

Solid State Structure
Lecture Notes

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1 Periodic functions, Fourier series and waves

1. As you will see, in this course we will be using quite a lot a mathematical tool known as Fourier series. For this reason, it seems appropriate to introduce this subject with some detail.

1.1 Periodic functions

2. Fourier series, at least limiting ourselves to the use of them we will make in this course, are defined for periodic functions (or functions that can be treated as such). Thus, we start by defining and analysing periodic functions.

3. A function of a single variable $f(x)$ (defined on the whole $\mathbb{R}$ axis) is periodic with fundamental period T if:

$$\exists T \in \mathbb{R} : f(x + kT) = f(x) \quad \forall x \in \mathbb{R}, \forall k \in \mathbb{Z} \quad (1)$$

The meaning of eq. 1 is the following: if we partition the x axis into intervals of amplitude T , then the graph of $f(x)$ repeats indentially in each interval (figure 1)

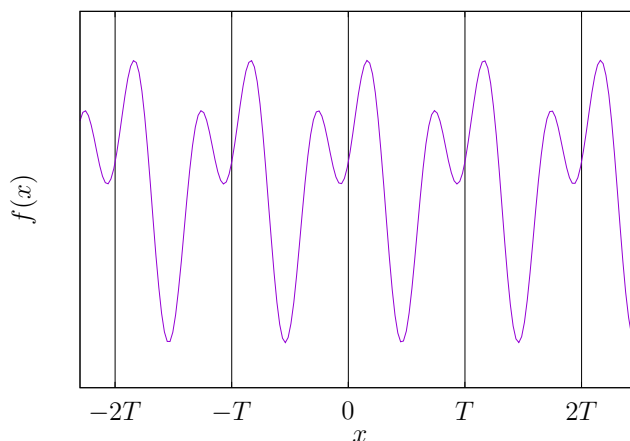


Figure 1: The graph of a periodic function. If the x axis is partitioned into intervals of amplitude T , then each interval contains exactly the same pattern.

4. Note that eq. 1 can be written in a simpler way:

$$\exists T \in \mathbb{R} : f(x + T) = f(x) \quad \forall x \in \mathbb{R} \quad (2)$$

Actually, 2 implies 1 and viceversa:

$$1 \iff 2$$

$1 \implies 2$ is trivial, since 1 holds $\forall k \in \mathbb{Z}$ and hence also when $k = 1$.

In order to prove the opposite, let's suppose that 2 holds. Then:

$$f(x + kT) = f(\overbrace{x + (k-1)T}^{x'} + T) \stackrel{\text{using 2}}{=} f(x + (k-1)T)$$

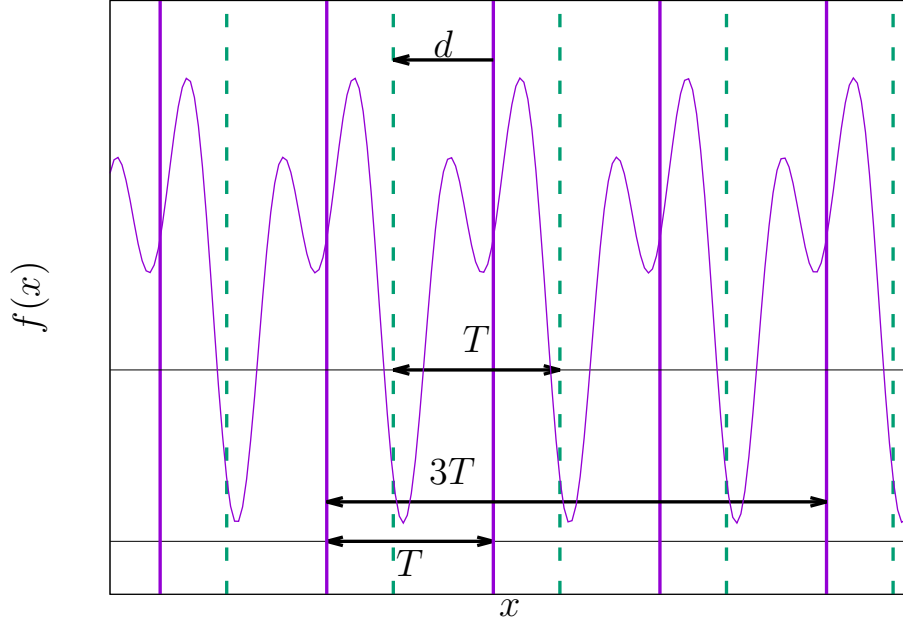


Figure 2: A T -periodic function of a single variable defines a monodimensional lattice whose primitive cell is the interval of amplitude T (full lines); in the figure a triple supercell (ie an interval of amplitude $3T$) is also shown. Note that if the original lattice (full lines) is shifted (translated) by an arbitrary amount (d) (dashed lines), the periodicity of $f(x)$ holds unchanged on the translated lattice.

$$= f\left(\overbrace{x + (k-2)T}^{x''} + T\right) = \overbrace{f(x + (k-2)T)}^{\text{using 2}} = \dots = f(x + T) = \overbrace{f(x)}^{\text{using 2}}$$

However, I think that definition 1 is more “descriptive”.

5. The period of a periodic function, T in 1, is the *minimum* number for which eq. 1 is satisfied: it is also called *fundamental period*.

Obviously, as eq. 1 clearly states, a periodic function with period T is also periodic with period $2T, 3T, 4T \dots$ and, equivalently, a periodic function with period $T/2, T/3, T/4, \dots$ is also periodic with period T .

6. Let’s now make a simple observation which will become more meaningful when we will deal with periodic functions in 2 or 3 dimensions.

The T -periodic function $f(x)$ defines a mono dimensional “*lattice*” on the x axisⁱ. This lattice consists of the infinite points equally spaced at a distance T (figure 2). For reasons that will become clear later, the lattice of T -spaced points associated with the periodic function $f(x)$ is called “*direct lattice*” (and the $\mathbb{R}$ space into which this direct lattice is immersed is called “*direct space*”): we will refer to the direct lattice with the symbol $\mathcal{R}$ throughout this course.

ⁱIn one only dimension, you’d probably find more appropriate to speak about a *grid*, rather than a *lattice*; however, since we will extend all the concepts introduced here to the case of functions of two or three variables, it is convenient to use a uniform jargon, valid for any dimensionality

T being the fundamental period of f , we call *primitive cell* or *elementary cell* of the (monodimensional) lattice induced by the periodicity of f any one of the intervals of amplitude T into which the x axis has been partitioned.

By virtue of the just introduced definition, we can say that the graph of the periodic function $f(x)$ repeats identical to itself in each primitive cell of the direct lattice. We can equivalently say that all the primitive cells of the lattice, together with their included portion of the graph of $f(x)$, are identical *replicas* of any one of them.

The generic point R of the direct lattice is given by:

$$R = kT \quad k \in \mathbb{Z} \quad (3)$$

where the point for $k = 0$ is taken as the origin.

Hence, the definition of a periodic function can be equivalently stated in the following terms.

Given a lattice $\mathcal{R}$ of equally spaced points R defined by eq. 3, the function $f(x)$ is periodic with period T if:

$$f(x + R) = f(x) \quad \forall x \in \mathbb{R}, \forall R \in \mathcal{R} \quad (4)$$

7. Supercell. We can further introduce the concept of *supercell* as an interval given by the union of two or more primitive cells. A double, triple etc. supercell means an interval of amplitude $2T$, $3T$, $\dots$, respectively. On the basis of 1, the graph of a T -periodic function $f(x)$ repeats identical not only in every primitive cell, but also in every supercell (of any size). Fig. 2 shows a triple supercell.

8. Note that the particular point of the x axis which is the origin of the $\mathcal{R}$ lattice (the point R when $k = 0$ in 3) is totally unimportant: the statements about the periodicity of the function f hold the same for any chosen origin.

In other words: once the amplitude T of the primitive cell of $\mathcal{R}$ is fixed, $\mathcal{R}$ itself can be arbitrarily translated without f losing its periodicity (as defined by 1). In fig. 2, the upper lattice has been translated by an arbitrary amount with respect to the lower lattice: the periodicity of the graph of the function is evident in each of the two lattices (and would hold for any other lattice defined by the same primitive cell).

What changes as a consequence of arbitrarily shifting the origin of the direct lattice $\mathcal{R}$ is only the content (i.e. the portion of the graph of f) of a(ny) primitive cell (fig. 2).

9. Frequency. We define the *frequency* ν of a T -periodic function $f(x)$ as the number of periods (or, if you want, the number of primitive cells) per unity of the x variable. In other words: how many times the interval of amplitude T is contained into the interval of amplitude 1.

Of course, the frequency is in general a positive real number, greater than 1 when $T < 1$ and less than 1 when $T > 1$.

Since the number of periods contained in T units of x is (trivially) 1, the frequency is given by:

$$\nu = \frac{[\text{n. of periods}]}{[\text{n. of } x \text{ units}]} = \frac{1}{T} \quad (5)$$

Note that, based on 5, the units used to measure the frequency are the inverse of those used to measure the period (or any other length on the x axis). For example: if the physical quantity reported on the x axis is length, measured in $\text{\AA}$, then the units for the frequency will be $\text{\AA}^{-1}$.

The just introduced frequency is also called *linear frequency*, to distinguish it from the *angular frequency*, to be defined in a while.

1.1.1 Two simple properties of the integral of a periodic function over a period

10. Since we will make use of them in the following, let's introduce now two strictly related properties enjoyed by the integral of a periodic function evaluated on an interval of amplitude equal to the period of the function (or, using the jargon introduced above: the integral of the function over a primitive cell).

1.1.1.1 Arbitrary translation of the integration interval

11. Given a T -periodic function $f(x)$, the following holds:

$$\int_a^{a+T} f(x) dx = \int_b^{b+T} f(x) dx \quad \forall a, b$$

that is: the integral of the function over an interval of amplitude T is invariant with respect to any translation of the integration interval.

This property is strictly related to what I said at point 8 regarding the ability to arbitrarily translate the lattice defined by a periodic function.

The informal/intuitive justification is:

- if the function is periodic and
- if the amplitude of the integration interval is equal to the period

then an arbitrary shift of the integration interval to the right makes you “lose” a portion of the graph on the left, but, at the same time, you “gain” an *identical* portion of the graph on the right, so that the area (i.e. the integral) under the graph of the function within the new integration interval does not change (and, of course, the same holds for an arbitrary shift to the left).

The formal proof (which I found on the web¹) goes like this.

Define the function:

$$H(z) = \int_z^{z+T} f(x) dx$$

(realize that this is a function of the single variable z)

If we call F any primitive function of f (primitive in the sense that $dF(x)/dx = f(x)$), then, by the fundamental rule of integration:

$$H(z) = F(z+T) - F(z)$$

Now take the first derivative with respect to z of both sides:

$$\frac{dH(z)}{dz} = \frac{dF(z+T)}{dz} - \frac{dF(z)}{dz}$$

For the first term on the right hand side (RHS), we have, with $u(z) = z + T$ and applying well known (I hope!) derivative rules:

$$\frac{dF(z+T)}{dz} = \frac{dF(u)}{dz} = \frac{dF(u)}{du} \overbrace{\frac{du}{dz}}^{=1} = f(u) = f(z+T) = f(z)$$

for f is T -periodic.

Thus, the derivative evaluates to:

$$\frac{dH(z)}{dz} = \frac{dF(z+T)}{dz} - \frac{dF(z)}{dz} = f(z) - f(z) = 0$$

But $dH/dz = 0$ means that $H(z)$ is the constant function, or:

$$H(a) = H(b) \quad \forall a, b \implies \int_a^{a+T} f(x) dx = \int_b^{b+T} f(x) dx \quad \forall a, b$$

1.1.1.2 Arbitrary translation of the function

12. This property is a consequence of the previous one.

Given a T -periodic function, the following holds:

$$\int_a^{a+T} f(x) dx = \int_a^{a+T} f(x+d) dx \quad \forall d \in \mathbb{R}$$

that is: the integral over an interval of amplitude T is invariant with respect to any translation of the function along the x axis (we will come back on what translating a function actually means in point 111, but you should already have previous knowledge that the graph of $f(x+d)$ is just that of $f(x)$, translated by d to the right, when $d < 0$, or to the left, when $d > 0$).

The proof of this property follows directly from the previous one.

Let's start with the integral:

$$\int_a^{a+T} f(x+d) dx \tag{6}$$

and perform the following change of variable:

$$y = x + d \tag{7}$$

Then:

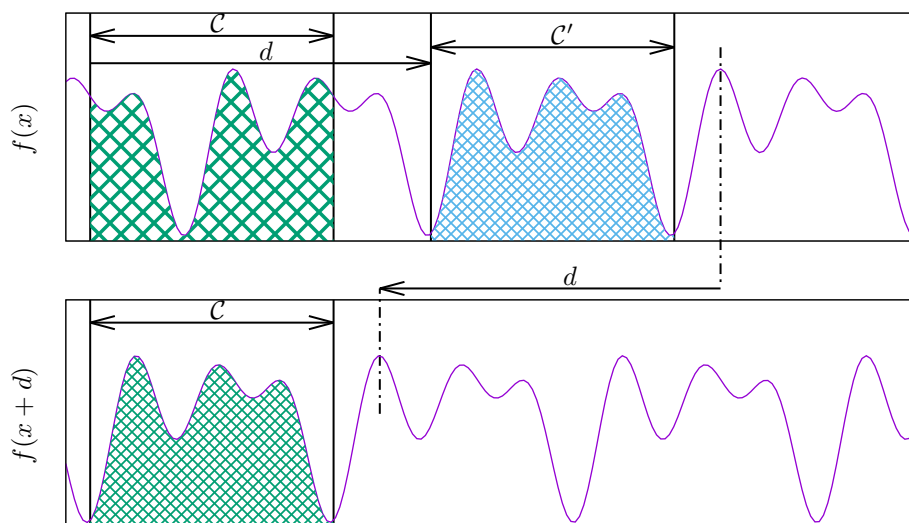
$$\begin{aligned} dx &= dy \\ x = a &\implies y = a + d \\ x = a + T &\implies y = a + d + T \end{aligned}$$

Thus, letting $a + d = b$, we have:

$$\int_a^{a+T} f(x+d) dx = \int_{a+d}^{a+d+T} f(y) dy = \int_b^{b+T} f(y) dy = \int_a^{a+T} f(y) dy = \int_a^{a+T} f(x) dx \tag{8}$$

where the penultimate equality follows from the property proved at the previous point 11. (in the last equality I have changed the variable name from y to x only to better evidence the relation with the starting integral)

Figure 3 is an attempt to graphically demonstrate this property. From the figure you should realize that translating the integration interval by d in a given direction (upper panel of the figure and property at point 11) is equivalent to translating the function to be integrated by d in the *opposite* direction (lower panel of the figure).



$$\int_C f(x) dx = \int_{C'} f(x) dx = \int_C f(x+d) dx$$

Figure 3: The integrals of a T -periodic function $f(x)$ over two primitive cells $\mathcal{C}$ and $\mathcal{C}'$, with $\mathcal{C}'$ translated by an arbitrary amount d to the right, are shown in the upper panel. These two integrals are equal, by the property of point 11.

In the lower panel it is shown that the integral of the function evaluated on $\mathcal{C}'$ (in the upper panel) can be equivalently evaluated on $\mathcal{C}$ by translating the function by the same amount d , but this time to the left. The integral evidenced in the lower panel is just:

$$\int_C f(x+d) dx.$$

We have proved the two above properties for a function of a single variable. However, even if we do not prove this, they still hold for a periodic function of any number of independent variables. We will introduce periodic functions of multiple variables on p. 31 and, in general, they will be a constant presence all over the course.

1.1.2 The sine and cosine functions and the Euler identity

13. You all know very well that the quintessential periodic functions are sine and cosine. The “natural” period of these functions is 2π :

$$\begin{aligned} \sin(x + k(2\pi)) &= \sin(x) \quad \forall x \in \mathbb{R} \quad \forall k \in \mathbb{Z} \\ \cos(x + k(2\pi)) &= \cos(x) \quad \forall x \in \mathbb{R} \quad \forall k \in \mathbb{Z} \end{aligned}$$

It is possible to turn the period of these functions into any real number T by multiplying the argument by $2\pi/T$.

The functions:

$$\sin\left(\frac{2\pi}{T}x\right) \text{ and } \cos\left(\frac{2\pi}{T}x\right)$$

are T -periodic, as can be easily verified:

$$\begin{aligned}\sin\left(\frac{2\pi}{T}(x+kT)\right) &= \sin\left(\frac{2\pi}{T}x + k(2\pi)\right) = \sin\left(\frac{2\pi}{T}x\right) \quad \forall x \in \mathbb{R} \quad \forall k \in \mathbb{Z} \\ \cos\left(\frac{2\pi}{T}(x+kT)\right) &= \cos\left(\frac{2\pi}{T}x + k(2\pi)\right) = \cos\left(\frac{2\pi}{T}x\right) \quad \forall x \in \mathbb{R} \quad \forall k \in \mathbb{Z}\end{aligned}$$

Since $\nu = 1/T$ is the linear frequency (eq. 5), it is useful to define the so called *angular frequency* as:

$$\omega = \frac{2\pi}{T} = 2\pi\nu \quad (9)$$

You can think of the angular frequency as a measure of how much the actual period T of a sine or cosine function differs from the “natural” period of 2π .

Based on the angular frequency definition, it is possible to write in a more compact form the T -periodic sine or cosine functions.

The functions:

$$\sin(\omega x) \text{ and } \cos(\omega x) \quad (10)$$

have period:

$$T = \frac{2\pi}{\omega} \quad (11)$$

and linear frequency:

$$\nu = \frac{\omega}{2\pi} \quad (12)$$

14. There exists a famous and elegant identity which connects the sine and cosine functions with the complex exponential function. This identity is called the “Euler identity” (from the name of the swiss mathematician, physicist and engineer who discovered it) and we will make use of it very often in this course.

The Euler identity is:

$$\exp(ix) = \cos(x) + i \sin(x) \quad \forall x \in \mathbb{R} \quad (13)$$

where i is the imaginary unit ($i^2 = -1$)ⁱⁱ

Note that:

$$\exp(-ix) = \exp(i(-x)) = \cos(-x) + i \sin(-x) = \cos(x) - i \sin(x) \quad (14)$$

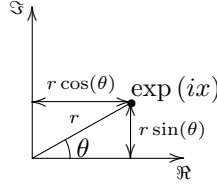
and thus it is customary to write the Euler identity more explicitly as:

$$\exp(\pm ix) = \cos(x) \pm i \sin(x) \quad (15)$$

15. You can find the derivation of the Euler identity in any math book. I will present here one of the derivations reported by Wikipedia.²

ⁱⁱI am assuming that you all have an elementary knowledge of complex numbers.

$\forall x \in \mathbb{R}$ the complex number $\exp(ix)$ is not null and can be written in polar form as:



$$\exp(ix) = r(x) \cos(\theta(x)) + ir(x) \sin(\theta(x)) \quad (16)$$

Note that it must be $r(x) > 0$ for the exponential in 16 is always $\neq 0$ (by definition, the modulus of the polar form of the complex number $a + ib$ is always ≥ 0 , being $r = \sqrt{a^2 + b^2}$).

Now take the derivative with respect to x of both sides:

$$i \exp(ix) = \cos(\theta) \frac{dr}{dx} - r \sin(\theta) \frac{d\theta}{dx} + i \sin(\theta) \frac{dr}{dx} + ir \cos(\theta) \frac{d\theta}{dx}$$

Substitute $\exp(ix)$ with its polar form and isolate the real and imaginary parts on both sides:

$$\begin{aligned} i(r \cos(\theta) + ir \sin(\theta)) &= \cos(\theta) \frac{dr}{dx} - r \sin(\theta) \frac{d\theta}{dx} + i \left(\sin(\theta) \frac{dr}{dx} + r \cos(\theta) \frac{d\theta}{dx} \right) \\ -r \sin(\theta) + ir \cos(\theta) &= \cos(\theta) \frac{dr}{dx} - r \sin(\theta) \frac{d\theta}{dx} + i \left(\sin(\theta) \frac{dr}{dx} + r \cos(\theta) \frac{d\theta}{dx} \right) \end{aligned}$$

By comparison of the real (or imaginary) parts on both sides we get:

$$\frac{dr}{dx} = 0 \rightarrow r(x) = \text{constant} \quad (17)$$

$$\frac{d\theta}{dx} = 1 \rightarrow \theta(x) = x + \theta(0) \quad (18)$$

Now: eq. 16 has to hold for *any* x , hence also when $x = 0$; in this case we obtain:

$$1 = r(0) \cos(\theta(0)) + ir(0) \sin(\theta(0))$$

This equality can be true if and only if:

$$\begin{aligned} \theta(0) &= 0 && \text{because (i) the imaginary part must be null and (ii) } r(0) \neq 0 \\ r(0) &= 1 && \text{because this is the only way the RHS can be } = 1, \text{ since } \cos(\theta(0)) = \cos 0 = 1 \end{aligned}$$

But then:

$$\begin{aligned} \theta(0) = 0 &\implies \theta = x \quad (\text{because } \theta(x) = x + \theta(0), \text{ eq. 18}) \\ r(0) = 1 &\implies r = 1 \quad \forall x \quad (\text{because } r = \text{constant}, \text{ eq. 17}) \end{aligned}$$

and thus eq. 16 just turns into the Euler identity 13.

16. As you can easily verify, the Euler identity can be inverted to obtain expressions for the sine and cosine functions as a combination of exponential functions.

Starting from:

$$\begin{aligned}\exp(ix) &= \cos(x) + i \sin(x) \\ \exp(-ix) &= \cos(x) - i \sin(x)\end{aligned}$$

add side by side to obtain:

$$\cos(x) = \frac{1}{2} (\exp(ix) + \exp(-ix)) \quad (19)$$

or subtract side by side to obtain:

$$\begin{aligned}\sin(x) &= \frac{1}{2i} (\exp(ix) - \exp(-ix)) \\ &= -\frac{i}{2} (\exp(ix) - \exp(-ix))\end{aligned} \quad (20)$$

We will make extensive use also of the above two results.

17. It is worthwhile to cast your mind back to three general and rather obvious properties of the exponential:

$$\exp(ix)$$

- The first one is that it is a function of a single real variable with values in the set of the complex numbers: actually, this is just what the Euler identity 13 tells us.

So: the domain is $\mathbb{R}$ and the codomain is $\mathbb{C}$:

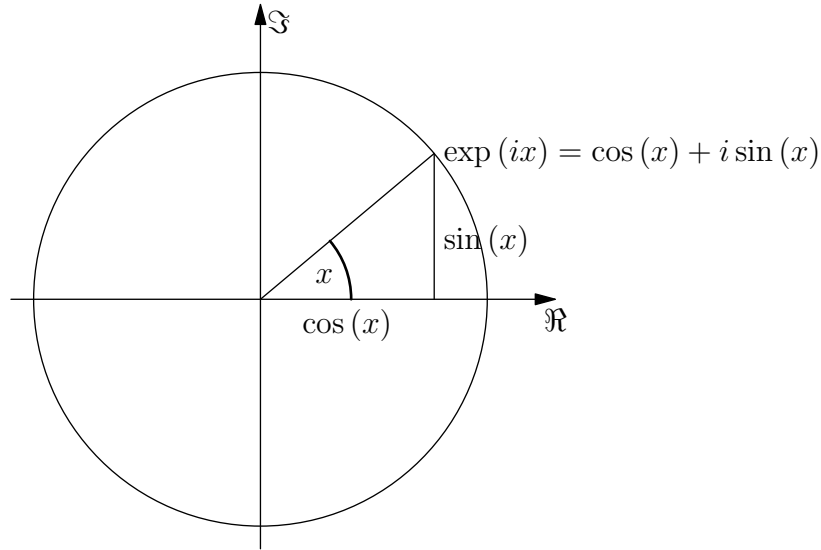
$$x \xrightarrow{\exp(ix)} \exp(ix) = \underbrace{\overbrace{\cos(x)}^{\Re(x)} + i \overbrace{\sin(x)}^{\Im(x)}}_{\in \mathbb{C}}$$

- The second remark is that, still based on the Euler identity, $\exp(ix)$ is a 2π -periodic function, since its real ($\cos(x)$) and imaginary ($\sin(x)$) parts are both 2π -periodic.

So it holds that:

$$\exp(i(x + k2\pi)) = \exp(ix) \quad \forall x \in \mathbb{R}, \forall k \in \mathbb{Z} \quad (21)$$

Since the real part of $\exp(ix)$ is $\cos(x)$ and its imaginary part is $\sin(x)$, the point representing $\exp(ix)$ on the complex plane is located on the trigonometric circle (of unit radius) and x can be geometrically thought of as being the angle made by the vector to said point and the real axis:



Hence the graph of $\exp(ix)$ on the complex plane is a circle of unit radius which gets traced as x changes and that “overlaps itself” with 2π periodicity.

Of course, and for exactly the same reason we already discussed for the sine and cosine functions, it is possible to impose an arbitrary period T to $\exp(ix)$ by multiplying its argument by $2\pi/T$:

$$\begin{aligned}\exp\left(i\frac{2\pi}{T}(x+kT)\right) &= \cos\left(\frac{2\pi}{T}(x+kT)\right) + i\sin\left(\frac{2\pi}{T}(x+kT)\right) \\ &= \cos\left(\frac{2\pi}{T}x + 2\pi k\right) + i\sin\left(\frac{2\pi}{T}x + 2\pi k\right) \\ &= \cos\left(\frac{2\pi}{T}x\right) + i\sin\left(\frac{2\pi}{T}x\right) = \exp\left(i\frac{2\pi}{T}x\right)\end{aligned}$$

- The third remark is:

$$\exp(i(2\pi n)) = \overbrace{\cos(2\pi n)}^{=1} + i\overbrace{\sin(2\pi n)}^{=0} = 1 \quad \forall n \in \mathbb{Z} \quad (22)$$

that is: the value of $\exp(ix)$ is the real number 1 when its argument is an integer multiple of 2π ⁱⁱⁱ

Again, you will see how much often we will make use of this (trivial) result.

1.2 The Fourier series in one dimension

18. We will now see how any periodic function^{iv} can be written as a series, which is called *Fourier series* (or *Fourier expansion*).

ⁱⁱⁱAll over the course, I will say “integer number” actually meaning a relative number $\in \mathbb{Z}$; the distinction between integers $\in \mathbb{N}$ or $\in \mathbb{Z}$ will always be clear from the context.

^{iv}Actually, it is not true that *any* periodic function can be Fourier expanded; however, in this course we will be dealing with “good” functions for which the Fourier series is always possible.

19. This introduction makes no claim to mathematical rigor, but I will carry out all the steps, because once in a lifetime it is good to do it.

We will perform the detailed derivation of the Fourier series only in one dimension (i.e. for functions of a single variable); we will then extend the 1D results for 2D and 3D functions with less details and more intuitively.

20. Let's focus on a T -periodic real function of a single real variable $f(x)$: our task is to write it as a series, that is, as a sum of infinite terms.

Since the function is T -periodic, it will be mandatory to expand it with functions having the same period T , or a period which is a submultiple of T . In this regard, remember that, based on 1, a periodic function of period $T' = T/k$, with $k \in \mathbb{N}$, is also trivially periodic with (super) period T (we noted this at point 5):

$$g(x + T) = g(x + kT') = g(x) \quad (23)$$

For the expansion we are after, it is not convenient to consider *non* periodic functions because they would not be able to reproduce the periodicity of $f(x)$ (also, realize that a periodic function with fundamental period αT , $\alpha > 1$, *cannot* be periodic with (fundamental) period T at the same time).

21. We could think of expanding our $f(x)$ with sines and cosines having periods $T, T/2, T/3, \dots$, each of them multiplied by a (x independent) coefficient, to be properly found (we'll see how).

$$\begin{aligned} f(x) &= C_1 \cos\left(\frac{2\pi}{T}x\right) + C_2 \cos\left(\frac{2\pi}{\frac{T}{2}}x\right) + \dots + S_1 \sin\left(\frac{2\pi}{T}x\right) + S_2 \sin\left(\frac{2\pi}{\frac{T}{2}}x\right) + \dots \\ &= \sum_{i=1}^{\infty} C_i \cos\left(\frac{2\pi}{\frac{T}{i}}x\right) + \sum_{i=1}^{\infty} S_i \sin\left(\frac{2\pi}{\frac{T}{i}}x\right) \\ &= \sum_{i=1}^{\infty} C_i \cos\left(\frac{2\pi i}{T}x\right) + \sum_{i=1}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) \end{aligned}$$

As just said, the C_i and S_i coefficients (assumed to be independent on x) have to be sorted out in some way, so that the above equality can be satisfied.

Indeed, deriving analytic expressions for the C_i and S_i coefficients is what we are going to achieve in the following.

22. There is still a problem. The sine and cosine functions oscillate above and below the $y = 0$ line. On the other hand, the function f to be expanded might be located anywhere along the y axis: so, to take this into account, we need to add a constant term to our proposed sum. This point is illustrated in fig. 4. We call it F_0 and, as was the case for the C_i and S_i coefficients, we assume that F_0 does not depend on x .

So, our final "proposal" for the expansion is:

$$f(x) = F_0 + \sum_{i=1}^{\infty} C_i \cos\left(\frac{2\pi i}{T}x\right) + \sum_{i=1}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) \quad (24)$$

23. Eq. 24 can work only if the F_0 , C_i and S_i coefficients do actually exist and can be determined. This is what we are going to verify now; however, before proceeding we need some simple results of general scope.

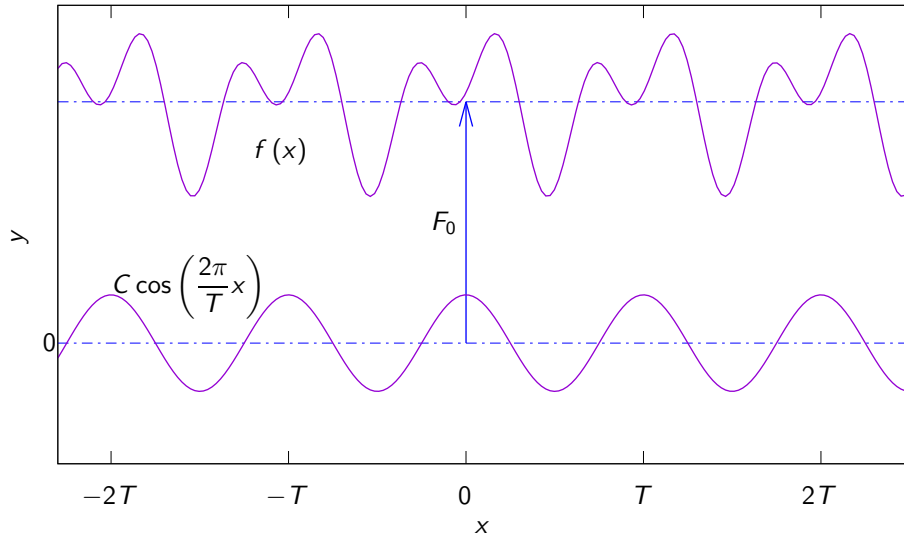


Figure 4: A T -periodic function $f(x)$ is “located” at a finite positive height with respect to the $y = 0$ horizontal line (upper plot); a simple cosine function $C \cos\left(\frac{2\pi}{T}x\right)$ with the same period is bound to oscillate around the $y = 0$ line (lower plot): there would be no way to expand $f(x)$ as a sum of such simple cosines (and/or sines). The only option is to shift the cosine (and/or sine) functions by an appropriate amount F_0 so that they oscillate in the same region of the cartesian plane where $f(x)$ is located. For the cosine function shown in the figure this would be achieved by considering $F_0 + C \cos\left(\frac{2\pi}{T}x\right)$ instead of $C \cos\left(\frac{2\pi}{T}x\right)$.

1.2.1 Some general results

1.2.1.1 An integral of the sine function

24. The following holds:

$$\int_a^{a+T} \sin\left(\frac{2\pi j}{T}x\right) dx = 0 \quad \forall j \in \mathbb{Z} \quad (25)$$

Let's verify it.

Perform the change of variable:

$$y = \frac{2\pi j}{T}x \quad (26)$$

Then:

$$dx = \frac{T}{2\pi j} dy \quad (27)$$

$$x = a \implies y = \frac{2\pi j}{T}a \quad (28)$$

$$x = a + T \implies y = \frac{2\pi j}{T}(a + T) = \frac{2\pi j}{T}a + 2\pi j \quad (29)$$

and thus:

$$\int_a^{a+T} \sin\left(\frac{2\pi j}{T}x\right) dx = \frac{T}{2\pi j} \int_{\frac{2\pi j}{T}a}^{\frac{2\pi j}{T}a+2\pi j} \sin(y) dy \quad (30)$$

$$= \frac{T}{2\pi j} \left(-\cos\left(\frac{2\pi j}{T}a + 2\pi j\right) - \left(-\cos\left(\frac{2\pi j}{T}a\right) \right) \right) \quad (31)$$

$$= \frac{T}{2\pi j} \left(-\cos\left(\frac{2\pi j}{T}a\right) - \left(-\cos\left(\frac{2\pi j}{T}a\right) \right) \right) = 0 \quad (32)$$

1.2.1.2 An integral of the cosine function

25. The following holds:

$$\int_a^{a+T} \cos\left(\frac{2\pi j}{T}x\right) dx = \begin{cases} 0 & \forall j \neq 0 \\ T & j = 0 \end{cases} \quad (33)$$

Also this one is easily verified:

when $j = 0$

$$\int_a^{a+T} \cos\left(\frac{2\pi j}{T}x\right) dx = \int_a^{a+T} dx = a + T - a = T \quad (34)$$

when $j \neq 0$ Similarly to the integral 25, we perform the change of variable:

$$y = \frac{2\pi j}{T}x \quad (35)$$

Then:

$$dx = \frac{T}{2\pi j} dy \quad (36)$$

$$x = a \implies y = \frac{2\pi j}{T} a \quad (37)$$

$$x = a + T \implies y = \frac{2\pi j}{T} (a + T) = \frac{2\pi j}{T} a + 2\pi j \quad (38)$$

and thus:

$$\int_a^{a+T} \cos\left(\frac{2\pi j}{T} x\right) dx = \frac{T}{2\pi j} \int_{\frac{2\pi j}{T} a}^{\frac{2\pi j}{T} a + 2\pi j} \cos(y) dy \quad (39)$$

$$= \frac{T}{2\pi j} \left(\sin\left(\frac{2\pi j}{T} a + 2\pi j\right) - \left(\sin\left(\frac{2\pi j}{T} a\right)\right) \right) \quad (40)$$

$$= \frac{T}{2\pi j} \left(\sin\left(\frac{2\pi j}{T} a\right) - \left(\sin\left(\frac{2\pi j}{T} a\right)\right) \right) = 0 \quad (41)$$

1.2.1.3 Prosthaphaeresis formula n.1

26.

$$\sin \alpha \sin \beta = \frac{1}{2} (\cos (\alpha - \beta) - \cos (\alpha + \beta)) \quad (42)$$

This gives us an opportunity to appreciate the usefulness of the Euler identity. Indeed, by using 20 we get:

$$\begin{aligned} \sin \alpha \sin \beta &= \frac{\exp(i\alpha) - \exp(-i\alpha)}{2i} \frac{\exp(i\beta) - \exp(-i\beta)}{2i} \\ &= - \frac{\exp(i(\alpha + \beta)) - \overbrace{\exp(-i(\alpha - \beta)) - \exp(i(\alpha - \beta))}^{-2 \cos(\alpha - \beta) \text{ by 19}} + \exp(-i(\alpha + \beta))}{4} \\ &= - \frac{\overbrace{\exp(i(\alpha + \beta)) + \exp(-i(\alpha + \beta))}^{2 \cos(\alpha + \beta) \text{ by 19}} - 2 \cos(\alpha - \beta)}{4} \\ &= \frac{1}{2} (\cos (\alpha - \beta) - \cos (\alpha + \beta)) \end{aligned} \quad (43)$$

1.2.1.4 Prosthaphaeresis formula n.2

27.

$$\sin \alpha \cos \beta = \frac{1}{2} (\sin (\alpha + \beta) + \sin (\alpha - \beta)) \quad (44)$$

Similar to what we did for the previous formula:

$$\begin{aligned}
\sin \alpha \cos \beta &= \frac{\exp(i\alpha) - \exp(-i\alpha)}{2i} \frac{\exp(i\beta) + \exp(-i\beta)}{2} \\
&= \frac{\exp(i(\alpha + \beta)) - \overbrace{\exp(-i(\alpha - \beta)) + \exp(i(\alpha - \beta))}^{2i \sin(\alpha - \beta) \text{ by 20}} - \exp(-i(\alpha + \beta))}{4i} \\
&= \frac{\overbrace{\exp(i(\alpha + \beta)) - \exp(-i(\alpha + \beta))}^{2i \sin(\alpha + \beta) \text{ by 20}} + 2i \sin(\alpha - \beta)}{4i} \\
&= \frac{1}{2} (\sin(\alpha + \beta) + \sin(\alpha - \beta))
\end{aligned} \tag{45}$$

1.2.1.5 Prosthaphaeresis formula n.3
28.

$$\cos \alpha \cos \beta = \frac{1}{2} (\cos(\alpha + \beta) + \cos(\alpha - \beta)) \tag{46}$$

Still using Euler identity:

$$\begin{aligned}
\cos \alpha \cos \beta &= \frac{\exp(i\alpha) + \exp(-i\alpha)}{2} \frac{\exp(i\beta) + \exp(-i\beta)}{2} \\
&= \frac{\exp(i(\alpha + \beta)) + \overbrace{\exp(-i(\alpha - \beta)) + \exp(i(\alpha - \beta))}^{2 \cos(\alpha - \beta) \text{ by 20}} + \exp(-i(\alpha + \beta))}{4} \\
&= \frac{\overbrace{\exp(i(\alpha + \beta)) + \exp(-i(\alpha + \beta))}^{2 \cos(\alpha + \beta) \text{ by 20}} + 2 \cos(\alpha - \beta)}{4} \\
&= \frac{1}{2} (\cos(\alpha + \beta) + \cos(\alpha - \beta))
\end{aligned} \tag{47}$$

1.2.2 The S_i coefficients

29. Now let's go back to eq. 24 and see how we can get an expression for the S_i coefficients. Multiply both sides of 24 by $\sin((2\pi j/T)x)$ and integrate over a period from a to $a+T$ (a is any real number):

$$\begin{aligned}
\int_a^{a+T} f(x) \sin\left(\frac{2\pi j}{T}x\right) dx &= F_0 \int_a^{a+T} \sin\left(\frac{2\pi j}{T}x\right) dx \\
&+ \sum_{i=1}^{\infty} C_i \int_a^{a+T} \cos\left(\frac{2\pi i}{T}x\right) \sin\left(\frac{2\pi j}{T}x\right) dx \\
&+ \sum_{i=1}^{\infty} S_i \int_a^{a+T} \sin\left(\frac{2\pi i}{T}x\right) \sin\left(\frac{2\pi j}{T}x\right) dx
\end{aligned} \tag{48}$$

Please note: j is a particular value chosen among all possible values of i ; since i varies from 1 to ∞ , the same holds for j : $1 \leq j < \infty$.

30. The first term on the RHS is always null, because of 25.

31. By application of 44 and taking 25 into account we realize that each term of the sum over the C_i 's is null:

$$\begin{aligned} & \int_a^{a+T} \cos\left(\frac{2\pi i}{T}x\right) \sin\left(\frac{2\pi j}{T}x\right) dx \\ &= \frac{1}{2} \int_a^{a+T} \left(\sin\left(\frac{2\pi(i+j)}{T}x\right) + \sin\left(\frac{2\pi(j-i)}{T}x\right) \right) dx = 0 \end{aligned} \quad (49)$$

$$\begin{aligned} &= \frac{1}{2} \overbrace{\int_a^{a+T} \sin\left(\frac{2\pi(i+j)}{T}x\right) dx}^{=0 \text{ by 25}} + \frac{1}{2} \overbrace{\int_a^{a+T} \sin\left(\frac{2\pi(j-i)}{T}x\right) dx}^{=0 \text{ by 25}} = 0 \end{aligned} \quad (50)$$

In the sum over the S_i 's, only the term with $i = j$ survives, by virtue of 42 and 33:

$$\begin{aligned} & \int_a^{a+T} \sin\left(\frac{2\pi i}{T}x\right) \sin\left(\frac{2\pi j}{T}x\right) dx \\ &= \frac{1}{2} \int_a^{a+T} \left(\cos\left(\frac{2\pi(i-j)}{T}x\right) - \cos\left(\frac{2\pi(j+i)}{T}x\right) \right) dx \\ &= \frac{1}{2} \overbrace{\int_a^{a+T} \cos\left(\frac{2\pi(i-j)}{T}x\right) dx}^{=0 \text{ when } i \neq j; =T/2 \text{ when } i=j, \text{ by 33}} - \frac{1}{2} \overbrace{\int_a^{a+T} \cos\left(\frac{2\pi(j+i)}{T}x\right) dx}^{\text{always null, by 33}} \\ &= \frac{1}{2} \int_a^{a+T} \cos\left(\frac{2\pi(i-j)}{T}x\right) dx - \frac{1}{2} \int_a^{a+T} \cos\left(\frac{2\pi(j+i)}{T}x\right) dx \end{aligned} \quad (51)$$

(the second integral is always null because $1 \leq i, j < \infty$, and thus it is always: $i + j \neq 0$)

32. Summarizing: the first term on the RHS of 48 is null; all the terms in the sum over the C_i 's are null and only the term with $i = j$ survives in the sum over the S_i and its value is $T/2$.

We thus obtain:

$$\begin{aligned} & \int_a^{a+T} f(x) \sin\left(\frac{2\pi j}{T}x\right) dx = S_j \left(\frac{T}{2}\right) \\ & S_j = \frac{2}{T} \int_a^{a+T} f(x) \sin\left(\frac{2\pi j}{T}x\right) dx \quad j \in \mathbb{N} \end{aligned} \quad (52)$$

What is the meaning of this result? Since we have obtained 52 starting from 24 and j is an *arbitrary* value of i chosen among all its possible values, eq. 52 defines all the S_j coefficients ($\forall j \geq 1$) for which 24 is satisfied.

1.2.3 The C_i coefficients

33. For the C_i 's we proceed in a strictly similar way.

Multiply both sides of 24 by $\cos((2\pi j/T)x)$ and integrate between a and $a + T$:

$$\int_a^{a+T} f(x) \cos\left(\frac{2\pi j}{T}x\right) dx = F_0 \int_a^{a+T} \cos\left(\frac{2\pi j}{T}x\right) dx$$

$$\begin{aligned}
& + \sum_{i=1}^{\infty} C_i \int_a^{a+T} \cos\left(\frac{2\pi i}{T}x\right) \cos\left(\frac{2\pi j}{T}x\right) dx \\
& + \sum_{i=1}^{\infty} S_i \int_a^{a+T} \sin\left(\frac{2\pi i}{T}x\right) \cos\left(\frac{2\pi j}{T}x\right) dx
\end{aligned} \tag{53}$$

(again: j is one chosen value among all possible values of i)

The first term on the RHS is null by 33 (j is always $\neq 0$) and the sum over the S_i 's is null by 50.

In the sum over the C_i 's, only the term with $i = j$ survives, by virtue of 46 and 33:

$$\begin{aligned}
& \int_a^{a+T} \cos\left(\frac{2\pi i}{T}x\right) \cos\left(\frac{2\pi j}{T}x\right) dx \\
& = \frac{1}{2} \int_a^{a+T} \left(\cos\left(\frac{2\pi(i+j)}{T}x\right) + \cos\left(\frac{2\pi(i-j)}{T}x\right) \right) dx \\
& = \underbrace{\frac{1}{2} \int_a^{a+T} \cos\left(\frac{2\pi(i+j)}{T}x\right) dx}_{\text{always null, by 33}} + \underbrace{\frac{1}{2} \int_a^{a+T} \cos\left(\frac{2\pi(i-j)}{T}x\right) dx}_{=0 \text{ when } i \neq j; =T/2 \text{ when } i=j, \text{ by 33}}
\end{aligned}$$

Summarizing:

$$\begin{aligned}
& \int_a^{a+T} f(x) \cos\left(\frac{2\pi j}{T}x\right) dx = C_j \left(\frac{T}{2}\right) \\
& C_j = \frac{2}{T} \int_a^{a+T} f(x) \cos\left(\frac{2\pi j}{T}x\right) dx \quad j \in \mathbb{N}
\end{aligned} \tag{54}$$

which defines the C_j coefficients such that 24 is satisfied.

1.2.4 The F_0 term

34. We still need to find F_0 .

Integrate both sides of 24 from a to $a + T$:

$$\int_a^{a+T} f(x) dx = \int_a^{a+T} F_0 dx + \sum_{i=1}^{\infty} C_i \int_a^{a+T} \cos\left(\frac{2\pi i}{T}x\right) dx + \sum_{i=1}^{\infty} S_i \int_a^{a+T} \sin\left(\frac{2\pi i}{T}x\right) dx$$

Trivially, all the terms of the two sums on the RHS are null by 33 and 25 (remember once again that i is always $\neq 0$).

The first integral on the RHS is also trivially equal to $F_0 T$ (remember that F_0 does not depend on x by hypothesis).

So:

$$\begin{aligned}
& \int_a^{a+T} f(x) dx = F_0 T \\
& F_0 = \frac{1}{T} \int_a^{a+T} f(x) dx
\end{aligned} \tag{55}$$

which defines F_0 .

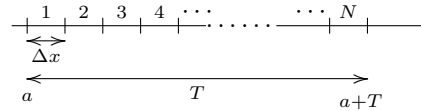
As one might have guessed, F_0 is *the average value* of the function $f(x)$ over a period.

Open parenthesis.

In general, not only for a periodic function, the following integral:

$$\frac{1}{T} \int_a^{a+T} f(x) dx$$

has the meaning of “average value of the function over the integration interval T ”. You can realize it by writing the integral as the limit of its finite form. Divide the integration interval T into N subintervals having the same amplitude Δx :



Then, calling x_i any x value within the i -th subinterval, we have:

$$\frac{1}{T} \int_a^{a+T} f(x) dx = \lim_{N \rightarrow \infty} \underbrace{\frac{1}{N \Delta x}}_T \sum_1^N f(x_i) \Delta x = \lim_{N \rightarrow \infty} \overbrace{\frac{\sum_1^N f(x_i)}{N}}^{\text{average of } N \text{ values}} = \langle f(x) \rangle$$

where $\langle f(x) \rangle$ is just the average of the values taken by f over the T interval.

Closed parenthesis.

Being the average value of the function $f(x)$ over the T interval, F_0 is the shift we must add to the sums of sines and cosines such that their oscillations take place in the same interval of the y axis where the graph of the function is located.

1.2.5 The Fourier series

35. Let's recap what we have found until now. We proposed a possible series expansion of the T -periodic function $f(x)$ (eq. 24). The expansion depends on certain coefficients (F_0, C_i, S_i) which, a priori, do not necessarily exist.

But we have just seen that those coefficients actually do exist and we have also found their expression.

It is thus “proved” that given a T -periodic function $f(x)$ it is always possible to expand it in a series in the following way:

$$\text{eq. 24: } f(x) = F_0 + \sum_{i=1}^{\infty} C_i \cos\left(\frac{2\pi i}{T} x\right) + \sum_{i=1}^{\infty} S_i \sin\left(\frac{2\pi i}{T} x\right)$$

$$\text{eq. 55: } F_0 = \frac{1}{T} \int_a^{a+T} f(x) dx$$

$$\text{eq. 54: } C_i = \frac{2}{T} \int_a^{a+T} f(x) \cos\left(\frac{2\pi i}{T} x\right) dx$$

$$\text{eq. 52: } S_i = \frac{2}{T} \int_a^{a+T} f(x) \sin\left(\frac{2\pi i}{T} x\right) dx$$

The series we have obtained is called *Fourier series* and it is difficult to overestimate its importance.

At the web site of this course you can download a small code (written in `octave`) which evaluates the first n terms of the Fourier expansion of an arbitray function.³

1.2.6 Equivalent forms of the Fourier series

There are several equivalent versions of the equations that define the Fourier series.

1.2.6.1 Particular values of the integration limits

36. Note that all the functions inside the integrals 55, 54 and 52 are T -periodic.

$f(x)$, in 55, is T -periodic by hypothesis.

As we noted at the beginning, all the functions:

$$\begin{aligned} &\cos\left(\frac{2\pi i}{T}x\right) \\ &\sin\left(\frac{2\pi i}{T}x\right) \end{aligned}$$

are T/i -periodic, and hence also T -periodic (point 5). It follows that all the functions inside the integrals 54 and 52 are T -periodic, being the product of T -periodic functions.

You can easily convince yourself about this.

Call $F(x)$ the function inside the integral in 54. Then:

$$\begin{aligned} F(x+T) &= f(x+T) \cos\left(\frac{2\pi i}{T}(x+T)\right) \\ &= f(x) \cos\left(\frac{2\pi i}{T}x + 2\pi i\right) \\ &= f(x) \cos\left(\frac{2\pi i}{T}x\right) \\ &= F(x) \end{aligned}$$

and similarly for the function inside integral 52.

For this reason, quite often the integration limits in 55, 54 and 52 are $[0, T]$ (that is: $a = 0$) or $[-T/2, T/2]$ (that is: $a = -T/2$); given the general property of point 11, it should be clear that a can be any real number.

1.2.6.2 $2T$ period

37. In other derivations, the period of the function $f(x)$ to be expanded is taken to be $2T$ (instead of T). In this case, the expressions 24, 55, 54 and 52 become:

$$f(x) = F_0 + \sum_{i=1}^{\infty} C_i \cos\left(\frac{\pi i}{T}x\right) + \sum_{i=1}^{\infty} S_i \sin\left(\frac{\pi i}{T}x\right) \quad (56)$$

$$F_0 = \frac{1}{2T} \int_a^{a+2T} f(x) dx \quad (57)$$

$$C_i = \frac{1}{T} \int_a^{a+2T} f(x) \cos\left(\frac{\pi i}{T} x\right) dx \quad (58)$$

$$S_i = \frac{1}{T} \int_a^{a+2T} f(x) \sin\left(\frac{\pi i}{T} x\right) dx \quad (59)$$

The reason why the period is some times taken as $2T$ is that, in this way, you have less 2 factors. Of course, in this cases, T is the *halfperiod* of the function.

1.2.6.3 A more compact form

38. You might happen to find a more compact expression of the Fourier series:

$$f(x) = \sum_{i=-\infty}^{\infty} C'_i \cos\left(\frac{2\pi i}{T} x\right) + \sum_{i=-\infty}^{\infty} S'_i \sin\left(\frac{2\pi i}{T} x\right) \quad (60)$$

with:

$$C'_i = \frac{1}{2} C_i = \frac{1}{T} \int_a^{a+T} f(x) \cos\left(\frac{2\pi i}{T} x\right) dx \quad (61)$$

$$S'_i = \frac{1}{2} S_i = \frac{1}{T} \int_a^{a+T} f(x) \sin\left(\frac{2\pi i}{T} x\right) dx \quad (62)$$

Note: the sums run from $-\infty$ to ∞ , the F_0 term is missing and in 61 and 62 $1/T$ has replaced $2/T$.

60, 61 and 62 are easily obtained from 24, 52 and 54.

Let's start from the first two terms on the RHS of 24:

$$F_0 + \sum_{i=1}^{\infty} C_i \cos\left(\frac{2\pi i}{T} x\right) \quad (63)$$

Realize that even if the sum in 24 starts from $i = 1$, we can arbitrarily extend the definition 54 to any (integer) value of i , i.e.:

$$C_i = \frac{2}{T} \int_a^{a+T} f(x) \cos\left(\frac{2\pi i}{T} x\right) dx \quad i \in \mathbb{Z} \quad (64)$$

(note the $i \in \mathbb{Z}$)

Based on the above, we add and subtract C_0 (as defined by extension of 54) in 63:

$$= F_0 - C_0 + C_0 + \sum_{i=1}^{\infty} C_i \cos\left(\frac{2\pi i}{T} x\right) \quad (65)$$

Now, trivially, it holds that:

$$C_0 = C_0 \overbrace{\cos\left(\frac{2\pi 0}{T} x\right)}^{=1} \quad (66)$$

so that we can include the positive C_0 term into the sum, making this latter start from 0, instead of 1:

$$= F_0 - C_0 + \sum_{i=0}^{\infty} C_i \cos \left(\frac{2\pi i}{T} x \right) \quad (67)$$

On the basis of the definitions of the C_i 's (eq. 54) and F_0 (eq. 55) it holds that:

$$C_0 = \frac{2}{T} \int_a^{a+T} f(x) \cos \left(\frac{2\pi \cdot 0}{T} x \right) dx = \frac{2}{T} \int_a^{a+T} f(x) dx = 2F_0 \quad (68)$$

so that we can continue with:

$$= -F_0 + \sum_{i=0}^{\infty} C_i \cos \left(\frac{2\pi i}{T} x \right) \quad (69)$$

The sum can be written as the difference between the following two:

$$= -F_0 + \sum_{i=-\infty}^{\infty} C_i \cos \left(\frac{2\pi i}{T} x \right) - \sum_{i=-\infty}^{-1} C_i \cos \left(\frac{2\pi i}{T} x \right) \quad (70)$$

In the second sum we can change the sign (and the order) of the limits if we also change the sign of the index in the sum terms:

$$= -F_0 + \sum_{i=-\infty}^{\infty} C_i \cos \left(\frac{2\pi i}{T} x \right) - \sum_{i=1}^{\infty} C_{-i} \cos \left(-\frac{2\pi i}{T} x \right) \quad (71)$$

where the C_{-i} 's are still defined by the extension of 54.

Now realize that the C_i 's are *even* functions of the index i , that is: $C_{-i} = C_i$. Actually, by definition:

$$C_{-i} = \frac{2}{T} \int_a^{a+T} f(x) \cos \left(-\frac{2\pi i}{T} x \right) dx = \frac{2}{T} \int_a^{a+T} f(x) \cos \left(\frac{2\pi i}{T} x \right) dx = C_i \quad (72)$$

because the cosine is an even function.

Skipping the intermediate equalities, we have arrived at:

$$F_0 + \sum_{i=1}^{\infty} C_i \cos \left(\frac{2\pi i}{T} x \right) = -F_0 + \sum_{i=-\infty}^{\infty} C_i \cos \left(\frac{2\pi i}{T} x \right) - \sum_{i=1}^{\infty} C_i \cos \left(\frac{2\pi i}{T} x \right) \quad (73)$$

(I have also replaced $\cos \left(-\frac{2\pi i}{T} x \right)$ with $\cos \left(\frac{2\pi i}{T} x \right)$, again thanks to even parity of the cos function)
So:

$$2F_0 + 2 \sum_{i=1}^{\infty} C_i \cos \left(\frac{2\pi i}{T} x \right) = \sum_{i=-\infty}^{\infty} C_i \cos \left(\frac{2\pi i}{T} x \right) \quad (74)$$

from which:

$$F_0 + \sum_{i=1}^{\infty} C_i \cos \left(\frac{2\pi i}{T} x \right) = \sum_{i=-\infty}^{\infty} \frac{1}{2} C_i \cos \left(\frac{2\pi i}{T} x \right) = \sum_{i=-\infty}^{\infty} C'_i \cos \left(\frac{2\pi i}{T} x \right) \quad (75)$$

with:

$$C'_i = \frac{1}{2}C_i = \frac{1}{T} \int_a^{a+T} f(x) \cos\left(\frac{2\pi i}{T}x\right) dx \quad (76)$$

which is exactly eq. 61.

We now consider the second sum in 24:

$$\sum_{i=1}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) \quad (77)$$

First off, realize that the sum value won't change if we augment it with an $i = 0$ term, since $\sin(0) = 0$ (S_0 is defined by extension of 52, letting $j \in \mathbb{Z}$, similar to what we did for the C 's).

$$= \sum_{i=0}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) \quad (78)$$

Now, as we did before, rewrite the sum as the difference between these two:

$$= \sum_{i=-\infty}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) - \sum_{i=-\infty}^{-1} S_i \sin\left(\frac{2\pi i}{T}x\right) \quad (79)$$

Again: in the second sum we can change the sign (and the order) of the limits if we also change the sign of the index in the sum terms:

$$= \sum_{i=-\infty}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) - \sum_{i=1}^{\infty} S_{-i} \sin\left(-\frac{2\pi i}{T}x\right) \quad (80)$$

Now realize that the S_i 's are *odd* functions of the index i , that is: $S_{-i} = -S_i$. Actually, by definition:

$$S_{-i} = \frac{2}{T} \int_a^{a+T} f(x) \sin\left(-\frac{2\pi i}{T}x\right) dx = -\frac{2}{T} \int_a^{a+T} f(x) \sin\left(\frac{2\pi i}{T}x\right) dx = -S_i \quad (81)$$

because the sine is an odd function.

Whence it must hold that:

$$S_{-i} \sin\left(-\frac{2\pi i}{T}x\right) = -S_i \left(-\sin\left(\frac{2\pi i}{T}x\right)\right) = S_i \sin\left(\frac{2\pi i}{T}x\right) \quad (82)$$

Substituting above we can continue with:

$$= \sum_{i=-\infty}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) - \sum_{i=1}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) \quad (83)$$

Eventually, skipping the intermediate equalities, we have arrived at:

$$\sum_{i=1}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) = \sum_{i=-\infty}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) - \sum_{i=1}^{\infty} S_i \sin\left(\frac{2\pi i}{T}x\right) \quad (84)$$

or:

$$2 \sum_{i=1}^{\infty} S_i \sin \left(\frac{2\pi i}{T} x \right) = \sum_{i=-\infty}^{\infty} S_i \sin \left(\frac{2\pi i}{T} x \right) \quad (85)$$

from which:

$$\sum_{i=1}^{\infty} S_i \sin \left(\frac{2\pi i}{T} x \right) = \sum_{i=-\infty}^{\infty} \frac{1}{2} S_i \sin \left(\frac{2\pi i}{T} x \right) = \sum_{i=-\infty}^{\infty} S'_i \sin \left(\frac{2\pi i}{T} x \right) \quad (86)$$

with:

$$S'_i = \frac{1}{2} S_i = \frac{1}{T} \int_a^{a+T} f(x) \sin \left(\frac{2\pi i}{T} x \right) dx \quad (87)$$

which is 62.

Obviously, substituting 75 and 86 into 24 we obtain 60.

1.2.6.4 The exponential form of the Fourier series

39. As you will see, we will not use the Fourier series in the form that we have introduced and discussed until now (ie as a sum of sines and cosines); instead, what we will be using all over this course is its so called *exponential form*.

This is a particular form of the Fourier series which is (of course!) perfectly equivalent to its expression in terms of sines and cosines, but is much more useful for doing the mathematical derivations you will encounter in this course.

We can derive the exponential form of the Fourier series starting from 60, which, based on 61 and 62, can be conveniently written as:

$$f(x) = \frac{1}{2} \sum_{n=-\infty}^{\infty} C_n \cos(\alpha_n) + S_n \sin(\alpha_n) \quad (88)$$

where, to make notation lighter, I have set:

$$\alpha_n = \frac{2\pi n}{T} x$$

(the index is now n to avoid any possible confusion with the imaginary unit i , which will be one of the ingredients of the final result; the C_n 's and S_n 's are defined by extension of 54 and 52, respectively, as already seen)

We start by re-writing the cosine and sine functions in 88 as a sum of complex exponentials on the basis of the Euler identity (eq. 19 and 20):

$$= \frac{1}{2} \sum_{n=-\infty}^{\infty} C_n \frac{\exp(i\alpha_n) + \exp(-i\alpha_n)}{2} - S_n \frac{i(\exp(i\alpha_n) - \exp(-i\alpha_n))}{2} \quad (89)$$

$$= \frac{1}{4} \sum_{n=-\infty}^{\infty} C_n (\exp(i\alpha_n) + \exp(-i\alpha_n)) - S_n (i(\exp(i\alpha_n) - \exp(-i\alpha_n))) \quad (90)$$

Now perform the multiplications and factor the exponentials out:

$$= \frac{1}{4} \sum_{n=-\infty}^{\infty} (C_n - iS_n) \exp(i\alpha_n) + (C_n + iS_n) \exp(-i\alpha_n) \quad (91)$$

Observe that, by 72 e 81, it holds that:

$$C_n + iS_n = C_{-n} - iS_{-n} \quad (92)$$

so that we can continue with:

$$= \frac{1}{4} \sum_{n=-\infty}^{\infty} (C_n - iS_n) \exp(i\alpha_n) + (C_{-n} - iS_{-n}) \exp(i\alpha_{-n}) \quad (93)$$

(note that I have also re-written: $\exp(-i\alpha_n) = \exp(i\alpha_{-n})$)

And now realize that, since the sum runs from $-\infty$ to ∞ , we can freely turn $-n$ into n without introducing any change: only *the order* of the terms will be different, but this has no effect on a summation.

Thus:

$$= \frac{1}{4} \sum_{n=-\infty}^{\infty} (C_n - iS_n) \exp(i\alpha_n) + (C_n - iS_n) \exp(i\alpha_n) \quad (94)$$

$$= \frac{1}{2} \sum_{n=-\infty}^{\infty} (C_n - iS_n) \exp(i\alpha_n) \quad (95)$$

$$= \sum_{n=-\infty}^{\infty} B_n \exp(i\alpha_n) \quad (96)$$

with:

$$B_n = \frac{1}{2} (C_n - iS_n) \quad (97)$$

$$= \frac{1}{2} \left(\frac{2}{T} \int_a^{a+T} f(x) \cos(\alpha_n) dx - i \frac{2}{T} \int_a^{a+T} f(x) \sin(\alpha_n) dx \right) \quad (98)$$

$$= \frac{1}{T} \int_a^{a+T} f(x) (\cos(\alpha_n) - i \sin(\alpha_n)) dx \quad (99)$$

$$= \frac{1}{T} \int_a^{a+T} f(x) \exp(-i\alpha_n) dx \quad (100)$$

and this is the final result.

In summary, the exponential form of the Fourier series is:

$$f(x) = \sum_{n=-\infty}^{\infty} B_n \exp(i\alpha_n) \quad (101)$$

$$B_n = \frac{1}{T} \int_a^{a+T} f(x) \exp(-i\alpha_n) dx \quad (102)$$

40. If you go back to 91 and re-write the first term (instead of the second) as:

$$(C_n - iS_n) \exp(i\alpha_n) = (C_{-n} + iS_{-n}) \exp(-i\alpha_{-n}) \quad (103)$$

(taking advantage, again, of the parity properties of the C_n 's and S_n 's) you will easily arrive at the equivalent form:

$$f(x) = \sum_{n=-\infty}^{\infty} B_n \exp(-i\alpha_n) \quad (104)$$

$$B_n = \frac{1}{T} \int_a^{a+T} f(x) \exp(i\alpha_n) dx \quad (105)$$

This shows that the exponential form of the Fourier series keeps its validity unaltered when we exchange the minus sign between the exponential in the sum and the one appearing in the definition of the B_n 's (compare 104 and 105 with 101 and 102)

41. You might ask at this point how can it be that a series containing complex terms can converge to a function which, until now, is supposed to be real.

A first (obvious) answer is: we started from 60, which is clearly a real (that is, non complex) expression; so, if we perform all the steps in the backward direction, we must re-obtain the real expression which we started from. Which means that if a function is real, then its Fourier expansion, even written in the complex exponential form, must return a real result (the ultimate reason why this is so is that, for real functions, all the imaginary parts of the Fourier series cancel with each other; and we will see this explicitly at point 103, in the light of a simple property which we will derive there.)

Moreover, it is also possible to prove (but we will not do this) that the complex exponential form of the Fourier series works unaltered for complex functions of a real variable, ie functions of type $f(x) = h(x) + ig(x)$; of course, in this latter case, the imaginary part of the expansion will not be null.⁴

1.3 The Fourier series in multiple dimensions

42. We now have to extend what we found for a function of a single variable to real functions of two or three variables, that is functions of type $f(x, y)$ or $f(x, y, z)$.

You will see that the extension of the Fourier series to the 2D or 3D cases is extremely elegant in the sense that the expressions which we have obtained for the monodimensional case remain basically the same, apart from few obvious changes due to the increased dimensionality.

43. We will not derive the multidimensional Fourier series with the same level of detail which we used for the monodimensional case. However, the extension of what we already know requires the introduction of concepts that will be of paramount importance for the rest of this course, because they constitute a fundamental theoretical tool to study not only the multidimensional Fourier expansion, but also a vast class of solid systems called *crystalline solids*.

44. In this part I will introduce the concepts of *Bravais lattice* (also called *direct lattice*) and *reciprocal lattice*.

I have already mentioned the direct lattice at point 6 for a periodic function of a single variable; on that instance, however, it might have been difficult to grasp the concrete meaning of it: even in common language, the word *net* or *lattice* is evocative of an object which is at least bidimensional (a fishing net, a lattice of alleys). The monodimensional lattice alluded to in point 6 is perfectly defined as a mathematical object, but tells us little from an intuitive point of view.

You will see now how the concept of a *lattice* becomes much more solid and concrete in two or three dimensions.

45. Note also that almost all the chemistry textbooks introduce the concepts of direct and reciprocal lattice as fundamental tools for the study of crystalline solids. This is absolutely correct, since the description of those systems cannot be done without a detailed presentation of these concepts.

However, it seems to me a good idea to introduce the definition of the two (strictly related) lattices starting from the (multidimensional) Fourier series. Mainly because this way the reciprocal lattice can be perceived as something which is “naturally” contained in the Fourier series, and not as a “mysterious” entity jumping out of the magician’s hat.

What I want to say here is that the concept of a reciprocal lattice always associated with a direct lattice, although being of fundamental importance in crystallography, is by no means peculiar of that field; it has, instead, a very broad spectrum of applications of which the Fourier analysis is just one among a multitude of examples (and, actually, Fourier analysis is a conceptual pillar in the study of crystalline solids).

I can add that in (at least) Kittel’s textbook,⁶ the reciprocal lattice is introduced starting from the Fourier series.

46. In this part I will make a first introduction and will come back with more details in the part concerning crystalline solids.

1.3.1 The reciprocal lattice in one dimension

47. To begin with, let us take the exponential form of the Fourier series for a T -periodic function of a single variable (eq. 101 and 102):

$$f(x) = \sum_{n=-\infty}^{\infty} B_n \exp\left(i \frac{2\pi n}{T} x\right) \quad (106)$$

$$B_n = \frac{1}{T} \int_a^{a+T} f(x) \exp\left(-i \frac{2\pi n}{T} x\right) dx$$

As already said in point 6, being T -periodic, the function f “naturally” defines a (monodimensional) lattice, whose primitive cell is the segment of amplitude T (figure 2). This “direct lattice” is made up by the infinite T -spaced values:

$$\dots - 2 \times T \quad - 1 \times T \quad 0 \times T \quad 1 \times T \quad 2 \times T \dots \quad (107)$$

If you now look closely at the Fourier expansion 106, you will realize very easily that it is completely defined by the infinite equally spaced values: $n(2\pi/T)$, $n \in \mathbb{Z}$:

$$\dots - 2 \times \left(\frac{2\pi}{T}\right) \quad - 1 \times \left(\frac{2\pi}{T}\right) \quad 0 \times \left(\frac{2\pi}{T}\right) \quad 1 \times \left(\frac{2\pi}{T}\right) \quad 2 \times \left(\frac{2\pi}{T}\right) \dots \quad (108)$$

What I want to say here is: any one of the $n(2\pi/T)$ points is all we need to “build” a corresponding term in the sum 106; namely, the exponential in the sum and the exponential in the expression for B_n ; everything else is “fixed” by the function to be expanded (which, of course, we assume to be known) and by the general prescription of the Fourier expansion.

Exactly like the T -spaced values which define the direct lattice, also these values do define a (monodimensional) lattice which we call *reciprocal lattice* and which we will represent with the

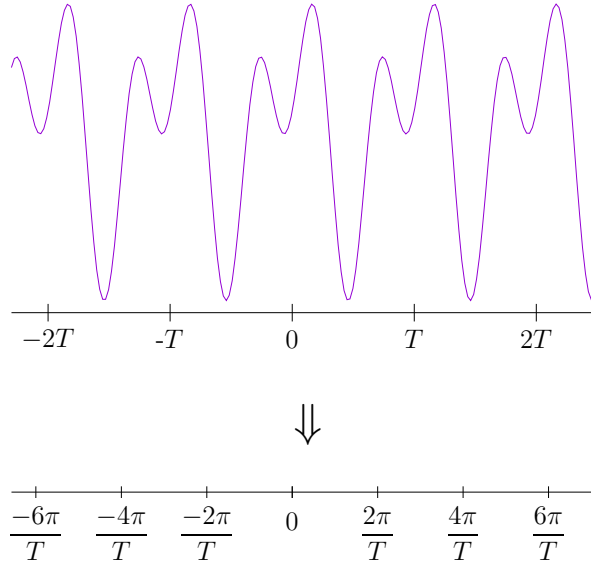


Figure 5: A T -periodic function defines not only a direct lattice, but also a corresponding reciprocal lattice, whose points are given by $n(2\pi/T)$. These values are the (infinite and equally spaced) angular frequencies which build up the Fourier expansion of the function.

symbol $\mathcal{R}^*$ from now on (figure 5). The primitive cell of the reciprocal lattice is the constant spacing of its constituent points, that is the segment of length $2\pi/T$.

It is also apparent that there exists a bijective (that is: one-to-one) map between the points of the reciprocal lattice and the terms of the Fourier expansion of the function f . For example, the point $7 \times 2\pi/T$ maps onto one (and only one) term of the Fourier series:

$$B_7 \exp \left(i \frac{2\pi}{T} 7x \right) \quad (109)$$

with:

$$B_7 = \frac{1}{T} \int_a^{a+T} f(x) \exp \left(-i \frac{2\pi}{T} 7x \right) dx \quad (110)$$

48. If you look back to the trigonometric form of the Fourier series (eq. 24) you realize a simple interpretation of the reciprocal lattice: the points of the reciprocal lattice (i.e. in 1D, the numbers $n(2\pi/T)$, $n \in \mathbb{Z}$) are the angular frequencies of all the sines and cosines into which a given T -periodic function can be Fourier expanded.

49. If we call k a generic point of the reciprocal lattice induced by the T -periodic function $f(x)$, that is:

$$k = n \frac{2\pi}{T} \quad (111)$$

then we can write its Fourier expansion as:

$$f(x) = \sum_{k \in \mathcal{R}^*} B_k \exp(ikx) \quad (112)$$

$$B_k = \frac{1}{T} \int_a^{a+T} f(x) \exp(-ikx) dx \quad (113)$$

where the sum runs over all the infinite (but discrete) k points of the reciprocal lattice. Note that k , as defined by 111, is a multiple of what we called “angular frequency” (at point 13) of the T -periodic function $f(x)$.

50. Remark: given the T -periodic function $f(x)$, the associated direct lattice is defined on the x axis (i.e. the whole set of real numbers, $\mathbb{R}$, used to represent the values of the independent variable x): as already mentioned, we call this the “direct space”; on the other hand, the reciprocal lattice is defined on a *different* axis, representing continuous values of the variable $z(2\pi/T)$ ($z \in \mathbb{R}$) (you can think of this variable as a “continuous angular frequency”); of course, the axis into which the points of the reciprocal lattice are “immersed” is, again, the whole set of real numbers, $\mathbb{R}$ (and we will refer to it as the “reciprocal space”): the points defining the reciprocal lattice are given by all the *integer* values of z : $z = -\infty, \dots, -2, -1, 0, 1, 2, \dots, \infty$. As just said (in 1D), both direct and reciprocal lattices are “immersed” in $\mathbb{R}$ ($\mathcal{R}, \mathcal{R}^* \subset \mathbb{R}$), the set of the real numbers: I mean that, in a purely mathematical sense, both the points of the direct lattice and those of the reciprocal lattice are real numbers; however, they represent different, although strictly related, physical quantities.

You can better realize that the two axes are different (in the sense that they represent different physical quantities) by noting that their units are correspondingly different. For instance, if the independent variable on which the function depends is a linear distance, then x (and the period of the function T) will have units of, say, $\text{\AA}$; on the other hand, the units of the quantity reported on the reciprocal axis will be, consistently, $\text{\AA}^{-1}$, i.e. the *inverse* of the units of the direct axis. This is one of many so called “reciprocity relations” between the direct and reciprocal lattice (and, actually, the reason why the reciprocal lattice is called like that).

51. Before proceeding, we can summarize the main points of our analysis (limited, until now, to functions of a single variable).

Any T -periodic function always induces *two* associated lattices (both “immersed” in $\mathbb{R}$):

the direct lattice whose points are given by:

$$nT, \quad n \in \mathbb{Z} \quad (114)$$

The direct lattice defines the periodicity of the function.

the reciprocal lattice whose points are given by:

$$n \frac{2\pi}{T}, \quad n \in \mathbb{Z} \quad (115)$$

The reciprocal lattice defines the Fourier expansion of the function. It is the set of all the discrete angular frequencies of the sines and cosines appearing in the Fourier expansion.

An important and useful interpretation of the reciprocal lattice is:

Any periodic function has an associated reciprocal lattice and each point of this reciprocal lattice gives a corresponding term of the Fourier expansion of the function.

For this reason, the reciprocal space is also called *Fourier space*.

1.3.2 Periodic functions in two and three dimensions

52. In the previous section we introduced the important concept of a reciprocal lattice for a function of a single variable, $f(x)$.

We will now see how all this can be extended to the case of functions of two or three variables.

Open parenthesis: notation.

When dealing with functions of two or three variables we will make use of the vectorial formalism, of which I am assuming that you all have a basic knowledge.

I will represent a function of three variables with either of the two equivalent notations:

$$f(x, y, z) \quad \text{or} \quad f(\vec{r}) \quad (116)$$

where $\vec{r} = (x, y, z)$ is the vector whose three components are (x, y, z) . In a cartesian reference system, $\vec{r}$ starts from the origin and reaches the point whose cartesian coordinates are (x, y, z) . $\vec{r}$ is also called *position vector*.

Of course, I will use the same notation also for functions of two variables x, y :

$$f(x, y) \quad \text{or} \quad f(\vec{r}) \quad (117)$$

with $\vec{r} = (x, y)$.

Closed parenthesis.

53. It is convenient to introduce the argument by first considering a periodic function of only two variables: $f(x, y)$. This is so because the graph of a 2D function can be easily represented (and thought of), while it is not so easy to deal with the graph of a 3D function.

As we already saw, 1D periodicity can be represented by a monodimensional direct lattice whose primitive cell is an interval of amplitude equal to the period: a 1D periodic function will assume identical values on all points of the x axis separated by an integer number of periods:

$$f(x + kT) = f(x) \quad \forall x \in \mathbb{R}, \forall k \in \mathbb{Z} \quad (\text{eq. 1})$$

or, indicating with $R = kT$ a generic point of the direct lattice $\mathcal{R}$:

$$f(x + R) = f(x) \quad \forall x \in \mathbb{R}, \forall R \in \mathcal{R} \quad (\text{eq. 4})$$

The extension of this description to the 2D case is straightforward and intuitive. Also the periodicity of a function of two independent variables can be described by a lattice which, however, in this case, is a bidimensional lattice (thus, a real network, even in the common sense of this term) immersed in $\mathbb{R}^2$. Similar to the monodimensional case, we call this *direct* (or *real* or even *Bravais*) *lattice* and we refer to the *continuous* $\mathbb{R}^2$ space as the *direct space*. Being bidimensional, this lattice is composed of (infinite) identical meshes: a single mesh is called *primitive or elementary cell* (symbol $\mathcal{C}$).

In general, the primitive cell of the direct lattice defining the periodicity of a 2D function is a *parallelogram*.

54. The most efficient mathematical description of the direct lattice (and thus of a periodic function of two variables) is obtained using the vector notation (refer to fig. 6). The primitive cell (that is, the single mesh) of the lattice is defined by two non parallel vectors $\vec{a}_1, \vec{a}_2$, corresponding to two consecutive sides of the parallelogram and called *primitive* or *generator* vectors of the lattice.

Being non parallel, the primitive vectors, thought of as elements of the $\mathbb{R}^2$ vector space, are linearly independent and thus constitute a *basis* (in the algebraic sense) of $\mathbb{R}^2$.

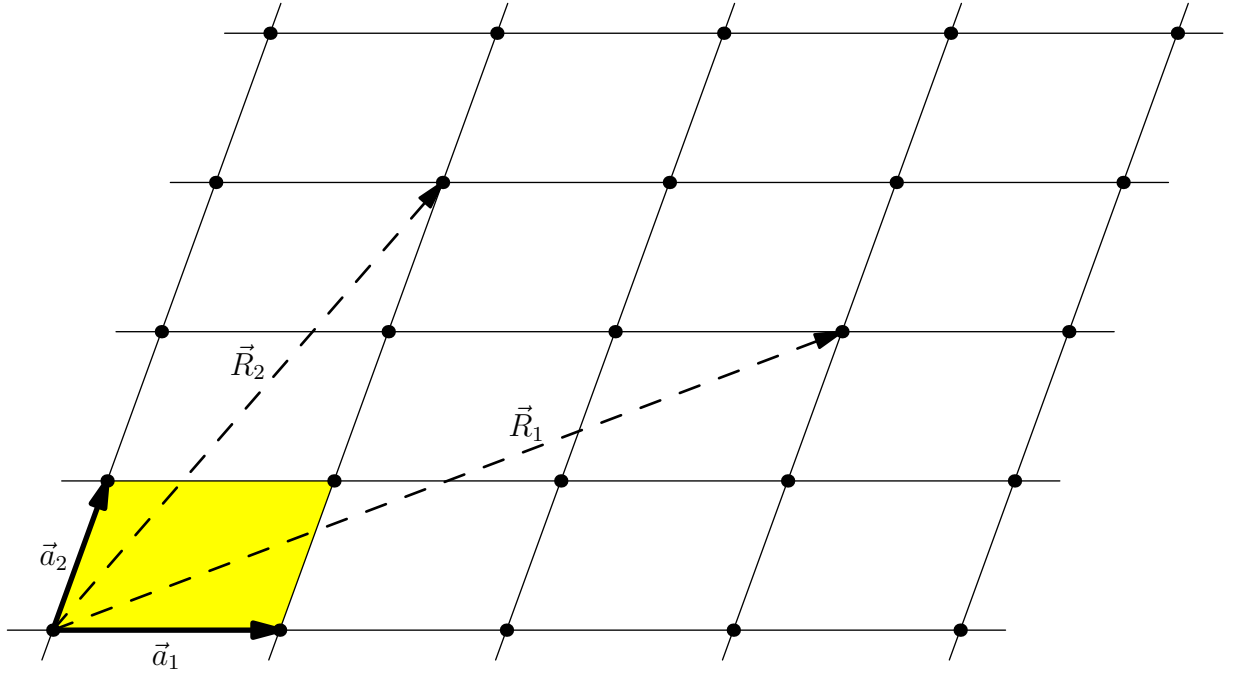


Figure 6: A portion of a bidimensional Bravais lattice. The primitive cell, defined by two non parallel vectors $\vec{a}_1, \vec{a}_2$, has been evidenced. Two (among the infinite) lattice points, $\vec{R}_1 = 3\vec{a}_1 + 2\vec{a}_2$ and $\vec{R}_2 = \vec{a}_1 + 3\vec{a}_2$, are also shown.

Any point of $\mathbb{R}^2$ can be reached with a proper linear combination of $\vec{a}_1, \vec{a}_2$. However, all (and only) the points of the direct lattice (which, of course, are elements of $\mathbb{R}^2$) are obtained by a linear combination of $\vec{a}_1, \vec{a}_2$ with integer coefficients.

That is, calling $\vec{R}$ the vector locating any lattice point, we have:

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 \quad n_1, n_2 \in \mathbb{Z} \quad (118)$$

We will say that a bidimensional function $f(x, y) = f(\vec{r})$ is periodic on a Bravais lattice defined by the two primitive vectors $\vec{a}_1, \vec{a}_2$ if:

$$f(\vec{r} + \vec{R}) = f(\vec{r} + n_1 \vec{a}_1 + n_2 \vec{a}_2) = f(\vec{r}) \quad \forall \vec{r} \in \mathbb{R}^2, \quad \forall n_1, n_2 \in \mathbb{Z} \quad (119)$$

or, equivalently and more concisely:

$$f(\vec{r} + \vec{R}) = f(\vec{r}) \quad \forall \vec{r} \in \mathbb{R}^2, \quad \forall \vec{R} \in \mathcal{R} \quad (120)$$

55. Note the formal correspondence of 120 with 4, which we wrote for the 1D case. On that instance, the primitive cell was a segment of the x axis and thus its complete definition only required a single scalar value, namely its linear amplitude T .

If you think of this amplitude as the modulus of a monodimensional vector $\vec{T}$ (having the fixed direction of the x axis), then “promoting” the scalar variable x to a “vector” of a single component, the condition of periodicity for a monodimensional function $f(\vec{x})$ can be expressed in vectorial notation in exactly the same form as 120:

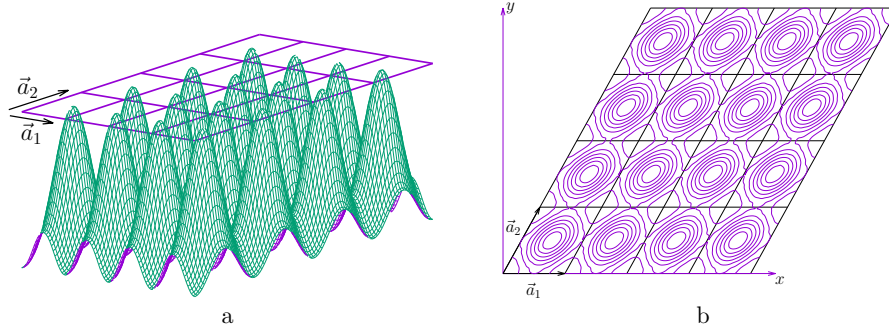


Figure 7: The 2D periodic function:

$$f(x, y) = 2g_0 \left(\cos\left(\frac{2\pi}{\lambda_x}x\right) + \cos\left(\frac{2\pi}{\lambda_y}y\right) \right) + 2g_1 \left(\cos\left(\frac{2\pi}{\lambda_x}x\right) + \cos\left(\frac{2\pi}{\lambda_y}y\right) \right)$$

and its associated Bravais lattice; a: the complete graph with the Bravais lattice evidenced (on top); b: the same graph represented on the x, y plane with isocurves. The two generator vectors of the lattice are also shown.

$$f(\vec{x} + \vec{R}) = f(\vec{x}) \quad \forall \vec{x} \in \mathbb{R}, \quad \forall \vec{R} \in \mathcal{R} \quad (121)$$

and the monodimensional analog of 118 becomes (eq. 3):

$$\vec{R} = k\vec{T} \quad k \in \mathbb{Z} \quad (122)$$

that is: a “linear combination” with an integer coefficient (k) of the single primitive vector $\vec{T}$, that locates all points in the monodimensional Bravais lattice.

56. In fig. 7a I have built the graph of a 2D periodic function highlighting the Bravais lattice which defines its periodicity. This latter can be more easily appreciated in fig. 7b, where the graph is represented on the x, y plane with isocurves (that is curves that are loci of the x, y points on which the value of the function is constant).

57. The 2D $\rightarrow$ 3D extension of the above concepts involves no additional difficulties.

The graph of a 3D periodic function repeats identical to itself in regions of $\mathbb{R}^3$ (instead of $\mathbb{R}^2$) space which are all identical parallelepipeds (instead of parallelograms).

A 3D periodic function $f(x, y, z) = f(\vec{r})$ induces a 3D Bravais lattice $\mathcal{R}$, whose primitive cell is a parallelepiped defined by three non coplanar primitive vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ which are three sides of the parallelepiped sharing a common vertex.

The generic point $\vec{R}$ of the lattice is located by a linear combination of the three primitive vectors *with integer coefficients*:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \quad n_1, n_2, n_3 \in \mathbb{Z} \quad (123)$$

(compare with 118)

Fig. 8 shows a portion of a 3D Bravais lattice, of which the primitive cell is also evidenced.

The condition of periodicity for a 3D function is expressed in a manner formally identical to that seen for a 2D function:

$$f(\vec{r} + \vec{R}) = f(\vec{r}) \quad \forall \vec{r} \in \mathbb{R}^3 \text{ e } \forall \vec{R} \in \mathcal{R} \quad (124)$$

(compare with 120)

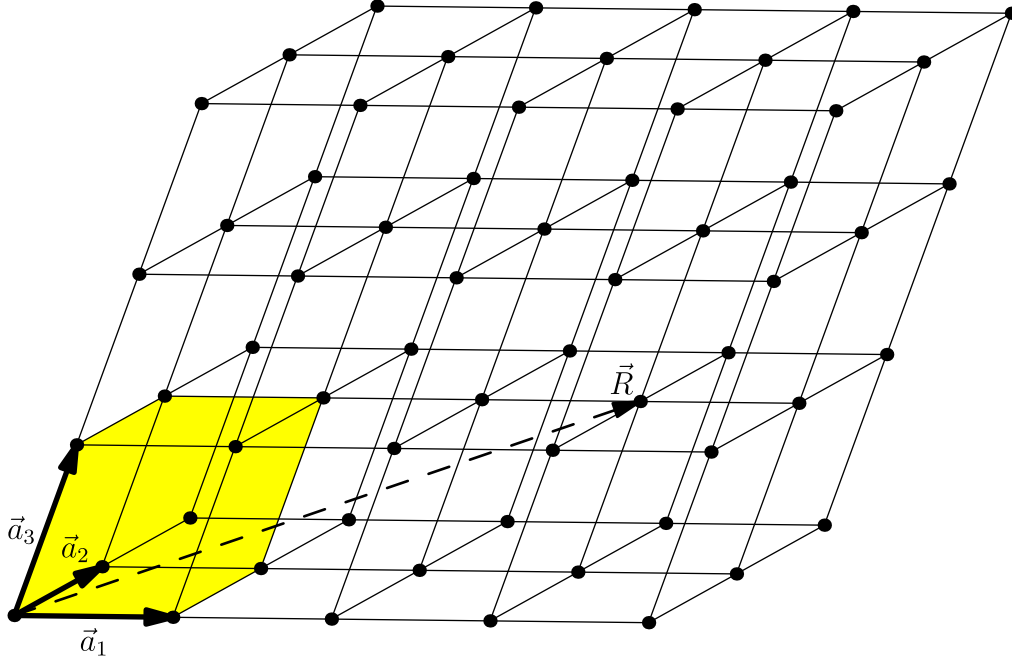


Figure 8: The portion of a 3D Bravais lattice. The primitive cell of the lattice, as defined by the three primitive vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ is evidenced. A lattice point located by the linear combination:

$$\vec{R} = 3\vec{a}_1 + \vec{a}_2 + \vec{a}_3$$
is also shown.

1.3.3 The fourier expansion of a function of two or three variables

58. We shall now derive the expression for the Fourier expansion of a 2D or 3D periodic function. As you will see, the final result is formally identical to the complex exponential form that we arrived at for a 1D function (eq. 112).

The derivation is very loose, but hopefully convincing enough and certainly, educationally, more effective than the bare-bones presentation of the end result.

In the following I have favored generality at the expense of the notation, which perhaps may be perceived as a bit heavy. However, if you “tune in” to the procedure, you should be able to follow with no difficulty.

Let’s focus on a periodic function of two or three variables:

$$f(\vec{r}), \vec{r} \in \mathbb{R}^D, D \in \{2, 3\} \quad (125)$$

The periodicity of f is mathematically described by a Bravais lattice $\mathcal{R}$, whose primitive cell is defined by the vectors $\vec{a}_j$, $j = 1, \dots, D$.

1.3.3.1 The proposal

59. For the Fourier expansion of a T –periodic monodimensional function we arrived at 112:

$$f(x) = \sum_k B_k \exp(ikx)$$

the sum running over the infinite points of the reciprocal lattice:

$$k = n \frac{2\pi}{T} \quad n \in \mathbb{Z}$$

By analogy, for the multidimensional case, we now propose:

$$f(\vec{r}) = \sum_{\vec{k}} B_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) \quad (126)$$

where the sum terms are indexed by $\vec{k}$ vectors which, for the moment, are still unknown (in 126, $\vec{k} \cdot \vec{r}$ is the dot (also called scalar) product of $\vec{k}$ and $\vec{r}$). Still in strict analogy with the 1D case, the $B_{\vec{k}}$ coefficients are assumed to be independent on $\vec{r}$.

Of course, this is a weak point of the derivation: why this formula? Who assures us that it is the right choice for the $D > 1$ cases?

The answer to these questions can be obtained in a mathematically rigorous way; however, we will content ourselves by verifying that 126 actually works, as we did in the monodimensional case ($D = 1$) in section 1.2.

Note, however, that the complex exponential is a periodic function (point 17) and thus is well suited for the series expansion of a periodic function.

60. For the 1D case we saw that:

$$k = n \frac{2\pi}{T}$$

was the necessary and sufficient condition for all the terms of the Fourier expansion to have the same periodicity as the function being expanded (point 20).

The same requirement has to be satisfied for the 2D or 3D case ($D > 1$); that is: the exponentials in 126:

$$\exp(i\vec{k} \cdot \vec{r}) \quad (127)$$

must have the same periodicity as the $f(\vec{r})$, if we want that our proposal 126 can actually work. However, in the multidimensional case finding the $\vec{k}$ vectors which satisfy the periodicity condition is not trivial.

Thus, differently from the 1D case, the validation of 126 requires the solution of two problems:

1. find the $\vec{k}$ vectors
2. find the expression for the corresponding $B_{\vec{k}}$'s.

1.3.3.2 The $\vec{k}$ vectors (first part)

61. As just said above, the $\vec{k}$ vectors in 126 must be such that the exponentials are periodic on the same Bravais lattice on which the function $f(\vec{r})$ is periodic.

Which is to say, based on 124:

$$\exp(i\vec{k} \cdot (\vec{r} + \vec{R})) = \exp(i\vec{k} \cdot \vec{r}) \quad \forall \vec{r} \in \mathbb{R}^D, \forall \vec{R} \in \mathcal{R} \quad (128)$$

Now: for the left hand side (LHS) it holds that:

$$\exp(i\vec{k} \cdot (\vec{r} + \vec{R})) = \exp(i\vec{k} \cdot \vec{r}) \exp(i\vec{k} \cdot \vec{R}) \quad (129)$$

and thus the periodicity condition amounts to require that:

$$\exp(i\vec{k} \cdot \vec{R}) = 1 \quad \forall \vec{R} \in \mathcal{R} \quad (130)$$

or, based on what we saw in point 17:

$$\vec{k} \cdot \vec{R} = 2\pi n \quad n \in \mathbb{Z} \quad \forall \vec{R} \in \mathcal{R} \quad (131)$$

The generic $\vec{R}$ vector of the Bravais lattice $\mathcal{R}$ is expressed as a linear combination (with integer coefficients) of the primitive vectors $\vec{a}_l$ (eq. 118 or 123):

$$\vec{R} = \sum_{l=1}^D n_l \vec{a}_l \quad (132)$$

(remember that D is the dimensionality of the function, or, equivalently, the number of its independent variables: 2 o 3; $D \in \{2, 3\}$)

In a similar way, we can express $\vec{k}$ with respect to a (presently still undefined) basis $\vec{b}_j$, $j = 1, \dots, D$ of $\mathbb{R}^D$:

$$\vec{k} = \sum_{j=1}^D m_j \vec{b}_j \quad (133)$$

(note: at this point the m_j coefficients can be any real numbers)

This way, eq. 131 becomes:

$$\vec{k} \cdot \vec{R} = \left(\sum_{j=1}^D m_j \vec{b}_j \right) \cdot \left(\sum_{l=1}^D n_l \vec{a}_l \right) = \sum_{j,l} m_j n_l \vec{b}_j \cdot \vec{a}_l = 2\pi n \quad (134)$$

(I have implied the variation limits of the j and l indices in the last sum)

Now: eq. 131 must hold *for every* $\vec{R}$ vector of the Bravais lattice, that is for every possible choice of the n_l integers in 134.

Keeping this in mind, realize that a sufficient condition for the validity of 134 is:

$$\begin{cases} \vec{b}_j \cdot \vec{a}_l = 2\pi \delta_{jl} \\ m_j \in \mathbb{Z} \end{cases} \quad (135)$$

where δ_{jl} is the (hopefully well known to all of you) *Kronecker delta*, whose definition is:

$$\delta_{jl} = \begin{cases} 1 & \text{if } j = l \\ 0 & \text{if } j \neq l \end{cases} \quad (136)$$

Indeed, if 135 holds, then:

$$\forall \vec{R} \in \mathcal{R} \quad \vec{k} \cdot \vec{R} = \sum_{j,l} m_j n_l \vec{b}_j \cdot \vec{a}_l = 2\pi \sum_{j,l} \overbrace{m_j n_l \delta_{jl}}^{=0 \text{ when } j \neq l} = 2\pi \sum_j \overbrace{m_j n_j}^{=n} = 2\pi n \quad n \in \mathbb{Z} \quad (137)$$

where the final equality is ensured by the hypothesis $m_j \in \mathbb{Z}$ (eq. 135).

Remark: the $\vec{k}$ vectors defined by 135 are solutions of 131 and thus they ensure that the exponential terms of the expansion 126 originally proposed have the same periodicity as $f(\vec{r})$; you might ask yourselves whether further solutions exist. In this regard, it is possible to prove (but we will not do this) that 135 is the only possible solution; that is, eq. 135 is sufficient *and necessary* condition for the validity of 134.

62. We have thus partially answered the first question: who are the $\vec{k}$'s?

The answer is only partial because the $\vec{k}$ vectors are defined by 133 and we still lack a practical “recipe” to build the $\vec{b}_j$ basis vectors.

We will solve this problem in a while.

For the moment note that the solution we found requires that the coefficients of the linear combination 133 cannot be any real numbers, but they must be instead integer numbers (eq. 135). From this it follows that the $\vec{k}$ vectors, exactly like the vectors of the Bravais lattice $\mathcal{R}$, define the points of another regular lattice which, as was the case for a 1D function, we will call the *reciprocal lattice* associated with $\mathcal{R}$ and we will represent with $\mathcal{R}^*$.

The $\vec{b}_j$'s are the primitive vectors of $\mathcal{R}^*$.

63. The meaning of the just introduced reciprocal lattice is identical to that seen in the 1D case: to every $\vec{k}$ vector of the reciprocal lattice $\mathcal{R}^*$ it corresponds a term in the Fourier expansion of the $f(\vec{r})$: refer to 126.

1.3.3.3 The $B_{\vec{k}}$ coefficients

64. Before showing how the generator vectors of the reciprocal lattice $\vec{b}_j$ (from which all the infinite $\vec{k}$ vectors are generated) can be actually obtained, we are already in the position to derive an expression for the $B_{\vec{k}}$ coefficients of the Fourier expansion 126.

As anticipated, you will see that the final expression will be formally identical to the one we got in the 1D case. Also the procedure is very similar.

65. Let's start from 126:

$$f(\vec{r}) = \sum_{\vec{k}} B_{\vec{k}} \exp(i\vec{k} \cdot \vec{r})$$

We pick one of the infinite $\vec{k}$ vectors and call it $\vec{k}'$. Multiply both sides of 126 by $\exp(-i\vec{k}' \cdot \vec{r})$ and integrate over the area ($D = 2$) or the volume ($D = 3$) V of a primitive cell:

$$\int_V f(\vec{r}) \exp(-i\vec{k}' \cdot \vec{r}) d\vec{r} = \int_V \exp(-i\vec{k}' \cdot \vec{r}) \sum_{\vec{k}} B_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) d\vec{r} \quad (138)$$

Open parenthesis.

I introduce here a notation which I will be using many times and that is used in almost every textbook.

When writing:

$$\int_Q \dots d\vec{r}$$

I mean a double or triple integral (depending on the dimensionality) evaluated on the surface or volume Q , respectively. The $d\vec{r}$ differential is a shorthand for “ $dx dy$ ” or “ $dx dy dz$ ”, respectively. Thus:

dimensionality	notation	meaning
2D	$\int_Q \dots d\vec{r}$	$\int_{x_1}^{x_2} \int_{y_1}^{y_2} \dots dx dy$
3D	$\int_Q \dots d\vec{r}$	$\int_{x_1}^{x_2} \int_{y_1}^{y_2} \int_{z_1}^{z_2} \dots dx dy dz$

Closed parenthesis.

In the RHS of the previous equation we can move the exponential term containing $\vec{k}'$ under the sum sign (it does not depend on $\vec{k}$); moreover, thanks to the linearity of the integral operator, we can swap the integral and the sum, which brings us to:

$$\int_V f(\vec{r}) \exp(-i\vec{k}' \cdot \vec{r}) d\vec{r} = \sum_{\vec{k}} \int_V B_{\vec{k}} \exp(i(\vec{k} - \vec{k}') \cdot \vec{r}) d\vec{r} \quad (139)$$

When $\vec{k} = \vec{k}'$ in the sum, the exponential is equal to 1 and the integral is trivial:

$$\vec{k} = \vec{k}' \implies \int_V B_{\vec{k}} \exp(i(\vec{k} - \vec{k}') \cdot \vec{r}) d\vec{r} = \int_V B_{\vec{k}'} d\vec{r} = B_{\vec{k}'} \int_V d\vec{r} = B_{\vec{k}'} V \quad (140)$$

So: let's factor out of the sum that particular term corresponding to $\vec{k} = \vec{k}'$:

$$\int_V f(\vec{r}) \exp(-i\vec{k}' \cdot \vec{r}) d\vec{r} = B_{\vec{k}'} V + \sum_{\vec{k} \neq \vec{k}'} \int_V B_{\vec{k}} \exp(i(\vec{k} - \vec{k}') \cdot \vec{r}) d\vec{r} \quad (141)$$

Now our next task is to show that all the terms in the sum for $\vec{k} \neq \vec{k}'$ are null, and thus the sum itself is null.

First realize that the $B_{\vec{k}}$'s do not depend on $\vec{r}$ and thus can be factored out of the integral; the sum in 141 becomes:

$$\sum_{\vec{k} \neq \vec{k}'} B_{\vec{k}} \int_V \exp(i(\vec{k} - \vec{k}') \cdot \vec{r}) d\vec{r}$$

66. Now we show that:

$$\vec{k} \neq \vec{k}' \implies \int_V \exp(i(\vec{k} - \vec{k}') \cdot \vec{r}) d\vec{r} = 0 \quad (142)$$

(pin this proof, because we will make use of it also in another section (p. 472))

Let $\vec{K} = \vec{k} - \vec{k}'$. Since the sum runs over all $\vec{k} \neq \vec{k}'$, $\vec{K}$ is $\neq 0$. So what we want to show is:

$$\int_V \exp(i(\vec{k} - \vec{k}') \cdot \vec{r}) d\vec{r} = \int_V \exp(i\vec{K} \cdot \vec{r}) d\vec{r} = 0 \quad \forall \vec{K} \neq 0 \quad (143)$$

First of all realize that $\vec{K} = \vec{k} - \vec{k}'$ is still a vector of $\mathcal{R}^*$ (just write explicitly two vectors of $\mathcal{R}^*$ as linear combinations of the primitive vectors with integer coefficients and take the difference).

67. Proving 143 in 1D is very simple.

In fact, in such case, the primitive cell of the direct lattice $\mathcal{R}$ is just a segment of the real axis of length T (fundamental period of the function); the variable $\vec{r}$ becomes a simple scalar and the generic non-null point $\vec{K} \in \mathcal{R}^*$ becomes the scalar $2\pi n/T$ (section 1.3.1) with $n \neq 0$:

$$V \longrightarrow T \quad (144)$$

$$\vec{r} \longrightarrow x \quad (145)$$

$$\vec{K} \longrightarrow \frac{2\pi}{T} n \quad (n \neq 0) \quad (146)$$

Under such conditions we have:

$$\begin{aligned} \int_V \exp(i\vec{K} \cdot \vec{r}) d\vec{r} &\longrightarrow \int_a^{a+T} \exp\left(i\frac{2\pi}{T} nx\right) dx \\ &= \int_a^{a+T} \cos\left(\frac{2\pi}{T} nx\right) dx + i \int_0^T \sin\left(\frac{2\pi}{T} nx\right) dx = 0 \end{aligned} \quad (147)$$

where the last equality follows from the (trivial) results which we presented when we introduced the Fourier series (eq. 25 and 33, and keep in mind that $n \neq 0$).

68. For the $D > 1$ case, I present here the proof offered by Ashcroft and Mermin:⁸ by admission of the authors themselves, it is not rigorous, but it is convincing.

If you are interested, I display a more formal proof in section 1.1 of the extracurricular part.

Being a term in the Fourier expansion of $f(\vec{r})$, which is, this latter, periodic on $\mathcal{R}$, the exponential $\exp(i\vec{K} \cdot \vec{r})$ is itself periodic on $\mathcal{R}$ (section 1.3.3) (remember that the complex exponential is, in general, a periodic function, point 17).

From this it follows that the integral evaluated on V (that is, the primitive cell of $\mathcal{R}$):

$$\int_V \exp(i\vec{K} \cdot \vec{r}) d\vec{r} \quad (148)$$

is invariant with respect to an arbitrary translation $\vec{d}$ of the function being integrated (we did prove this only for the 1D case in point 12, but I also told you that this property holds true also in $\mathbb{R}^n$).

Thus, for any vector $\vec{d}$ (not necessarily a vector of $\mathcal{R}$) it must hold that:

$$\int_V \exp(i\vec{K} \cdot \vec{r}) d\vec{r} = \int_V \exp(i\vec{K} \cdot (\vec{r} + \vec{d})) d\vec{r} \quad \forall \vec{d} \in \mathbb{R}^D \quad (149)$$

which can be rearranged as:

$$\begin{aligned} \int_V \exp(i\vec{K} \cdot \vec{r}) d\vec{r} &= \int_V \exp(i\vec{K} \cdot \vec{r}) \exp(i\vec{K} \cdot \vec{d}) d\vec{r} \\ &= \exp(i\vec{K} \cdot \vec{d}) \int_V \exp(i\vec{K} \cdot \vec{r}) d\vec{r} \quad \forall \vec{d} \in \mathbb{R}^D \end{aligned}$$

$$(1 - \exp(i\vec{K} \cdot \vec{d})) \int_V \exp(i\vec{K} \cdot \vec{r}) d\vec{r} = 0 \quad \forall \vec{d} \in \mathbb{R}^D \quad (150)$$

This equality must be true for *any* $\vec{d}$ vector; but, since $\vec{K} \neq 0$, the factor multiplying the integral cannot be null for *any* $\vec{d}$ vector, and thus it is the integral that must inevitably be null.

But this implies, as anticipated, that the whole sum in 141 is null.

69. In the end, eq. 141 reduces to:

$$\int_V f(\vec{r}) \exp(-i\vec{k}' \cdot \vec{r}) d\vec{r} = B_{\vec{k}'} V \quad (151)$$

or:

$$B_{\vec{k}'} = \frac{1}{V} \int_V f(\vec{r}) \exp(-i\vec{k}' \cdot \vec{r}) d\vec{r} \quad (152)$$

and since $\vec{k}'$ was arbitrary, we can replace k' with k and our final result is:

$$B_{\vec{k}} = \frac{1}{V} \int_V f(\vec{r}) \exp(-i\vec{k} \cdot \vec{r}) d\vec{r} \quad (153)$$

70. If you compare eq. 153 just obtained with 113 for the 1D case, you should immediately appreciate the formal equivalence: the length of the integration interval T in the monodimensional case has become the area (2D) or the volume (3D) for the multidimensional case and the simple product “ kx ” has turned into a scalar product of vectors “ $\vec{k} \cdot \vec{r}$ ”; apart from that, the two expressions are just identical.

We have solved the second problem mentioned on p. 39.

1.3.3.4 The $\vec{k}$ vectors (second part)

71. We are left to find the expression for the primitive vectors $\vec{b}_j$ of the reciprocal lattice $\mathcal{R}^*$. Remember that these vectors define all the points of $\mathcal{R}^*$ through 133.

What we are going to do in this section is to find the expression of the $\vec{b}_j$'s as a function of the primitive vectors $\vec{a}_j$ of the *direct* lattice $\mathcal{R}$: that is, given a $f(\vec{r})$ function periodic over a Bravais lattice defined by primitive vectors $\vec{a}_l$, we will sort out the expression of the primitive vectors of the associated *reciprocal* lattice $\mathcal{R}^*$ as a function of the $\vec{a}_l$'s.

72. The starting point is condition 135.

73. A first approach to the problem might be analytical: by writing the $\vec{b}_j$'s and $\vec{a}_l$'s in terms of their cartesian components and performing the scalar products in 135, a linear system for the unknown components of the $\vec{b}_j$ vectors is obtained.

For the $D = 3$ case, letting:

$$\begin{aligned} \vec{a}_l &= (a_{lx}, a_{ly}, a_{lz}) \\ \vec{b}_j &= (b_{jx}, b_{jy}, b_{jz}) \end{aligned}$$

condition 135 becomes:

$$\begin{aligned} \vec{b}_1 \cdot \vec{a}_1 &= b_{1x}a_{1x} + b_{1y}a_{1y} + b_{1z}a_{1z} = 2\pi \\ \vec{b}_1 \cdot \vec{a}_2 &= b_{1x}a_{2x} + b_{1y}a_{2y} + b_{1z}a_{2z} = 0 \\ \vec{b}_1 \cdot \vec{a}_3 &= b_{1x}a_{3x} + b_{1y}a_{3y} + b_{1z}a_{3z} = 0 \\ \vec{b}_2 \cdot \vec{a}_1 &= b_{2x}a_{1x} + b_{2y}a_{1y} + b_{2z}a_{1z} = 0 \\ \vec{b}_2 \cdot \vec{a}_2 &= b_{2x}a_{2x} + b_{2y}a_{2y} + b_{2z}a_{2z} = 2\pi \\ \vec{b}_2 \cdot \vec{a}_3 &= b_{2x}a_{3x} + b_{2y}a_{3y} + b_{2z}a_{3z} = 0 \\ \vec{b}_3 \cdot \vec{a}_1 &= b_{3x}a_{1x} + b_{3y}a_{1y} + b_{3z}a_{1z} = 0 \\ \vec{b}_3 \cdot \vec{a}_2 &= b_{3x}a_{2x} + b_{3y}a_{2y} + b_{3z}a_{2z} = 0 \\ \vec{b}_3 \cdot \vec{a}_3 &= b_{3x}a_{3x} + b_{3y}a_{3y} + b_{3z}a_{3z} = 2\pi \end{aligned}$$

For the $D = 2$ case, letting:

$$\begin{aligned}\vec{a}_l &= (a_{lx}, a_{ly}) \\ \vec{b}_j &= (b_{jx}, b_{jy})\end{aligned}$$

condition 135 becomes:

$$\begin{aligned}\vec{b}_1 \cdot \vec{a}_1 &= b_{1x}a_{1x} + b_{1y}a_{1y} &= 2\pi \\ \vec{b}_1 \cdot \vec{a}_2 &= b_{1x}a_{2x} + b_{1y}a_{2y} &= 0 \\ \vec{b}_2 \cdot \vec{a}_1 &= b_{2x}a_{1x} + b_{2y}a_{1y} &= 0 \\ \vec{b}_2 \cdot \vec{a}_2 &= b_{2x}a_{2x} + b_{2y}a_{2y} &= 2\pi\end{aligned}$$

As said above, a linear system (of D^2 dimension) is obtained whose solution gives the unknown components of the $\vec{b}_j$'s (of course, the components of the $\vec{a}_l$ are assumed to be known).

If you are interested, the solution of the system for the simpler 2D case is detailed in section 1.2 of the extracurricular part of these notes.

74. The analytical approach is laborious and the final result of little practical use, as you can realize if you browse the conclusion of section 1.2 in the extracurricular part.

The sought expression of the $\vec{b}_j$ vectors can be derived in an extremely more elegant and useful way by tackling condition 135 with methods and elementary notions of vectorial algebra.

Let's start again from 135.

One first implication of it is that, when indices are different, $\vec{b}_j$ and $\vec{a}_l$ must be orthogonal (so that their scalar product is null).

In other words:

$$\begin{array}{lll} \text{when...} & \dots \text{it must be} & \\ D = 2 & \begin{array}{l} \vec{b}_1 \perp \vec{a}_2 \\ \vec{b}_2 \perp \vec{a}_1 \end{array} & \\ D = 3 & \begin{array}{ll} \vec{b}_1 \perp \vec{a}_2 & \vec{b}_1 \perp \vec{a}_3 \\ \vec{b}_2 \perp \vec{a}_3 & \vec{b}_2 \perp \vec{a}_1 \\ \vec{b}_3 \perp \vec{a}_1 & \vec{b}_3 \perp \vec{a}_2 \end{array} & \end{array} \quad (154)$$

At this point it is convenient to treat the 2D and 3D cases separately.

The 3D case (simpler)

75. For the threedimensional case it is fairly simple to guess how the above orthogonality conditions can be satisfied.

By definition, the cross product of two vectors $\vec{a}_l$ and $\vec{a}_p$ is a vector orthogonal to both $\vec{a}_l$ and $\vec{a}_p$, or, in equivalent terms, orthogonal to the plane defined by $\vec{a}_l$ and $\vec{a}_p$. Thus, if $\vec{b}_j$ must be

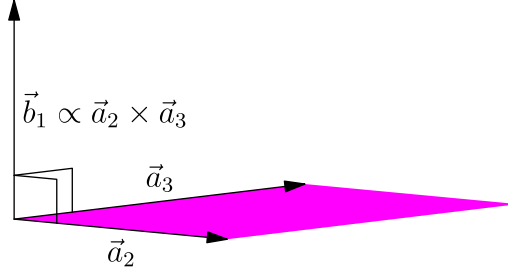


Figure 9: The $\vec{a}_2 \times \vec{a}_3$ vector is, by definition, orthogonal to both $\vec{a}_2$ and $\vec{a}_3$ and thus, if we take $\vec{b}_1$ proportional to it, condition 154:

$$\vec{b}_1 \perp \vec{a}_2 \quad \vec{b}_1 \perp \vec{a}_3$$

is satisfied.

orthogonal to both $\vec{a}_l$ e $\vec{a}_p$, it is sufficient to take it proportional (i.e. in the same direction) to the cross product $\vec{a}_l \times \vec{a}_p$ (figure 9).

In summary, for the $D = 3$ case, the orthogonality conditions 154 will be satisfied when:

$$\vec{b}_j \propto \vec{a}_l \times \vec{a}_p \quad \text{with } \{j, l, p\} \text{ cyclic permutation of } \{1, 2, 3\} \quad (155)$$

or, equivalently:

$$\vec{b}_j = \xi_j (\vec{a}_l \times \vec{a}_p) \quad (156)$$

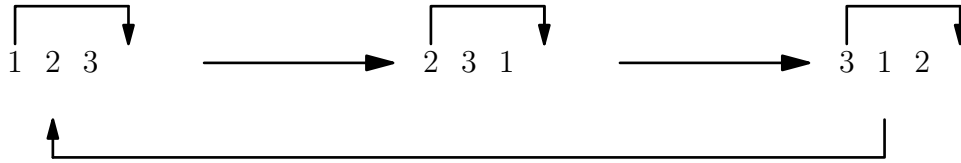
where ξ_j is a proportionality constant (a simple scalar $\in \mathbb{R}$).

Open parenthesis.

You all should know what a “cyclic permutation” is: for the $\{1, 2, 3\}$ set there are three possible cyclic permutations, namely:

$$\{1, 2, 3\} \quad \{2, 3, 1\} \quad \{3, 1, 2\}$$

Basically: for a given sequence of the elements of the set, you get the “following” cyclic permutation by moving the first element to the last place (hence for a set of three elements there are three possible distinct cyclic permutations):



Closed parenthesis.

Coming back to 156 and taking $\vec{b}_1$ as an explicit example (figure 9), eq. 156 becomes:

$$\vec{b}_1 = \xi_1 (\vec{a}_2 \times \vec{a}_3) \quad (157)$$

The $\vec{a}_2 \times \vec{a}_3$ vector is, *by definition of cross product*, orthogonal to the plane defined by $\vec{a}_2$ and $\vec{a}_3$ and thus, in particular, it is orthogonal to these two vectors. Hence, if we take $\vec{b}_1$ proportional

to $\vec{a}_2 \times \vec{a}_3$, the corresponding condition in 154 is automatically satisfied (I am assuming that you know that being proportional to one another means that two vectors have the same direction). Obviously, the same reasoning applies to $\vec{b}_2$ and $\vec{b}_3$. We thus arrive at:

$$\begin{aligned}\vec{b}_1 &= \xi_1 (\vec{a}_2 \times \vec{a}_3) \\ \vec{b}_2 &= \xi_2 (\vec{a}_3 \times \vec{a}_1) \\ \vec{b}_3 &= \xi_3 (\vec{a}_1 \times \vec{a}_2)\end{aligned}$$

We are left to find the three proportionality constants ξ_j . To this end, we start again from 135, this time, however, considering the $j = l$ case, which we did not use yet. For $\vec{b}_1$ the condition is:

$$\vec{b}_1 \cdot \vec{a}_1 = 2\pi$$

Substituting the expression found above we get:

$$\begin{aligned}\xi_1 \overbrace{(\vec{a}_2 \times \vec{a}_3) \cdot \vec{a}_1}^{\text{scalar}} &= 2\pi \\ \xi_1 &= \frac{2\pi}{(\vec{a}_2 \times \vec{a}_3) \cdot \vec{a}_1}\end{aligned}$$

(beware: $(\vec{a}_2 \times \vec{a}_3) \cdot \vec{a}_1$ is just a scalar and so the above equation is trivially of the type: $\xi_1 p = q$, with $p, q \in \mathbb{R}$)

Back substitution of ξ_1 just found gives us:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{(\vec{a}_2 \times \vec{a}_3) \cdot \vec{a}_1}$$

Of course, ξ_2 and ξ_3 are found in an identical way and we arrive at:

$$\begin{aligned}\vec{b}_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{(\vec{a}_2 \times \vec{a}_3) \cdot \vec{a}_1} \\ \vec{b}_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{(\vec{a}_3 \times \vec{a}_1) \cdot \vec{a}_2} \\ \vec{b}_3 &= 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{(\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3}\end{aligned}$$

As I said: we have found the expressions of the $\vec{b}_j$'s as a function of the $\vec{a}_l$'s.

76. The final result is usually presented in a form which is easier to remember, taking advantage of the commutative property enjoyed by the scalar product:

$$\vec{v}_1 \cdot \vec{v}_2 = \vec{v}_2 \cdot \vec{v}_1$$

and of the invariance of the so called “triple product” with respect to any cyclic permutation of the involved vectors:

$$\vec{v}_1 \cdot \vec{v}_2 \times \vec{v}_3 = \vec{v}_2 \cdot \vec{v}_3 \times \vec{v}_1 = \vec{v}_3 \cdot \vec{v}_1 \times \vec{v}_2 \quad (158)$$

The proof of the commutativity of the scalar product is trivial.

The proof of the invariance of the triple product with respect to any cyclic permutation is presented in section 1.3 of the extracurricular part.

By taking advantage of these two properties, the final result for the expressions of the primitive vectors of the reciprocal lattice $\mathcal{R}^*$ as a function of the primitive vectors of the direct lattice $\mathcal{R}$ for the 3D case can be rewritten as:

$$\begin{aligned} \vec{b}_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \\ \vec{b}_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \\ \vec{b}_3 &= 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \end{aligned} \quad (159)$$

(I have also dropped the parentheses in the denominator: realize that they are redundant)

As I said above, the above written form makes the formulas easier to remember and write: the denominator is always the same with indices in sequence: 1, 2, 3; the indices of the $\vec{b}_j$'s in the LHS and the $\vec{a}_i$'s in the numerator of the RHS are cyclically permuted: (1, 2, 3), (2, 3, 1), (3, 1, 2).

The 2D case (somehow more cumbersome)

77. Let's now turn our attention to the bidimensional case ($D = 2$).

First of all: based on what we have done in the previous case, you might be tempted to write something like:

$$\vec{b}_j \propto \vec{a}_1 \times \vec{a}_2 \quad j = 1, 2 \quad (160)$$

But this would not make sense for multiple reasons:

- in the first place, for $D = 2$, the vectors we are dealing with are bidimensional while the cross product (at least as far as we consider it in this course) is defined for threedimensional vectors only
- even if we were able to solve the cross product problem in some way, then, if we took $\vec{b}_1$ orthogonal to both $\vec{a}_1$ and $\vec{a}_2$, we would then have $\vec{b}_1 \cdot \vec{a}_2 = 0$, which is good, but also:

$$\vec{b}_1 \cdot \vec{a}_1 = 0$$

which is *not* good (see 135)

- if both the $\vec{b}_1$ and $\vec{b}_2$ primitive reciprocal vectors were orthogonal to the plane defined by $\vec{a}_1$ and $\vec{a}_2$, then they would be parallel to each other, hence linearly dependent: they could not be a basis of $\mathbb{R}^2$, contrary to what 133 requires

78. On the other hand, the orthogonality conditions contained into 154 make us intensely desire to take advantage of the cross product, just like we did for the $D = 3$ case.

So: let's start by “promoting” the bidimensional vectors of the $D = 2$ case to corresponding three-dimensional ones. In other words: let's “immerse” the $\mathbb{R}^2$ space, where the Bravais lattice lives in this case, into the $\mathbb{R}^3$ space.

Just to fix ideas and make our life easier, even if this would not be strictly required, we can introduce a 3D cartesian reference system xyz and make the plane defined by $\vec{a}_1$ and $\vec{a}_2$ be coincident with the xy plane: this way the components of the direct primitive vectors as promoted to 3D become:

$$\begin{aligned}\vec{a}_1 &= (a_{1x}, a_{1y}, 0) \\ \vec{a}_2 &= (a_{2x}, a_{2y}, 0)\end{aligned}$$

that is: the x and y components are the same as in $\mathbb{R}^2$, while the third z component is simply null.

79. And now this is our plan.

We will take advantage of being in 3D to obtain expressions for the reciprocal primitive vectors starting from 135, in a way very similar to what we did for the “genuine” 3D case.

However, we will do this in such a way that the two obtained reciprocal primitive vectors, $\vec{b}_1$ and $\vec{b}_2$, lay on the $\Pi_{\vec{a}_1\vec{a}_2}$ plane defined by $\vec{a}_1$ and $\vec{a}_2$, that is: their components will be:

$$\begin{aligned}\vec{b}_1 &= (b_{1x}, b_{1y}, 0) \\ \vec{b}_2 &= (b_{2x}, b_{2y}, 0)\end{aligned}$$

Please realize that, in general, if two 3D vectors of type:

$$\begin{aligned}\vec{v}_j &= (v_{jx}, v_{jy}, 0) \\ \vec{v}_l &= (v_{lx}, v_{ly}, 0)\end{aligned}$$

do satisfy:

$$\vec{v}_j \cdot \vec{v}_l = 2\pi\delta_{jl}$$

then the same condition will be satisfied also for the 2D vectors:

$$\begin{aligned}\vec{v}_j &= (v_{jx}, v_{jy}) \\ \vec{v}_l &= (v_{lx}, v_{ly})\end{aligned}$$

In math notation:

$$(v_{jx}, v_{jy}, 0) \cdot (v_{lx}, v_{ly}, 0) = 2\pi\delta_{jl} \implies (v_{jx}, v_{jy}) \cdot (v_{lx}, v_{ly}) = 2\pi\delta_{jl} \quad (161)$$

80. Let's focus on the $\vec{b}_1$ reciprocal primitive vector.

The conditions it must satisfy in the present 2D case are (eq. 135):

$$\begin{aligned}\vec{b}_1 \cdot \vec{a}_2 &= 0 \\ \vec{b}_1 \cdot \vec{a}_1 &= 2\pi\end{aligned}$$

Thanks to the 3D promotion, we can now use the cross product.
However, simply defining:

$$\vec{b}_1 = \xi_1 (\vec{a}_1 \times \vec{a}_2) \quad (162)$$

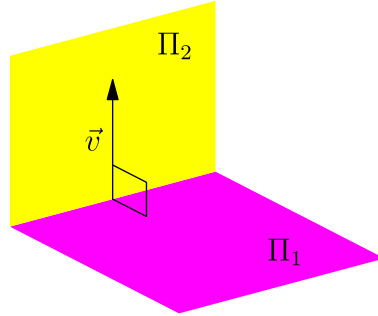
that is: taking $\vec{b}_1$ proportional to the cross product of $\vec{a}_1$ and $\vec{a}_2$, cannot work in this case. Why? Because, if on the one side this choice actually makes $\vec{b}_1$ orthogonal to $\vec{a}_2$, on the other side the problems outlined above in point 77 are still there. Moreover, if we were to use 162, $\vec{b}_1$ would not be contained in the $\Pi_{\vec{a}_1 \vec{a}_2}$ plane, being orthogonal to it.

However, the idea of using (in some way) the $(\vec{a}_1 \times \vec{a}_2)$ cross product is not a bad one. By definition of cross product, the $(\vec{a}_1 \times \vec{a}_2)$ vector is orthogonal to the $\Pi_{\vec{a}_1 \vec{a}_2}$ plane. Now: consider the plane $\Pi_\perp$, defined by the $(\vec{a}_1 \times \vec{a}_2)$ and $\vec{a}_2$ vectors. Obviously, $(\vec{a}_1 \times \vec{a}_2)$ is contained into the $\Pi_\perp$ plane (by construction!).

In general (no formal proof given):

$$\vec{v} \perp \Pi_1, \vec{v} \in \Pi_2 \implies \Pi_2 \perp \Pi_1 \quad (163)$$

in simple words: if a vector $\vec{v}$ is orthogonal to a plane Π_1 and, at the same time, is contained in a plane Π_2 , then the Π_1 and Π_2 planes are mutually orthogonal:



In our present case:

$$\begin{aligned}\vec{v} &\rightarrow (\vec{a}_1 \times \vec{a}_2) \\ \Pi_1 &\rightarrow \Pi_{\vec{a}_1 \vec{a}_2} \\ \Pi_2 &\rightarrow \Pi_\perp\end{aligned} \quad (164)$$

As said above: $(\vec{a}_1 \times \vec{a}_2)$ is orthogonal to $\Pi_{\vec{a}_1 \vec{a}_2}$ by definition of cross product, and is contained in $\Pi_\perp$ by construction.

But then (refer to fig. 10), the vector:

$$\vec{a}_2 \times (\vec{a}_1 \times \vec{a}_2)$$

1. is orthogonal to $\vec{a}_2$, by definition of cross product

2. and lays on the $\Pi_{\vec{a}_1\vec{a}_2}$ plane, because it is orthogonal to $\Pi_{\perp}$ which, in turn, is orthogonal to $\Pi_{\vec{a}_1\vec{a}_2}$

and this is exactly what we need.

In the end, the $\vec{b}_1 \cdot \vec{a}_2 = 0$ orthogonality condition will be satisfied if we take $\vec{b}_1$ proportional to the $\vec{a}_2 \times (\vec{a}_1 \times \vec{a}_2)$ vector, that is:

$$\vec{b}_1 = \xi_1 \vec{a}_2 \times (\vec{a}_1 \times \vec{a}_2) \quad (165)$$

where, as usual, ξ_1 is the proportionality constant, still to be found.

Remark: the parentheses in 165 are *not* redundant because the cross product does not enjoy the associative property. To convince yourself it is enough to consider the following cross product:

$$\vec{v}_1 \times (\vec{v}_1 \times \vec{v}_2)$$

If $\vec{v}_1$ and $\vec{v}_2$ are not parallel, then the triple cross product is guaranteed to be $\neq 0$; on the other hand, the:

$$(\vec{v}_1 \times \vec{v}_1) \times \vec{v}_2$$

product is obviously null.

Note also that the $\vec{b}_1$ vector as defined above cannot be orthogonal to $\vec{a}_1$ at the same time: if that was the case, then $\vec{a}_1$ and $\vec{a}_2$ would be parallel, but this is not possible because they are the primitive vectors of the direct lattice, thus linearly independent (alternatively, you can think that $\vec{a}_1$ and $\vec{a}_2$ are two consecutive sides of a parallelogram, and as such they cannot share the same direction). $\vec{b}_1$ not being parallel to $\vec{a}_1$ reassures us, since we know that it must be $\vec{b}_1 \cdot \vec{a}_1 = 2\pi$.

81. Very much like what we did in the (genuine) 3D case, the proportionality constant ξ_1 is determined by the condition:

$$\vec{b}_1 \cdot \vec{a}_1 = 2\pi$$

which we did not yet consider.

By substituting for $\vec{b}_1$ expression 165 we get:

$$\xi_1 \overbrace{\vec{a}_2 \times (\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_1}^{\text{scalar}} = 2\pi \quad (166)$$

$$\xi_1 = 2\pi \frac{1}{\vec{a}_2 \times (\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_1} \quad (167)$$

(as already noted for the 3D case, realize that $\vec{a}_2 \times (\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_1$ is a simple scalar and thus the equation is a trivial algebraic equation)

The final result for $\vec{b}_1$ is:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times (\vec{a}_1 \times \vec{a}_2)}{\vec{a}_2 \times (\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_1} \quad (168)$$

Obviously, the procedure for $\vec{b}_2$ is identical (do it by exercise) and leads to:

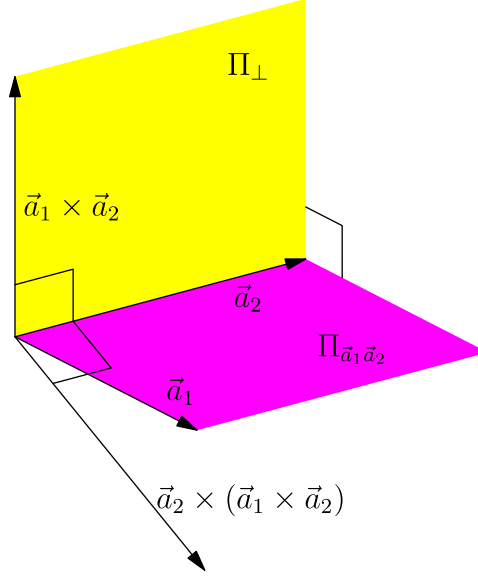


Figure 10: The $(\vec{a}_1 \times \vec{a}_2)$ vector is orthogonal to the $\Pi_{\vec{a}_1 \vec{a}_2}$ plane and thus the $\Pi_{\perp}$ plane, defined by the $(\vec{a}_1 \times \vec{a}_2)$ and $\vec{a}_2$ vectors, is orthogonal to $\Pi_{\vec{a}_1 \vec{a}_2}$. From this it follows that the $\vec{a}_2 \times (\vec{a}_1 \times \vec{a}_2)$ vector (i) is orthogonal to $\vec{a}_2$ and (ii) lays on the $\Pi_{\vec{a}_1 \vec{a}_2}$ plane.

$$\vec{b}_2 = 2\pi \frac{\vec{a}_1 \times (\vec{a}_1 \times \vec{a}_2)}{\vec{a}_1 \times (\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_2} \quad (169)$$

82. Usually, the expressions for $\vec{b}_1$ and $\vec{b}_2$ are reworked such that they become formally identical to the ones we derived for the 3D case.

Let:

$$\vec{a}_3 = \vec{a}_1 \times \vec{a}_2 \quad (170)$$

Then we can rewrite the two expressions as:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_2 \times \vec{a}_3 \cdot \vec{a}_1} \quad (171)$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_1 \times \vec{a}_3}{\vec{a}_1 \times \vec{a}_3 \cdot \vec{a}_2} \quad (172)$$

Again, thanks to the commutative property of the scalar product, the expression for $\vec{b}_1$ can be put in the following form:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad (173)$$

In the expression for $\vec{b}_2$ we can swap $\vec{a}_1$ and $\vec{a}_3$ in the cross product, so that it changes sign (you know it: the cross product is *anticommutative*: $\vec{v}_1 \times \vec{v}_2 = -\vec{v}_2 \times \vec{v}_1$) and taking advantage once

more of the commutativity of the scalar product and of the invariance of the triple product with respect to cyclic permutations (point 76) we arrive at:

$$\vec{b}_2 = 2\pi \frac{-\vec{a}_3 \times \vec{a}_1}{-\vec{a}_3 \times \vec{a}_1 \cdot \vec{a}_2} = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_3 \times \vec{a}_1 \cdot \vec{a}_2} = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot \vec{a}_3 \times \vec{a}_1} = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad (174)$$

Ultimately:

$$\begin{aligned} \vec{b}_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \\ \vec{b}_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \end{aligned} \quad (175)$$

As you can see, in this form the expressions for $\vec{b}_1$ and $\vec{b}_2$ in the 2D case are identical to the ones for $\vec{b}_1$ and $\vec{b}_2$ in the 3D case (eq. 159).

Of course, as it should be clear from the whole procedure, in the 2D case the $\vec{a}_1$, $\vec{a}_2$, $\vec{b}_1$, $\vec{b}_2$ vectors are actually bidimensional vectors, which have been “promoted” to three-dimensional vectors for the convenience of being able to make use of the cross product.

Moreover, while in the 3D case the $\vec{a}_3$ vector has no relation with $\vec{a}_1$ and $\vec{a}_2$, in the 2D case $\vec{a}_3$ is *defined* by $\vec{a}_1$ and $\vec{a}_2$ via 170.

As already said, if the plane containing the Bravais lattice defining the periodicity of the function expanded in Fourier series is made coincident with the xy plane of a 3D cartesian reference system xyz , then the primitive vectors of the (bidimensional) reciprocal lattice are obtained by simply suppressing the third (null) component of the “promoted” vectors appearing in 175.

You can appreciate the elegance of the vectorial approach by comparing the final result for $\vec{b}_1$ and $\vec{b}_2$ with the corresponding expressions obtained by the analytical procedure in section 1.2 of the extracurricular part.

83. You can also verify the validity of 175 with this small `octave` code:

```
# octave start
## INPUT STARTS HERE
a1=[0.6,1/3];
a2=[6/7,3/11];
## INPUT ENDS HERE
## promote a1 and a2 to 3D
## (p stands for 3D "promoted")
a1p=[a1,0];
a2p=[a2,0];
## evaluate b1p and b2p
a3p=cross(a1p,a2p);
den=dot(a1p,cross(a2p,a3p));
b1p=2*pi*cross(a2p,a3p)/den;
b2p=2*pi*cross(a3p,a1p)/den;
## verify result
# dot products in 3D
printf("verifying result in 3D:\n");
printf("=====\n");
printf("a1p=[%.2f,%.2f,%.2f]\n",a1p);
```

```

printf("a2p=[%.2f,%.2f,%.2f]\n",a2p);
printf("b1p=[%.2f,%.2f,%.2f]\n",b1p);
printf("b2p=[%.2f,%.2f,%.2f]\n",b2p);
printf("%+15s %5.2f\n","b1p.a2p:",dot(b1p,a2p));
printf("%+15s %5.2f\n","b1p.a1p/(2pi):",dot(b1p,a1p)/(2*pi));
printf("%+15s %5.2f\n","b2p.a1p:",dot(b2p,a1p));
printf("%+15s %5.2f\n","b2p.a2p/(2pi):",dot(b2p,a2p)/(2*pi));
# dot products in 2D
b1=[b1p(1),b1p(2)];
b2=[b2p(1),b2p(2)];
printf("\nverifying result in 2D:\n");
printf("=====\n");
printf("a1=[%.2f,%.2f]\n",a1);
printf("a2=[%.2f,%.2f]\n",a2);
printf("b1=[%.2f,%.2f]\n",b1);
printf("b2=[%.2f,%.2f]\n",b2);
printf("%+15s %5.2f\n","b1.a2:",dot(b1,a2));
printf("%+15s %5.2f\n","b1.a1/(2pi):",dot(b1,a1)/(2*pi));
printf("%+15s %5.2f\n","b2.a1:",dot(b2,a1));
printf("%+15s %5.2f\n","b2.a2/(2pi):",dot(b2,a2)/(2*pi));
# octave end

```

1.3.3.5 The geometrical interpretation of the reciprocal primitive lattice vectors

84. The obtained formulas for the reciprocal primitive lattice vectors for the 2D and 3D cases (eq. 159 and 175) can be geometrically interpreted in a simple way.

The *direction* of the $\vec{b}_j$'s is immediately derived from the conditions 154 which we used to obtain them.

In the 2D case, the direction of $\vec{b}_1$ is orthogonal to $\vec{a}_2$ and the direction of $\vec{b}_2$ is orthogonal to $\vec{a}_1$. In the 3D case, $\vec{b}_1$ must be orthogonal to both $\vec{a}_2$ and $\vec{a}_3$: this means that $\vec{b}_1$'s direction will be the normal to the plane defined by $\vec{a}_2$ and $\vec{a}_3$; since $\vec{a}_2$ and $\vec{a}_3$ identify a particular face of the parallelepiped which constitutes the direct primitive cell, $\vec{b}_1$'s direction is simply obtained as the normal to that particular face of the direct primitive cell; in a similar way, $\vec{b}_2$'s direction will be the normal to the face of the direct primitive cell defined by $\vec{a}_3$ and $\vec{a}_1$ and $\vec{b}_3$'s direction will be the normal to the face of the direct primitive cell defined by $\vec{a}_1$ and $\vec{a}_2$.

85. Regarding the *modulus* of the $\vec{b}_j$'s, it is better to consider separately the 2D and 3D cases.

The 2D case

86. Let's consider $\vec{b}_1$ (the procedure for $\vec{b}_2$ is identical).

$\vec{b}_1$'s modulus is the modulus of the RHS of the corresponding expression in 175:

$$|\vec{b}_1| = b_1 = 2\pi \frac{|\vec{a}_2 \times \vec{a}_3|}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|} \quad (176)$$

Remember that $\vec{a}_3 = \vec{a}_1 \times \vec{a}_2$ (eq. 170) and thus $\vec{a}_3 \perp \vec{a}_2$ (keep in mind that in 175 the $\vec{b}_j$ and $\vec{a}_i$ vectors have been promoted to threedimensional vectors).

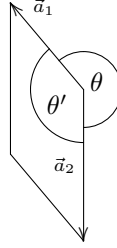
Thus, performing the cross product in the numerator we get:

$$|\vec{a}_2 \times \vec{a}_3| = a_2 a_3 \sin\left(\frac{\pi}{2}\right) = a_2 a_3 \quad (177)$$

In the denominator, let θ be the angle defined by $\vec{a}_1$ and $\vec{a}_2$.
Without loss of generality, we can always assume:

$$\theta < \pi \quad (178)$$

because if it was $\theta > \pi$, then we could not build any primitive cell and we would be required to consider θ 's 2π complement as the angle between $\vec{a}_1$ and $\vec{a}_2$, that is $\theta' < \pi$ below:



(trivially, $\theta = \pi$ is not allowed, since $\vec{a}_1, \vec{a}_2$ cannot be parallel (they must be linearly independent))
Since, by definition, $\vec{a}_3$ is orthogonal to the plane identified by $\vec{a}_1$ and $\vec{a}_2$, the vector $\vec{a}_2 \times \vec{a}_3$:

- lays on the plane defined by $\vec{a}_1$ and $\vec{a}_2$ (review what we said on p. 51 and also fig.10)
- is orthogonal to $\vec{a}_2$ (trivially)
- has modulus $a_2 a_3$ (because $\vec{a}_2$ and $\vec{a}_3$ make an angle of $\pi/2$ radians)

But then, as shown in figure 11, for any relative orientation of the three vectors $\vec{a}_1, \vec{a}_2, \vec{a}_2 \times \vec{a}_3$ it always holds that:

$$|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| = A a_3 \quad (179)$$

where A is the area of the direct primitive cell (that is, the area of the parallelogram identified by $\vec{a}_1, \vec{a}_2$).

Ultimately, the $\vec{b}_1$'s modulus is:

$$b_1 = 2\pi \frac{|\vec{a}_2 \times \vec{a}_3|}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|} = 2\pi \frac{a_2 a_3}{A a_3} = 2\pi \frac{a_2}{A} \quad (180)$$

Obviously, the procedure for $\vec{b}_2$ is identical and leads to:

$$b_2 = 2\pi \frac{a_1}{A}$$

87. So, the practical “recipe” to build and visualize the reciprocal primitive cell starting from the direct one in the 2D case reduces to this:

$\Rightarrow$ $\vec{b}_1$ is obtained by drawing on the plane defined by $\vec{a}_1$ and $\vec{a}_2$ a vector orthogonal to the side of the direct primitive cell corresponding to $\vec{a}_2$ and having modulus:

$$b_1 = 2\pi \frac{a_2}{A} \quad (181)$$

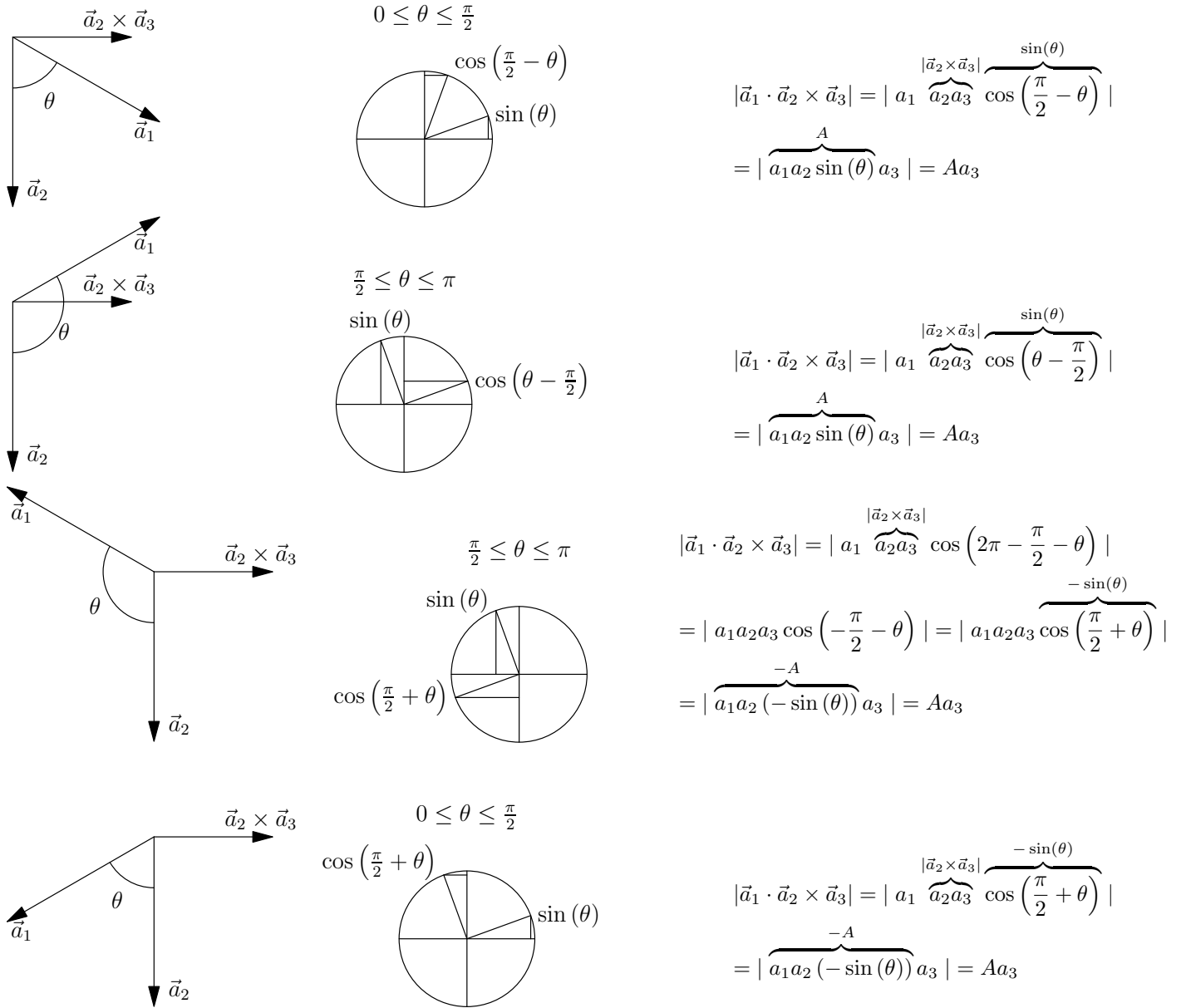


Figure 11: For any possible relative orientation of the three vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_2 \times \vec{a}_3$ (left column) one always gets:

$$|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| = A a_3$$

where A is the area of the parallelogram defined by $\vec{a}_1$, $\vec{a}_2$. The central column of the table helps to remember the trigonometric relations used in the right column.

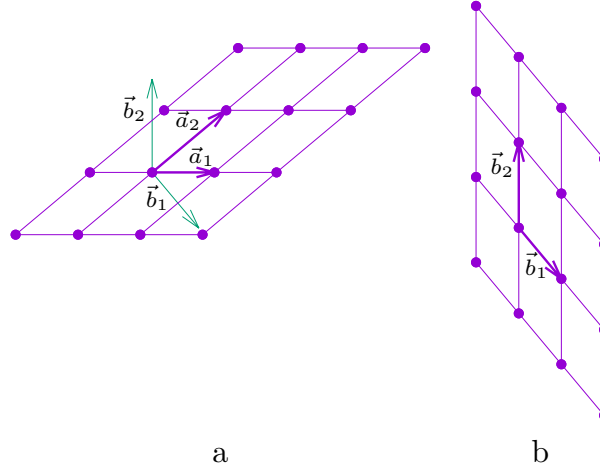


Figure 12: a: how to build the vectors defining the reciprocal primitive cell: $\vec{b}_1$ is orthofonal to $\vec{a}_2$ and $\vec{b}_2$ is orthogonal to $\vec{a}_1$; b: the reciprocal lattice associated with the direct lattice in (a) and generated by $\vec{b}_1$ and $\vec{b}_2$.

$\Rightarrow$ $\vec{b}_2$ is obtained by drawing on the plane defined by $\vec{a}_1$ and $\vec{a}_2$ a vector orthogonal to the side of the direct primitive cell corresponding to $\vec{a}_1$ and having modulus:

$$b_2 = 2\pi \frac{a_1}{A} \quad (182)$$

The procedure is shown in fig. 12.

88. It is worth noting that we completely neglect to consider the *sense* of the $\vec{b}_1$ and $\vec{b}_2$ vectors: in fact, it is totally irrelevant. The two $\vec{b}_i$ vectors having direction and modulus as defined above will generate exactly the same reciprocal lattice, irrespective of their particular sense; you should convince yourself about this by looking at figure 12b.

The 3D case

89. Let's develop our reasoning for the vector $\vec{b}_1$ (for $\vec{b}_2$ and $\vec{b}_3$ the procedure is identical, of course).

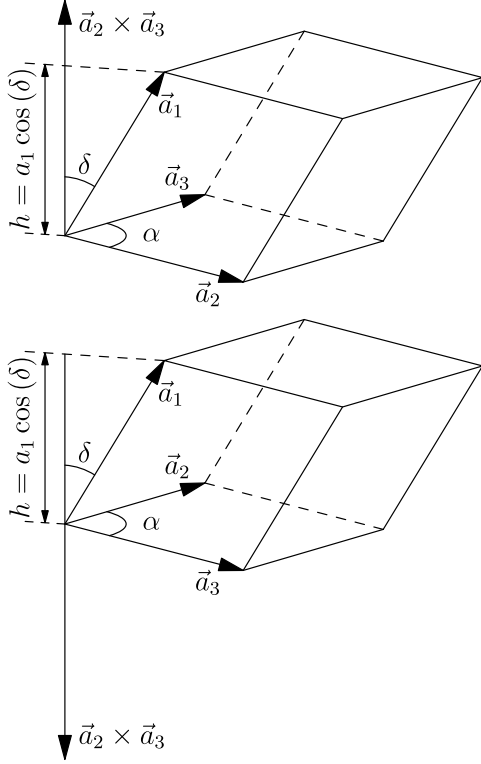
Let α be the angle between $\vec{a}_2$ and $\vec{a}_3$.

Note that in the 2D case analyzed above, α was always a right angle, *by construction*. Differently, now $\vec{a}_3$ is not defined as a function of $\vec{a}_1$ and $\vec{a}_2$: it simply is the third direct primitive vector, because now the direct Bravais lattice is three-dimensional; thus, the angle between $\vec{a}_2$ and $\vec{a}_3$ has now any value. However, as said at point 86, we can always assume: $\alpha < \pi$.

Then, explicitly performing the cross product in the numerator, we get:

$$b_1 = |\vec{b}_1| = 2\pi \frac{|\vec{a}_2 \times \vec{a}_3|}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|} = 2\pi \frac{a_2 a_3 \sin(\alpha)}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|} = 2\pi \frac{A_{23}}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|} \quad (183)$$

where (last equality) A_{23} is just the area of the face of the direct primitive cell defined by $\vec{a}_2$, $\vec{a}_3$. It is now simple to realize that the denominator is just the volume of the direct primitive cell. In the first place, realize that for the relative orientation of the three direct primitive vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ only the two possibilities shown in figure 13 do actually exist (basically, the three vectors can only make a *right* or *left* trio). And then, as shown in the same figure, it always holds:



$$\begin{aligned}
 |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| &= |a_1 (a_2 a_3 \sin(\alpha)) \cos(\delta)| \\
 &= \underbrace{|a_1 \cos(\delta)|}_h \underbrace{a_2 a_3 \sin(\alpha)}_{A_{23}} = |h A_{23}| = V
 \end{aligned}$$

$$\begin{aligned}
 |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| &= |a_1 (a_2 a_3 \sin(\alpha)) \cos(\pi - \delta)| \\
 &= \underbrace{|-a_1 \cos(\delta)|}_{-h} \underbrace{a_2 a_3 \sin(\alpha)}_{A_{23}} = |-h A_{23}| = V
 \end{aligned}$$

Figure 13: For any possible orientation of the three vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ we always have:

$$|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| = h A_{23} = V$$

where A_{23} is the basal area, h is the height and V is the volume of the parallelepiped identified by $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$.

$$|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| = V \quad (184)$$

$\vec{b}_1$'s modulus thus becomes:

$$b_1 = 2\pi \frac{A_{23}}{V} \quad (185)$$

As said above, the procedure for $\vec{b}_2$ and $\vec{b}_3$ is the same.

90. In conclusion, given the three vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ which define the primitive cell of the direct lattice:

$\Rightarrow$ $\vec{b}_1$ is orthogonal to the face of the direct primitive cell corresponding to $\vec{a}_2$ and $\vec{a}_3$ and has modulus:

$$b_1 = 2\pi \frac{a_2 a_3 \sin(\alpha)}{V} = 2\pi \frac{A_{23}}{V} \quad (186)$$

where α is the angle between $\vec{a}_2$ and $\vec{a}_3$ and A_{23} is the area of the $\vec{a}_2$, $\vec{a}_3$ face of the direct primitive cell.

$\Rightarrow$ $\vec{b}_2$ is orthogonal to the face of the direct primitive cell corresponding to $\vec{a}_3$ and $\vec{a}_1$ and has modulus:

$$b_2 = 2\pi \frac{a_3 a_1 \sin(\beta)}{V} = 2\pi \frac{A_{31}}{V} \quad (187)$$

where β is the angle between $\vec{a}_1$ and $\vec{a}_3$ and A_{31} is the area of the of the $\vec{a}_3, \vec{a}_1$ face of the direct primitive cell.

$\Rightarrow$ $\vec{b}_3$ is orthogonal to the face of the direct primitive cell corresponding to $\vec{a}_1$ and $\vec{a}_2$ and has modulus:

$$b_3 = 2\pi \frac{a_1 a_2 \sin(\gamma)}{V} = 2\pi \frac{A_{12}}{V} \quad (188)$$

where γ is the angle between $\vec{a}_1$ and $\vec{a}_2$ and A_{12} is the area of the of the $\vec{a}_1, \vec{a}_2$ face of the direct primitive cell.

As already pointed out for the 2D case, the reciprocal lattice generated by the three $\vec{b}_i$ vectors is totally independent on their particular sense: what actually matters is only their direction and modulus.

You can easily verify by exercise that in the simplest possible case where the direct primitive vectors are mutually orthogonal and share the same modulus a , the three reciprocal primitive vectors derived from them are themselves mutually orthogonal (with $\vec{b}_1$ orthogonal to the $\vec{a}_2 \vec{a}_3$ plane, and hence parallel to $\vec{a}_1$, etc.) and share the same modulus equal to $2\pi/a$ (here is another reciprocity relation between the direct and reciprocal lattices).

91. By the way, figure 13 offers an alternative proof (less formal than the one I present in section 1.3 of the extracurricular part, but perhaps simpler and more intuitive) of the invariance property with respect to cyclic permutations enjoyed by the triple product.

Go back to figure 13 and call A the configuration corresponding to the parallelepiped in the upper panel and B the one corresponding to the parallelepiped in the lower panel.

As shown in the figure, one has:

$$\begin{aligned} \text{case } A : \quad & \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = V \\ \text{case } B : \quad & \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = -V \end{aligned} \quad (189)$$

(note that in case B the result is now $-V$ because we are not taking the absolute value)

Now: let Π be the “horizontal” plane to which the $\vec{a}_2 \vec{a}_3$ face of the two parallelepipeds is parallel in figure 13 (i.e. the plane of the table on which the parallelepipeds are resting).

If you rotate each parallelepiped such that the face parallel to Π is the $\vec{a}_1, \vec{a}_2$ or the $\vec{a}_3, \vec{a}_1$, then re-applying identical steps to those we performed in point 89, you will get:

$$\begin{aligned} \text{case } A : \quad & \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = \vec{a}_2 \cdot \vec{a}_3 \times \vec{a}_1 = \vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2 = V \\ \text{case } B : \quad & \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = \vec{a}_2 \cdot \vec{a}_3 \times \vec{a}_1 = \vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2 = -V \end{aligned} \quad (190)$$

which just proves that the triple product is invariant with respect to any cyclic permutation of the involved vectors.

1.3.3.6 Summary of what we have seen so far

92. For the Fourier expansion of the function of two or three variables:

$$f(\vec{r}) \quad \vec{r} \in \mathbb{R}^D \quad D \in \{2, 3\}$$

periodic on a Bravais lattice $\mathcal{R}$ defined by the primitive vectors $\vec{a}_l, l \in \{1, \dots, D\}$, we proposed (eq. 126):

$$f(\vec{r}) = \sum_{\vec{k}} B_{\vec{k}} \exp(i\vec{k} \cdot \vec{r})$$

which is formally identical (apart from obvious changes due to the increased dimensionality) to the complex exponential form which we discussed for the case of a function of a single variable (eq. 101).

Our proposal can work if and only if we are able to find expressions for:

- $\Rightarrow$ the $\vec{k}$ vectors of the reciprocal lattice $\mathcal{R}^*$, defined by the primitive vectors $\vec{b}_j, j \in \{1, \dots, D\}$
- $\Rightarrow$ the corresponding $B_{\vec{k}}$ coefficients

93. Since each exponential term of the proposed series expansion *must* be periodic on the direct lattice $\mathcal{R}$, the primitive vectors $\vec{b}_j$ of the reciprocal lattice *must* satisfy condition 135:

$$\vec{b}_j \cdot \vec{a}_l = 2\pi\delta_{jl}$$

94. Based on conditions 135 we have derived the expressions for the $\vec{b}_j$ primitive vectors of the reciprocal lattice:

$$D = 2 \text{ (eq. 175)} \quad \left\{ \begin{array}{lcl} \vec{a}_3 & = & \vec{a}_1 \times \vec{a}_2 \\ \vec{b}_1 & = & 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \\ \vec{b}_2 & = & 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \end{array} \right.$$

$$D = 3 \text{ (eq. 159)} \quad \left\{ \begin{array}{lcl} \vec{b}_1 & = & 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \\ \vec{b}_2 & = & 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \\ \vec{b}_3 & = & 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \end{array} \right.$$

95. With a procedure very similar to that used in the 1D case, we have derived the expressions for the $B_{\vec{k}}$ coefficients (eq. 153):

$$B_{\vec{k}} = \frac{1}{V} \int_V f(\vec{r}) \exp(-i\vec{k} \cdot \vec{r}) d\vec{r}$$

96. This way, the Fourier expansion of the function $f(\vec{r})$:

$$f(\vec{r}) = \sum_{\vec{k}} B_{\vec{k}} \exp(i\vec{k} \cdot \vec{r})$$

is fully defined:

- $\Rightarrow$ given the function $f(\vec{r})$ periodic on the Bravais lattice $\mathcal{R}$, the $\vec{a}_l$ direct primitive vectors are well defined

- ⇒ from the $\vec{a}_i$'s we are able to derive the $\vec{b}_j$ primitive vectors of the reciprocal lattice $\mathcal{R}^*$ via 175 or 159
- ⇒ once we know the reciprocal primitive vectors, we can generate the infinite $\vec{k}$ reciprocal vectors via 133
- ⇒ for each $\vec{k}$ point we know how to build the corresponding coefficient of the Fourier expansion, via 153

1.3.4 An equivalent definition of reciprocal lattice

97. Up to this point we have defined the reciprocal lattice $\mathcal{R}^*$ of a given direct lattice $\mathcal{R}$ as the set of points of $\mathbb{R}^D$, $D \in \{1, 2, 3\}$, each of which uniquely defines one term of the Fourier expansion of a $\mathcal{R}$ periodic function.

98. However, based on the results we have obtained in this section, it is possible to state an equivalent definition of reciprocal lattice, perhaps more abstract, but extremely useful from a mathematical standpoint.

We have seen how eq. 137 follows from 135. Eq. 137 holds for any point of the direct lattice $\mathcal{R}$, that is:

$$\vec{k} \in \mathcal{R}^* \implies \vec{k} \cdot \vec{R} = 2\pi n, \quad n \in \mathbb{Z}, \quad \forall \vec{R} \in \mathcal{R} \quad (191)$$

The wording of 191 sounds like this: if $\vec{k}$ is a reciprocal lattice point, then the scalar product of $\vec{k}$ with *any* vector of the direct lattice is equal to an integer multiple of 2π .

99. It is possible to prove rather easily that the opposite statement also holds, that is:

$$\vec{k} \cdot \vec{R} = 2\pi n, \quad n \in \mathbb{Z}, \quad \forall \vec{R} \in \mathcal{R} \implies \vec{k} \in \mathcal{R}^* \quad (192)$$

whose translation in words is: if the scalar product of a vector $\vec{k} \in \mathbb{R}^D$ with *any* vector $\vec{R} \in \mathcal{R}$ is equal to an integer multiple of 2π , then $\vec{k}$ is a point of the reciprocal lattice $\mathcal{R}^*$ associated with $\mathcal{R}$.

In order to prove 192 it is enough to show that for a generic vector of $\mathbb{R}^D$ *not belonging* to the reciprocal lattice $\mathcal{R}^*$ eq. 191 *does not* hold.

In fact, we already know that all points of $\mathcal{R}^*$ do satisfy 191; if for a generic vector $\vec{d}$ not belonging to $\mathcal{R}^*$ eq. 191 is not satisfied, then this means that eq. 191 holds for all *and only* the vectors of $\mathcal{R}^*$ and thus 192 remains proved.

100. Since 191 must hold for every vector $\vec{R} \in \mathcal{R}$, in order to prove that 191 does not hold for a generic vector $\vec{d}$ *not belonging* to $\mathcal{R}^*$, it is enough to find *at least* one point of $\mathcal{R}$ whose scalar product with $\vec{d}$ *is not* an integer multiple of 2π .

In math language:

$$\vec{d} \notin \mathcal{R}^* \implies \exists \vec{R} \in \mathcal{R} : \vec{d} \cdot \vec{R} = 2\pi x, \quad x \notin \mathbb{Z} \quad (193)$$

101. Just to make notation lighter, let's focus on the $D = 3$ case (of course, everything remains valid also for $D \in \{1, 2\}$).

Let's take a point $\vec{d} \in \mathbb{R}^3$ not being part of the reciprocal lattice $\mathcal{R}^*$.

Now: all the points of $\mathcal{R}^*$ are linear combinations of the reciprocal primitive vectors $\vec{b}_j$ with *integer coefficients* (eq. 133 and 135).

However, the reciprocal primitive vectors, which, recall, are linearly independent, do form a basis of $\mathbb{R}^3$ in general and thus $\vec{d}$ can be expressed as a linear combination of them.

But, since $\vec{d} \notin \mathcal{R}^*$, in the linear combination *at least one of the coefficients will be non-integer* (if all three coefficients were integer numbers, then $\vec{d}$ would be a vector of $\mathcal{R}^*$ by definition, but this can not be, by hypothesis).

The vector $\vec{d}$ can thus be written as:

$$\vec{d} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3 \quad (194)$$

where at least one among x_1, x_2, x_3 is not an integer number.

Let $j \in \{1, 2, 3\}$ be the index for which $x_j \notin \mathbb{Z}$. We can then rewrite $\vec{d}$ as:

$$\vec{d} = x_j \vec{b}_j + \sum_{\substack{i=1 \\ i \neq j}}^3 x_i \vec{b}_i \quad (195)$$

so evidencing the term of the linear combination containing the non-integer coefficient.

Now: trivially, the direct primitive vector $\vec{a}_j$ is a vector of the direct lattice $\mathcal{R}$.

But then we have:

$$\vec{d} \cdot \vec{a}_j = \left(x_j \vec{b}_j + \sum_{\substack{i=1 \\ i \neq j}}^3 x_i \vec{b}_i \right) \cdot \vec{a}_j = x_j \overbrace{\vec{b}_j \cdot \vec{a}_j}^{=2\pi} + \sum_{\substack{i=1 \\ i \neq j}}^3 x_i \overbrace{\vec{b}_i \cdot \vec{a}_j}^{=0} = x_j 2\pi \quad x_j \notin \mathbb{Z} \quad (196)$$

that is: we have found a vector of $\mathcal{R}$ (namely: $\vec{a}_j$) whose scalar product with $\vec{d}$ is *not* an integer multiple of 2π .

This means that 191 does not hold for $\vec{d}$ and thus eq. 191 holds for all *and only* the vectors of $\mathcal{R}^*$; which, as said above, proves 192.

Ultimately, we can safely claim:

$$\vec{k} \in \mathcal{R}^* \iff \vec{k} \cdot \vec{R} = 2\pi n, \quad n \in \mathbb{Z}, \quad \forall \vec{R} \in \mathcal{R}$$

and this, as anticipated, allows the following equivalent definition of reciprocal lattice:

Given a direct Bravais lattice $\mathcal{R}$ whose points (i.e. vectors) are $\vec{R}$, we define the reciprocal lattice $\mathcal{R}^*$ associated with it as the set of *all and only* the vectors $\vec{k}$ which satisfy:

$$\vec{k} \cdot \vec{R} = 2\pi n \quad n \in \mathbb{Z} \quad \forall \vec{R} \in \mathcal{R} \quad (197)$$

1.3.5 Some useful properties of the Fourier series

We conclude this part about the Fourier series by presenting some of its properties which we will happen to use in the following.

1.3.5.1 Real functions

102. If $f(\vec{r})$ is a real function (that is: $f(\vec{r}) : \mathbb{R}^D \rightarrow \mathbb{R}^D$), then the coefficients of its Fourier expansion:

$$f(\vec{r}) = \sum_{\vec{k}} B_{\vec{k}} \exp(i\vec{k} \cdot \vec{r})$$

where $\vec{k} \in \mathcal{R}^*$, are related with each other by the following relation:

$$B_{-\vec{k}} = B_{\vec{k}}^*$$

($B_{\vec{k}}^*$ is the complex conjugate of $B_{\vec{k}}$)

The opposite statement also applies, and thus:

$$\overbrace{f(\vec{r}) = (f(\vec{r}))^*}^{\text{i.e.: } f(\vec{r}) \text{ is real}} \iff B_{-\vec{k}} = B_{\vec{k}}^* \quad (198)$$

Let's prove the two sides of the implication.

$$\boxed{f(\vec{r}) = (f(\vec{r}))^* \implies B_{-\vec{k}} = B_{\vec{k}}^*}$$

Suppose $f(\vec{r})$ is real.

The expression for the the Fourier coefficient $B_{\vec{k}}$ is:

$$B_{\vec{k}} = \frac{1}{V} \int_V \exp(-i\vec{k} \cdot \vec{r}) f(\vec{r}) d\vec{r}$$

where V is the volume (or the area, in the 2D case) of the direct primitive cell and $d\vec{r} = dxdydz$ (or $d\vec{r} = dxdy$, in the 2D case) is the infinitesimal volume (area) element.

The complex conjugate of $B_{\vec{k}}$ is:

$$B_{\vec{k}}^* = \left[\frac{1}{V} \int_V \exp(-i\vec{k} \cdot \vec{r}) f(\vec{r}) d\vec{r} \right]^*$$

Remark It is trivial to verify that the conjugation operator is linear; that is: given two real numbers x_1, x_2 and two complex numbers z_1, z_2 , it always holds:

$$[x_1 z_1 + x_2 z_2]^* = x_1 z_1^* + x_2 z_2^* \quad (199)$$

Remark It is also trivial to verify that, given two complex numbers z_1, z_2 , we have:

$$[z_1 z_2]^* = z_1^* z_2^* \quad (200)$$

Remark With $h(\vec{r})$ and $g(\vec{r})$ real functions, the following holds:

$$\begin{aligned} \left[\int h(\vec{r}) + ig(\vec{r}) d\vec{r} \right]^* &= \left[\int h(\vec{r}) d\vec{r} + i \int g(\vec{r}) d\vec{r} \right]^* \\ &= \int h(\vec{r}) d\vec{r} - i \int g(\vec{r}) d\vec{r} = \int h(\vec{r}) - ig(\vec{r}) d\vec{r} \\ &= \int [h(\vec{r}) + ig(\vec{r})]^* d\vec{r} \end{aligned}$$

that is the integral operator is “transparent” to the conjugation operator:

$$\left[\int \dots \right]^* = \int [\dots]^* \quad (201)$$

Thus, based on 199, 200 and 201:

$$\begin{aligned}
B_{\vec{k}}^* &= \frac{1}{V} \left[\int_V \exp \left(-i\vec{k} \cdot \vec{r} \right) f(\vec{r}) d\vec{r} \right]^* = \frac{1}{V} \int_V \left[\exp \left(-i\vec{k} \cdot \vec{r} \right) f(\vec{r}) \right]^* d\vec{r} \\
&\text{(here we take advantage of the hypothesis that } f(\vec{r}) \text{ is real)} \\
&= \frac{1}{V} \int_V f(\vec{r}) \left[\exp \left(-i\vec{k} \cdot \vec{r} \right) \right]^* d\vec{r} \\
&= \frac{1}{V} \int_V f(\vec{r}) \exp \left(i\vec{k} \cdot \vec{r} \right) d\vec{r} = \frac{1}{V} \int_V f(\vec{r}) \exp \left(-i \left(-\vec{k} \right) \cdot \vec{r} \right) d\vec{r} = B_{-\vec{k}}
\end{aligned}$$

and that's it.

$$\boxed{B_{-\vec{k}} = B_{\vec{k}}^* \implies f(\vec{r}) = (f(\vec{r}))^*}$$

Let's write the two expressions for $B_{-\vec{k}}$ and $B_{\vec{k}}^*$:

$$\begin{aligned}
B_{-\vec{k}} &= \frac{1}{V} \int_V \exp \left(i\vec{k} \cdot \vec{r} \right) f(\vec{r}) d\vec{r} \\
B_{\vec{k}}^* &= \left[\frac{1}{V} \int_V \exp \left(-i\vec{k} \cdot \vec{r} \right) f(\vec{r}) d\vec{r} \right]^* = \frac{1}{V} \int_V \left[\exp \left(-i\vec{k} \cdot \vec{r} \right) f(\vec{r}) \right]^* d\vec{r} \\
&= \frac{1}{V} \int_V \exp \left(i\vec{k} \cdot \vec{r} \right) f(\vec{r})^* d\vec{r}
\end{aligned}$$

(we have made use again of the remarks 199, 200 and 201)

By comparison of the expressions for $B_{-\vec{k}}$ and $B_{\vec{k}}^*$ and recalling that by hypothesis $B_{-\vec{k}} = B_{\vec{k}}^*$ we get:

$$f(\vec{r}) = f(\vec{r})^*$$

or, as sought, $f(\vec{r})$ is real.

103. This property also allows us to show formally (if it would be ever needed) the reason why it is possible to expand a real function with the complex exponential form of the Fourier series. In fact, when the expanded function is real, for all the pairs of terms corresponding to $-\vec{k}$ and $\vec{k}$ we have:

$$\begin{aligned}
f(\vec{r}) &= \sum_{\vec{k}} B_{\vec{k}} \exp \left(i\vec{k} \cdot \vec{r} \right) \\
&= \dots + B_{-\vec{k}} \exp \left(i \left(-\vec{k} \right) \cdot \vec{r} \right) + \dots + B_{\vec{k}} \exp \left(i\vec{k} \cdot \vec{r} \right) \dots \\
&\quad \text{by the property just seen:} \\
&= \dots + B_{\vec{k}}^* \exp \left(-i\vec{k} \cdot \vec{r} \right) + \dots + B_{\vec{k}} \exp \left(i\vec{k} \cdot \vec{r} \right) \dots \\
&= \dots + B_{\vec{k}}^* \left(\exp \left(i\vec{k} \cdot \vec{r} \right) \right)^* + \dots + B_{\vec{k}} \exp \left(i\vec{k} \cdot \vec{r} \right) \dots \\
&= \dots + \left(B_{\vec{k}} \left(\exp \left(i\vec{k} \cdot \vec{r} \right) \right) \right)^* + \dots + B_{\vec{k}} \exp \left(i\vec{k} \cdot \vec{r} \right) \dots
\end{aligned}$$

$$\begin{aligned} \text{let: } B_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) &= a + ib \\ &= \dots + a - i\cancel{b} + \dots + a + i\cancel{b} \dots \end{aligned}$$

That is, as I anticipated in point 41, all the imaginary parts do cancel each other.

1.3.5.2 Real and even functions

104. The Fourier coefficients of the expansion of a real and even function are real and even (with respect to $\vec{k}$).

That is: given the Fourier expansion:

$$f(\vec{r}) = \sum_{\vec{k}} B_{\vec{k}} \exp(i\vec{k} \cdot \vec{r})$$

with $\vec{k} = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$ vector of the reciprocal lattice, it holds:

$$\overbrace{f(\vec{r}) = (f(\vec{r}))^*}^{f \text{ real}} \text{ and } \overbrace{f(\vec{r}) = f(-\vec{r})}^{f \text{ even}} \implies \overbrace{B_{\vec{k}} = B_{\vec{k}}^*}^{B \text{ real}} \text{ and } \overbrace{B_{\vec{k}} = B_{-\vec{k}}}^{B \text{ even}} \quad (202)$$

We prove this property in only one dimension: if you are interested, I present the proof for a function of three variables in section 1.4 of the extracurricular part.

For the monodimensional case we have:

$$\begin{aligned} \vec{k} &\rightarrow k = \frac{2\pi n}{T} \quad n \in \mathbb{Z} \quad (T = \text{period}) \\ \vec{r} &\rightarrow x \quad (\text{scalar variable}) \end{aligned}$$

and thus:

$$B_k = \frac{1}{T} \int_a^{a+T} f(x) \exp(-ikx) dx \quad (\text{eq. 102})$$

Perform the change of variable:

$$u = -x$$

Then:

$$\begin{aligned} x &= -u \\ dx &= -du \\ x = a &\rightarrow u = -a \\ x = a + T &\rightarrow u = -(a + T) \end{aligned}$$

Hence:

$$B_k = \frac{1}{T} \int_{-a}^{-(a+T)} f(-u) \exp(iku) (-du)$$

But $f(x)$ is even by hypothesis, so:

$$B_k = -\frac{1}{T} \int_{-a}^{-(a+T)} f(u) \exp(iku) du$$

Eventually: swap the integration limits (so the integral changes sign), add $2a + T$ to both integration limits (we are allowed to do this because the argument of the integral is a T -periodic function, point 17, and thus the property presented in point 11 applies) and rearrange the argument of the exponential:

$$B_k = \frac{1}{T} \int_{-(a+T)}^{-a} f(u) \exp(iku) du = \frac{1}{T} \int_a^{a+T} f(u) \exp(-i(-k)u) du = B_{-k} \quad (203)$$

and this proves the even parity.

Finally, combining the result just obtained with 198 (which applies since f is real by hypothesis), we get:

$$\left. \begin{array}{l} B_k = B_{-k} \\ B_{-k} = B_k^* \end{array} \right\} \implies B_k = B_k^* \quad (204)$$

and this proves that the coefficients are real.

1.3.5.3 Real and odd functions

105. The Fourier coefficients of the expansion of a real and odd function are imaginary and odd (with respect to $\vec{k}$).

That is: given the Fourier expansion:

$$f(\vec{r}) = \sum_{\vec{k}} B_{\vec{k}} \exp(i\vec{k} \cdot \vec{r})$$

where $\vec{k} = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$ is a vector of the reciprocal lattice, the following holds:

$$\overbrace{f(\vec{r}) = (f(\vec{r}))^*}^{f \text{ real}} \text{ and } \overbrace{f(\vec{r}) = -f(-\vec{r})}^{f \text{ odd}} \implies \overbrace{B_{\vec{k}} = -B_{\vec{k}}^*}^{B \text{ imaginary}} \text{ and } \overbrace{B_{\vec{k}} = -B_{-\vec{k}}}^{B \text{ odd}} \quad (205)$$

Also for this one I present the proof in only one dimension (the corresponding demonstration for the 3D case is reported in section 1.5 of the extracurricular part).

Similar to what we already saw at point 104, in one dimension we have:

$$\begin{aligned} \vec{k} &\rightarrow k = \frac{2\pi n}{T} \quad n \in \mathbb{Z} \quad (T = \text{period}) \\ \vec{r} &\rightarrow x \quad (\text{scalar variable}) \end{aligned}$$

and thus:

$$B_k = \frac{1}{T} \int_a^{a+T} f(x) \exp(-ikx) dx \quad (\text{eq. 102})$$

Like the previous case, we perform the following change of variable:

$$u = -x$$

Then:

$$\begin{aligned} x &= -u \\ dx &= -du \\ x = a &\rightarrow u = -a \\ x = a + T &\rightarrow u = -(a + T) \end{aligned}$$

and:

$$B_k = \frac{1}{T} \int_{-a}^{-(a+T)} f(-u) \exp(iku) (-du)$$

But f is odd by hypothesis ($f(u) = -f(-u)$) and so:

$$B_k = \frac{1}{T} \int_{-a}^{-(a+T)} f(u) \exp(iku) du$$

Like the previous case: swap the integration limits (so the integral changes sign), add $2a + T$ to both integration limits (we are allowed to do this because the argument of the integral is a T -periodic function, point 17, and thus the property presented in point 11 applies) and rearrange the argument of the exponential:

$$B_k = -\frac{1}{T} \int_{-(a+T)}^{-a} f(u) \exp(iku) du = -\frac{1}{T} \int_a^{a+T} f(u) \exp(-i(-k)u) du = -B_{-k} \quad (206)$$

and this proves the odd parity.

Finally, combining the result just obtained with 198 (which applies since f is real by hypothesis), we get:

$$\left. \begin{aligned} B_k &= -B_{-k} \\ B_{-k} &= B_k^* \end{aligned} \right\} \implies B_k = -B_k^* \quad (207)$$

and this proves that the coefficients are pure imaginary numbers.

106. In a very similar way it is possible to prove two more properties of the Fourier series, but we skip the demonstration because we will not use them.

Here is a summary of all these properties:

if $f(\vec{r})$ is ...	then the $B_{\vec{k}}$'s are ...	ref: property ...
real	$B_{-\vec{k}} = B_{\vec{k}}^*$	198
real and even	real and even	202
real and odd	imaginary and odd	205
imaginary and even	imaginary and even	N/D
imaginary and odd	real and odd	N/D

1.4 Some reminders about waves

107. Before going to the next part let's recall some fundamentals about *waves* and their mathematical representation. This seems appropriate to me, since in the following we will be dealing very often with typical wave functions.

108. In general, a *wave* is the change (with respect to a reference value) of some physical quantity defined in every point of a space region (of course, the region can also be infinite and/or coincide with the entire space). The essential and peculiar feature of a wave is that the variation of the quantity defining it depends not only on space position, but also on time. In other words, for a fixed point in space, the physical quantity that defines the wave in that point varies with time. Thus, in general and for what we are concerned with, the mathematical definition of a wave is that of a function of four coordinates: the three spatial coordinates plus time:

$$f(x, y, z, t) = f(\vec{r}, t) \quad (208)$$

109. A well known example is that of sea waves. In this case the space where the wave is defined is bidimensional, that is the sea surface; the varying physical quantity is the height of the water with respect to the average height value of the sea surface; the time dependence is easily verified: if you fix your eyes on a given point of the surface, you will see that its height with respect to the average height value of the sea surface varies periodically as a function of time.

Sea waves are an example of so called *traveling waves*. If you follow the crest of a particular sea wave you see it moving (with approximately constant speed). The same holds for any other part of the wave, but looking at the crest is simpler. Of course, you all know very well that if it is true that sea waves do travel, it is also true that the sea itself does not: if there was an actual sea movement, then the sea shore (thought of as the boundary between sea and land) would not exist...

110. Another example of wave is that which is generated when we pluck a guitar string: in this case the space where the wave is defined is monodimensional (the string line) and, in a way very similar to the example of sea waves, the variation of the physical quantity to be considered is the displacement of the string with respect to its rest position. This displacement is different for different points of the string and, for a fixed point, it varies with time. This kind of wave, differently from the sea waves, is a *standing* (or *stationary*) *wave*. The difference between traveling and standing waves is that the latter do not move and this becomes apparent if you consider that the two extrema of the guitar string (which are part of it) do not move (of course). Every point of the string oscillates in time, but the position of the oscillation maximum (or minimum) along the string does not change.

1.4.1 Traveling waves

111. Let's begin to delve into the mathematical description of a traveling wave.

Basically, the problem is: how can we mathematically describe a function of position whose graph "travels" (moves) as a function of time?^v

To make our lives easier, let's concentrate on a function of a single spatial coordinate, $f(x)$, and let's ask ourselves how can we translate the graph of the function along the x axis.

This is actually quite easy (refer to figure 14): given the graph of $f(x)$, the graph of $f(x - t)$, with $t > 0$, is identical to that of $f(x)$, but shifted by t in the positive direction (that is: to the right) of the x axis.

^vAs I have already noted, what actually moves in a traveling wave is not the medium in which the wave manifests itself (e.g. the sea water), but rather the *mathematical description* (that is: the *graph*) of the variation of the physical quantity which originates the wave. When I will say that a traveling wave moves or displaces itself, I will always mean the movement or displacement of its graph: the so called waveform.

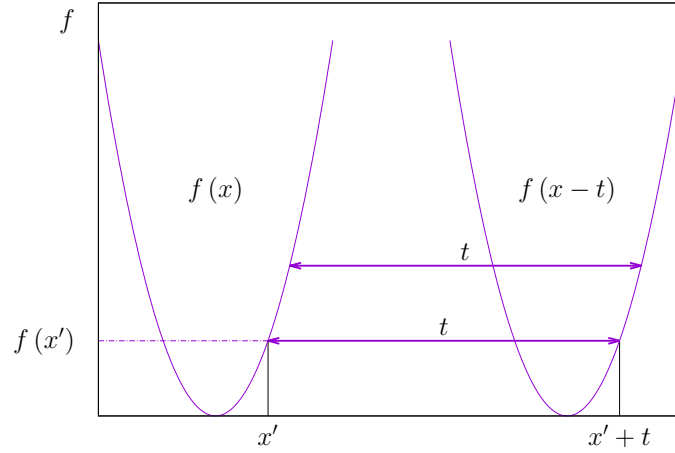


Figure 14: The graph of the function $f(x-t)$ is identical to that of the function $f(x)$, but it is translated by t in the positive direction (i.e. to the right) of the x axis with respect to the latter.

To see why this is so, consider the value $f(x')$ taken by the original, unshifted function for $x = x'$; clearly, the function $f(x-t)$ takes that same value when $x = x' + t$, for:

$$f((x' + t) - t) = f(x') \quad (209)$$

and since this holds $\forall x'$, it follows that the graph of $f(x-t)$ is obtained by shifting to the right the one of $f(x)$ by the amount t .

Of course, with a similar reasoning, you realize that the graph of the function $f(x+t)$ ($t > 0$) is identical to that of the function $f(x)$, but shifted by the amount t in the negative direction (i.e. to the left) of the x axis.

112. If you now think of t no more as a constant, but as a second variable on which the function depends, you have obtained a traveling wave: for fixed t , the function will have a given graph (represented on the cartesian plane); as t increases the graph moves (i.e. “travels”) to the right or to the left, depending on the sign of t .

For us, t will always represent time.

113. We are still missing a detail.

If we define the traveling wave simply as:

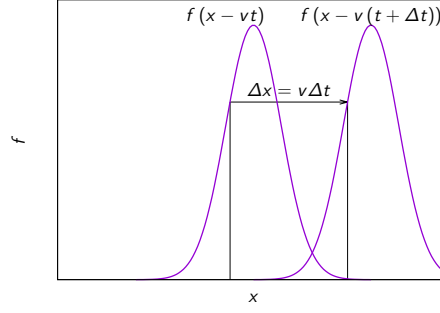
$$f(x \pm t) \quad (210)$$

then in a given time interval, the shift of the graph is always the same. On the other hand, we all know that traveling waves do travel at different speeds (just compare the velocity at which a sea wave moves with that of an electromagnetic wave, which is also a traveling wave).

If a traveling wave has to move at different possible velocities, then we have to multiply the variable t by a factor v able to increase or decrease the translation experienced by the graph of the wave for the same time interval:

$$f(x \pm vt) \quad (211)$$

It should be evident that the factor v so introduced is just the velocity with which the wave moves along the x axis. In a time interval Δt a given point of the graph of f moves by $\Delta x = v\Delta t$ along x and thus:



$$\Delta x = v\Delta t \implies v = \frac{\Delta x}{\Delta t} \quad (212)$$

1.4.2 Sinusoidal traveling waves

114. The traveling waves which we will be dealing with in this course will always be sinusoidal periodic waves of constant velocity, that is waves in which the function $f(\vec{r}, t)$ is a sinusoidal function periodic in both space $\vec{r}$ and time t . This means that, for a fixed time, the graph of f as a function of the spatial coordinate is sinusoidal; and, similarly, for a fixed point in space the graph of f as a function of time (in that point) is also sinusoidal.

115. The simplest mathematical expression for a sinusoidal monodimensional wave traveling to the right is:

$$f(x, t) = A \cos \left(\overbrace{\frac{2\pi}{\lambda}(x - vt)}^{\text{phase}} + \Phi_0 \right) \quad (213)$$

The argument of the cosine is called the *phase* of the wave.

Note that representing a sinusoidal wave with a cosine or a sine function is just the same, since one representation can be converted into the other by just adding a constant to the phase:

$$\cos(\alpha) = \sin\left(\alpha + \frac{\pi}{2}\right)$$

A is called the *amplitude* of the wave and it is the maximum value taken by the variation of the physical quantity represented by the wave function (the wave takes values in the interval $[-A, A]$, corresponding to the -1 and 1 values of the cosine, respectively).

Φ_0 is called *initial phase* and defines the initial amplitude of the wave, that is for $x = t = 0$:

$$f(0, 0) = A \cos(\Phi_0)$$

Most of the time, in this course, the initial phase will be null ($\Phi_0 = 0$); that is, we will be dealing with sinusoidal waves of the type:

$$f(x, t) = A \cos\left(\frac{2\pi}{\lambda}(x - vt)\right) \quad (214)$$

The sinusoidal behavior of the wave with respect to the spatial variable x (for fixed t) and with respect to the time variable t (for fixed x) contained in 214 is shown in figure 15 where I have

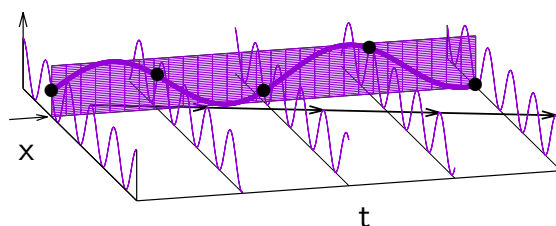


Figure 15: In this figure I have drawn the graph of the sinusoidal wave:

$$f(x, t) = A \cos\left(\frac{2\pi}{\lambda}(x - vt)\right);$$

the five parallel cosines are sections of the graph at five different equispaced time values; the four arrows connect the *same* crest of the five cosines to emphasize the movement of the wave; the arrows are on the same straight line because the wave velocity is constant. The shadowed section shows the behavior as a function of time for a fixed value of x (as shown by the small arrow); the black dots are the intersections of the five cosine traces with $x = \text{constant}$ plane.

represented the monodimensional periodic wave 214 (which moves in the positive direction of the x axis) at different times; in the figure I have evidenced both the space and time periodicities. You can find a more interactive version of the same figure on the web site of this course.⁹

116. Since a sinusoidal wave is periodic in both space (x) and time (t), there will be two periods (a “spatial” period and a “time” period), two corresponding frequencies etc. For this reason the quantities which refer to the spatial variable(s) and those which refer to time have different names (note that this problem did not arise when we introduced periodic functions in general, in section 1.1)

If you rewrite 214 as:

$$f(x, t) = A \cos\left(\frac{2\pi}{\lambda}x - \frac{2\pi}{\frac{\lambda}{v}}t\right) \quad (215)$$

and keep in mind what we said in point 13, then you should immediately realize that the period with respect to x is λ : however, in the case of a wave, the name “period” is used to denote the period with respect to the time t ; for this reason, the period with respect to x is called *wave length*. The origin of the name should be clear: it is the distance (just the actual distance, measured in m, mm, Å etc) between two corresponding and consecutive points of the spatial representation of the wave (that is: f as a function of x at fixed t).

The quantity:

$$f = \frac{1}{\lambda} \quad (216)$$

is called *spatial frequency* to distinguish it from the “temporal frequency”, or simply “frequency”, which is used for the time dependence of the wave. The spatial frequency is just what we defined in general as “linear frequency” for a periodic function (eq. 5) and refers to the function f thought of as a periodic function of x at fixed t .

Likewise:

$$k = \frac{2\pi}{\lambda} = 2\pi f \quad (217)$$

is what we defined as “angular frequency” for a simple periodic function (eq. 9). Like for the period, also this name is reserved for the corresponding temporal quantity and thus, in the case of a wave, k is called *wave number*.

When x changes by λ (at fixed t), the phase of the wave changes by:

$$\text{phase change} = \left(\frac{2\pi}{\lambda} (x + \lambda) - \frac{2\pi}{\lambda} t \right) - \left(\frac{2\pi}{\lambda} x - \frac{2\pi}{\lambda} t \right) = 2\pi \quad (218)$$

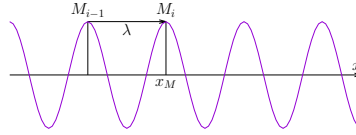
from which a physical meaning of the wave number can be derived: it is the phase change (in radians) per unit change of x (at fixed t):

$$\frac{\text{phase change in radians}}{x \text{ change}} = \frac{2\pi}{\lambda} = k \quad (219)$$

117. Still from 215 it can be seen that the temporal period, simply called *period*, that is the period of the wave thought of as a periodic function of t at fixed x , is:

$$T = \frac{\lambda}{v} \quad (220)$$

This relation shows that period and wave length are related and this should not come as a surprise. Suppose to fix x at the value x_M of a crest (i.e. maximum) of the wave at a fixed time:



If the wave moves at a constant velocity v , then the time Δt it takes for the crest M_{i-1} (that is, the crest immediately before M_i on the left) to reach x_M must be $\Delta t = \lambda/v$, because λ is the distance that M_{i-1} must cover. On the other hand, this is also the time it takes for the function $f(x_M, t)$ (that is: $f(x, t)$ thought of as a periodic function of t at fixed $x = x_M$) to complete a whole cycle, that is: its temporal period T ; so we have:

$$T = \Delta t = \lambda/v$$

(I have tried to better highlight this concept with an animated graph that you can find on the web site of the course¹⁰)

The quantity:

$$\nu = \frac{1}{T} = \frac{v}{\lambda} \quad (221)$$

is called *frequency* and is the same quantity we defined for periodic functions in general (eq. 5). For the case of a wave, it refers to the function f thought of as a periodic function of t at fixed x .

Finally, what we called *angular frequency* for a generic periodic function of a single variable (eq. 9) is used here for the temporal dependence of the wave:

$$\omega = \frac{2\pi}{T} = 2\pi\nu \quad (222)$$

118. In summary, the quantities that define the mathematical expression of a sinusoidal traveling wave are:

$f(x, t) = A \cos\left(\frac{2\pi}{\lambda}(x - vt)\right)$			
A		amplitude	
v		velocity	
spatial quantities		temporal quantities	
λ	wave length	$T = \frac{\lambda}{v}$	period
$f = \frac{1}{\lambda}$	spatial frequency	$\nu = \frac{1}{T} = \frac{v}{\lambda} = vf$	frequency
$k = \frac{2\pi}{\lambda} = 2\pi f$	wave number	$\omega = \frac{2\pi}{T} = 2\pi\nu$	angular frequency

Making use of the definitions of wave number and angular frequency, eq. 214 can be rewritten in more compact form as:

$$f(x, t) = A \cos(kx - \omega t) \quad (223)$$

1.4.3 Stationary waves

119. A stationary wave is a wave for which the spatial part does *not* “travel”, that is: its spatial graph does not translate with time (I introduced stationary waves in point 110). The simplest mathematical form of a monodimensional stationary wave is (with initial amplitude A):

$$f(x, t) = A \cos(kx) \cos(\omega t) \quad (224)$$

where A , k and ω have been already defined above.

Note the difference with respect to a traveling wave (eq. 223): the spatial and temporal coordinates are “separated”, that is: they do not appear in the same sinusoidal function. On p. 69 we saw in general that the necessary condition for a wave to travel is just that x and t be always combined together as $(x \pm vt)$ inside the function which mathematically describes the wave (eq. 211).

In a stationary wave this condition is not satisfied.

You can easily realize that the graph of a stationary wave does not undergo any translation along the x axis as a function of time. The points of the x axis where the function is null are called the *nodes* of the stationary wave. Trivially, they are given by:

$$f(x, t) = 0 \iff kx_n = \frac{\pi}{2} + n\pi \implies x_n = \frac{1}{k} \left(\frac{\pi}{2} + n\pi \right) \quad n \in \mathbb{Z} \quad (225)$$

From 224 it is clear that f will be null for the x values shown above *for any t value*. Of course, this means that the nodes of the function do not change their position as time passes; but then, if the nodes are fixed in time, the same must hold for the whole graph, which remains thus “localized” on the x axis and does not travel.

So: what are the changes in the graph as a function of time?

We have just seen that the nodes stay fixed: in other words, in the points of the x axis given by 225, the graph is independent on time.

Now consider a point x_0 of the x axis which is not a node. The behavior of f at x_0 as a function of time is:

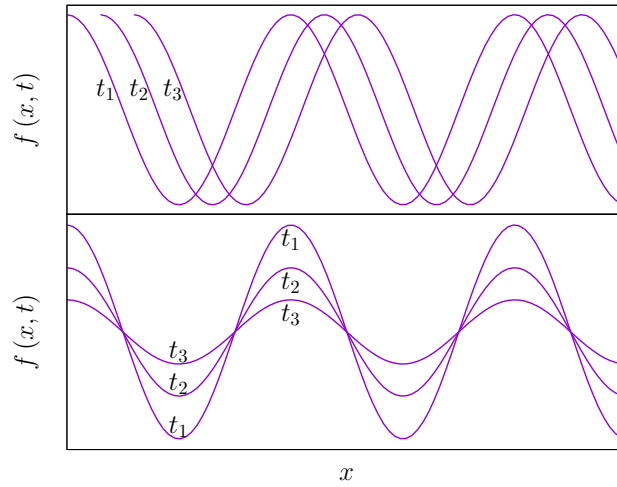


Figure 16: A traveling wave (up) and a stationary wave (down) at three different successive time values t_1 , t_2 , t_3 .

$$x_0 \neq x_n \implies f(x_0, t) = A \cos(kx_0) \cos(\omega t) \quad (226)$$

which is an harmonic oscillation of amplitude $A \cos(kx_0)$ and angular frequency ω .

So: at every point (different from a node) of a space region where a stationary wave is defined, the quantity represented by the wave varies periodically in time, but the graph of the wave does not translate.

This behavior is compared with that of a traveling wave in figure 16.

1.4.4 Multidimensional waves: traveling plane waves

120. For what regards this course, we will encounter only one type of multidimensional traveling waves, which are the extension to two or three dimensions of the simple sinusoidal wave 223. ^{vi}Such type of waves belong to a general class of multidimensional waves called *plane waves*.

The mathematical form of a traveling sinusoidal plane wave in 2D or 3D is:

$$f(\vec{r}, t) = A \cos(k\vec{r} \cdot \vec{n} - \omega t) \quad (227)$$

Of course, for the 2D case, $\vec{r}$ will be a vector of two spatial components $\vec{r} = (x, y)$; for the 3D case, $\vec{r}$ will be a vector of three spatial components $\vec{r} = (x, y, z)$.

As already mentioned, $\vec{r}$ is a position vector which locates a given point in the (2D or 3D) space where the physical quantity represented by the wave varies as a function of time; $\vec{n}$ is a versor of constant direction: as we will better explain at point 125, $\vec{n}$ defines the *propagation direction* of the sinusoidal plane wave, that is the direction along which the graph of the plane wave moves as a function of time.

The parameters A , k and ω have the same meaning as the monodimensional case (but with a clarification regarding k which we will make in a moment).

^{vi}When speaking about mono, bi or threedimensional waves I always mean the dimensionality of the *spatial* part; however, keep in mind that a wave whose spatial part depends, for instance, on a single variable x , from a purely mathematical standpoint, is a function of *two* variables: namely x and t

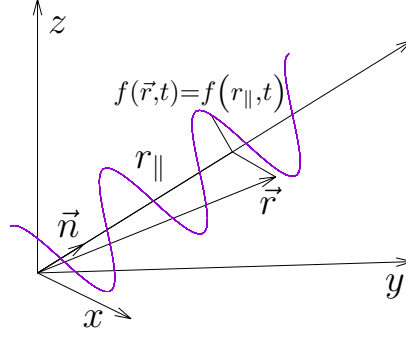


Figure 17: The value taken by the plane wave $f(\vec{r}, t)$ in the generic point $\vec{r}$ at fixed t can be obtained by projecting $\vec{r}$ along the direction of $\vec{n}$ and calculating $f(r_{\parallel}, t)$, where $r_{\parallel}$ is the modulus of the projection.

1.4.4.1 Time dependence

121. First of all it is easy to realize that at a given fixed point in space, that is for fixed $\vec{r}$, the temporal part of a plane wave, that is the time dependence of the physical quantity represented by the plane wave at that point, is a simple periodic function of a single variable, the time t , with angular frequency ω :

$$f(\vec{r}, t) \equiv f(t) = A \cos(\overbrace{k\vec{r} \cdot \vec{n}}^{\text{constant}} - \omega t) \quad (228)$$

1.4.4.2 Wave number in the propagation direction

122. We now want to understand how the waveform depends on the spatial coordinate, that is: what is the graph of $f(\vec{r}, t)$ as a function of $\vec{r}$ at fixed t ?

We will focus on the 3D case (i.e. $\vec{r}$ is a three component vector): adapting the discussion to the 2D case should be trivial.

First of all let's realize that k is the wave number *in the direction of the versor $\vec{n}$* (you will see in a moment that $\vec{n}$ defines the propagation direction of the plane wave, that is the direction in which the whole graph moves as time passes).

Make reference to figure 17.

Given any space point $\vec{r}$, the dependence of $f(\vec{r}, t)$ on that point is contained into the scalar product $k\vec{r} \cdot \vec{n}$.

Now: it is always possible to decompose the position vector $\vec{r}$ into two components $\vec{r}_{\parallel}$ and $\vec{r}_{\perp}$, parallel and orthogonal, respectively, to $\vec{n}$:

$$\vec{r} = \vec{r}_{\parallel} + \vec{r}_{\perp} \quad (229)$$

Then:

$$f(\vec{r}, t) = A \cos(k\vec{r} \cdot \vec{n} - \omega t) = A \cos(k(\vec{r}_{\parallel} + \vec{r}_{\perp}) \cdot \vec{n} - \omega t) \quad (230)$$

$$= A \cos \left(\overbrace{k(\vec{r}_{\parallel} \cdot \vec{n})}^{=|\vec{r}_{\parallel}|=r_{\parallel}} + \overbrace{k(\vec{r}_{\perp} \cdot \vec{n})}^{=0} - \omega t \right) \quad (231)$$

$$= A \cos(kr_{\parallel} - \omega t) = f(r_{\parallel}, t) \quad (232)$$

The meaning of 232 is the following.

The value taken by $f(\vec{r}, t)$ on the generic 3D space point $\vec{r}$ is equal to that taken by the function $f(r_{\parallel}, t)$ of a single scalar spatial coordinate on a cartesian plane containing the vector $\vec{n}$ and in which the abscissa is the scalar distance from the origin, measured along the direction of $\vec{n}$ (that is, precisely, $r_{\parallel}$).

Put into equivalent terms: the value of $f(\vec{r}, t)$ taken on the generic point $\vec{r}$ can always be obtained by projecting $\vec{r}$ along the direction of $\vec{n}$ (the scalar product $\vec{r} \cdot \vec{n}$ does exactly this) and calculating $f(r_{\parallel}, t)$, where $r_{\parallel}$ is the modulus of the projection.

This is what I have attempted to show in figure 17.

If you followed the above discussion, you should realize that a three-dimensional plane wave is “representable” as a *monodimensional* traveling wave propagating, with wave number k and angular frequency ω , along the direction of the versor $\vec{n}$.

An important concept which emerges from this discussion is that, in general, the wave number of a multidimensional plane wave *depends* on direction: it will be k in the direction of the versor $\vec{n}$, but will have a different value in a different direction. This aspect is further clarified in section 1.6 of the extracurricular part.

Of course, for the monodimensional wave 232 the wave number defines a corresponding wave length given by:

$$k = \frac{2\pi}{\lambda} \quad (233)$$

This wave length will thus be the wave length in the direction of the versor $\vec{n}$.

1.4.4.3 Wave fronts

123. A very useful concept which we will be using when dealing with plane waves is that of *wave front*. In general, a wave front of any multidimensional wave (not necessarily a plane wave) is defined as the locus of the space points on which the phase of the wave takes a constant value at a given time (trivially, being the locus of constant phase, a wave front will also be the locus of a constant value of the wave; the opposite is not true, though: constant value does not imply constant phase; compare $\cos(k\vec{r} \cdot \vec{n} - \omega t)$ and $\cos(k\vec{r} \cdot \vec{n} - \omega t + 2\pi)$: value is the same, but phases differ by 2π).

Plane waves are called like that because their wave fronts are planes orthogonal to the direction of the versor $\vec{n}$ (and thus parallel to each other).

In fact, also considering point 122, all the $\vec{r}$ vectors whose tips lie on a plane Π orthogonal to $\vec{n}$ share the same projection along the direction of $\vec{n}$ (refer to figure 18):

But then, at a given fixed time t , the value taken by the phase of the wave (that is: the argument of the cosine) will be the same for all the points of Π (eq. 232):

$$\Pi \perp \vec{n} \implies \vec{r} \cdot \vec{n} = r_{\parallel} = \text{constant} \quad \forall \vec{r} \in \Pi \quad (234)$$

$$\implies \text{phase} = k\vec{r} \cdot \vec{n} - \omega t = kr_{\parallel} - \omega t = \text{constant} \quad \forall \vec{r} \in \Pi \quad (\text{at fixed time}) \quad (235)$$

That is: Π is a wave front.

Obviously, this argument can be applied to any plane which is orthogonal to $\vec{n}$ and thus any plane which is orthogonal to $\vec{n}$ is a wave front of the plane wave.

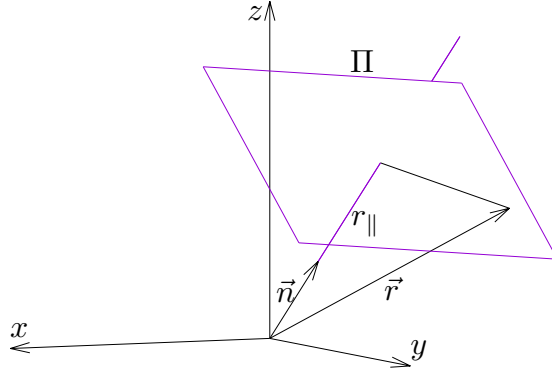


Figure 18: All the vectors leaning against the plane Π , orthogonal to the direction of the vector $\vec{n}$, share the same projection $r_{||}$ along the direction of $\vec{n}$. $r_{||}$ is also the distance of Π from the origin.

Note that $r_{||}$ is also the distance of Π from the origin (the distance of a plane from a point is the length of the segment going from the point to the plane and being orthogonal to the plane). Clearly, the particular value taken by $f(\vec{r}, t)$ on different planes will be, in general, different, but the important point is that the value of the phase (and thus the value of $f(\vec{r}, t)$) will be the same on all the points of the *same* plane.

124. Since the phase of a plane wave is the argument of a cosine (eq. 227) it is clear that an infinite family of wave fronts on which the plane wave takes the same value must exist, corresponding to infinite phase values differing by an integer multiple of 2π :

$$\begin{aligned} A \cos(k\vec{r} \cdot \vec{n} - \omega t) &= A \cos(k\vec{r} \cdot \vec{n} - \omega t \pm 1 \times 2\pi) \\ &= A \cos(k\vec{r} \cdot \vec{n} - \omega t \pm 2 \times 2\pi) = \dots = A \cos(k\vec{r} \cdot \vec{n} - \omega t \pm j \times 2\pi) = \dots \end{aligned}$$

As you can easily guess, the spacing of such wave fronts is equal to the wave length λ in the direction of $\vec{n}$.

To see this in a formal way, let Π_1 and Π_2 be any two *consecutive* wave fronts belonging to the family on which the phase values differ by an integer multiple of 2π .

Since Π_1 and Π_2 are consecutive, their corresponding constant phase values will differ by 2π :

$$|\text{phase on } \Pi_1 - \text{phase on } \Pi_2| = 2\pi \quad (236)$$

$$|(kr_{||,1} - \omega t) - (kr_{||,2} - \omega t)| = 2\pi \quad (237)$$

where $r_{||,1}$ and $r_{||,2}$ are the constant values of the moduli of the projection of any point of Π_1 and Π_2 , respectively, along $\vec{n}$, i.e. the distances of Π_1 and Π_2 from the origin (as discussed in point 123; see also fig. 18). In math symbols:

$$r_{||,1} = \vec{r} \cdot \vec{n} \quad \forall \vec{r} \in \Pi_1 \quad (238)$$

$$r_{\parallel,2} = \vec{r} \cdot \vec{n} \quad \forall \vec{r} \in \Pi_2 \quad (239)$$

Thus:

$$|r_{\parallel,1} - r_{\parallel,2}| \quad (240)$$

is the spacing of the two wave fronts, which can be worked out as:

$$|(kr_{\parallel,1} - \omega t) - (kr_{\parallel,2} - \omega t)| = 2\pi \quad (241)$$

$$|k(r_{\parallel,1} - r_{\parallel,2})| = 2\pi \quad (242)$$

$$\frac{2\pi}{\lambda} |r_{\parallel,1} - r_{\parallel,2}| = 2\pi \quad (243)$$

$$|r_{\parallel,1} - r_{\parallel,2}| = \lambda \quad (244)$$

i.e. the spacing of any two consecutive wave fronts sharing a common value of the plane wave is equal to the wave length (in the direction of $\vec{n}$), as anticipated.

1.4.4.4 Propagation direction

125. As promised in point 120, I'll now show you that the propagation direction of the plane wave 227 is actually that of the versor $\vec{n}$.

Take a particular wave front Π . As already seen in the previous point, this is a plane orthogonal to $\vec{n}$.

Since at time t the phase of the plane wave takes the same value on all points of Π , it must hold:

$$k\vec{r} \cdot \vec{n} - \omega t = kr_{\parallel} - \omega t = Q \quad (\text{constant}) \quad \forall \vec{r} \in \Pi \quad (245)$$

But this means that Π *moves away from the origin along the direction of $\vec{n}$* as time passes. In fact:

$$\text{distance of } \Pi \text{ from the origin} = r_{\parallel} = \frac{Q}{k} + \frac{\omega}{k}t \quad (246)$$

which shows that the distance of the wave front from the origin ($r_{\parallel}$) increases linearly with time. The propagation velocity is the velocity at which $r_{\parallel}$ varies with time, that is:

$$v = \frac{dr_{\parallel}}{dt} = \frac{\omega}{k} = \frac{\lambda}{T} \quad (247)$$

which is what it has to be (eq. 220).

126. It follows from the above that a useful way to visualize a traveling plane wave is to imagine all its wave fronts corresponding, for instance, to the maxima, moving in the direction of the versor $\vec{n}$ and remaining, of course, parallel to each other and orthogonal to $\vec{n}$ itself.

It should be clear that the wave fronts for a *bidimensional* plane wave are straight lines (instead of planes) on the xy plane: in figure 19 I have represented a bidimensional plane wave evidencing the wave fronts corresponding to the maxima (hence the phase is $k\vec{r} \cdot \vec{n} - \omega t = 2\pi m$, $m \in \mathbb{Z}$) and the propagation direction of the wave.

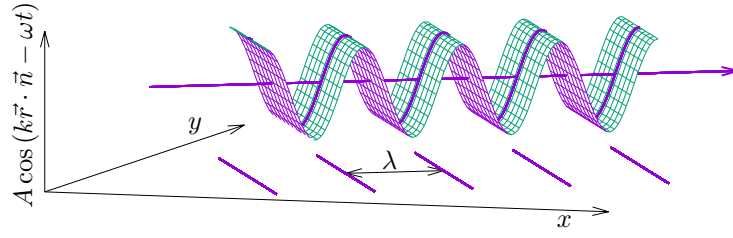


Figure 19: A bidimensional plane wave at a fixed time. The wave is propagating in the direction given by:

$$\vec{n} = (\cos(\pi/6), \sin(\pi/6))$$

evidenced by the arrow. On the surface which is the graph of the plane wave I have also highlighted its projection onto the plane which is orthogonal to xy and contains the propagation direction: as you can see, this projection is a simple monodimensional sinusoidal wave having the same wave length. On the xy plane I have also shown the wave fronts corresponding to the maxima.

1.4.4.5 Bravais lattice for (the spatial part of) a plane wave

127. As we saw in point 122, the spatial part of a plane wave can be visualized as a monodimensional periodic function with wave number k and corresponding wave length λ in the propagation direction (that is, the direction of $\vec{n}$).

On the other hand, the spatial part of a plane wave is just a periodic function of three coordinates (at a fixed time) and we saw that, in general, such a function defines a Bravais lattice in space (point 57).

You might wonder how this Bravais lattice can be derived and visualized for the spatial part of a given plane wave. Indeed, this can be done analytically and I used to include the derivation in this section.

However, due to the insufficient amount of time available for this course, I had to move this (interesting) insight to the extracurricular part (section 1.6).

1.4.4.6 Wave vector

128. For the rest of this course we will always use a more compact form for the expression of a plane wave. By defining the *wave vector* as:

$$\vec{k} = k\vec{n} = \frac{2\pi}{\lambda}\vec{n} \quad (248)$$

we can write the plane wave as:

$$f(\vec{r}, t) = A \cos(\vec{k} \cdot \vec{r} - \omega t) \quad (249)$$

With this notation, eq. 249 is formally identical to 223, the only difference being the vectorial nature of the product in the spatial part.

1.4.5 Stationary plane waves

129. Similar to what we have seen for the monodimensional case (point 119), also in 2D or 3D we can have stationary plane waves, whose simplest mathematical form is:

$$f(\vec{r}, t) = A \cos(\vec{k} \cdot \vec{r}) \cos(\omega t) \quad (250)$$

Again, note how the spatial and temporal parts are separated, and this is what determines the stationary character of the wave.

The same remarks we did for the monodimensional case hold in multiple dimensions.

In particular, the nodes of a stationary plane wave (which, in multiple dimensions, are not points, but straight lines on the cartesian plane (2D) or planes in the cartesian space (3D)) are time invariant: that is, the loci of the points where the plane wave takes the null value remain localized in the same regions of the plane or space, independently on time.

On a fixed point $\vec{r}_0$ not belonging to a node the plane wave harmonically oscillates as a function of time, with an amplitude equal to $A \cos(\vec{k} \cdot \vec{r}_0)$; I mean that the values taken by the plane wave do oscillate remaining inside the interval $\left[-A \cos(\vec{k} \cdot \vec{r}_0), A \cos(\vec{k} \cdot \vec{r}_0)\right]$, that is:

$$-A \cos(\vec{k} \cdot \vec{r}_0) \leq f(\vec{r}_0, t) \leq A \cos(\vec{k} \cdot \vec{r}_0) \quad (251)$$

1.4.6 The complex exponential form of traveling sinusoidal waves

130. An extremely useful formalism to deal with sinusoidal waves is their representation with a complex exponential function.

Consider the plane wave:

$$f(\vec{r}, t) = A \cos(\vec{k} \cdot \vec{r} - \omega t) \quad (252)$$

By making use of the Euler identity (eq. 13) it is evident that such wave can be regarded as the real part of the exponential:

$$A \exp\left(i(\vec{k} \cdot \vec{r} - \omega t)\right) = A \cos(\vec{k} \cdot \vec{r} - \omega t) + iA \sin(\vec{k} \cdot \vec{r} - \omega t) \quad (253)$$

Hence, a plane wave can be written in the form:

$$f(\vec{r}, t) = A \exp\left(i(\vec{k} \cdot \vec{r} - \omega t)\right) \quad (254)$$

being understood that only the real part has a physical meaning.

The reason why this representation is so useful is that the algebraic manipulations with the exponential function are so much more comfortable than those with trigonometric functions (by the way, this is also the reason why the Fourier expansion is very often used in its exponential form, eq. 101–102)

The usual procedure is to write a sinusoidal wave in complex exponential form, perform all the algebra required to solve a given problem, and eventually convert back to the trigonometric representation by taking the real part of the obtained complex result:

$$A \cos(\vec{k} \cdot \vec{r} - \omega t) = \Re\left(A \exp\left(i(\vec{k} \cdot \vec{r} - \omega t)\right)\right) \quad (255)$$

In the following we will often use the complex exponential form of the traveling waves.

Moreover, I will use the term “plane wave” even when referring only to the spatial part. It should be clear that the exponential:

$$\exp\left(i\vec{k} \cdot \vec{r}\right) \quad (256)$$

can always be considered as the spatial part of a plane wave whose complete expression is obtained multiplying the former by $\exp(-i\omega t)$ (and by an amplitude factor A):

$$A \exp(i \vec{k} \cdot \vec{r}) \exp(-i\omega t) = A \exp(i (\vec{k} \cdot \vec{r} - \omega t)) \quad (257)$$

In this regard, if you review eq. 126, you realize that the terms of the Fourier expansion of a periodic function are nothing but spatial parts of plane waves with wave vector values corresponding to the points of the Bravias lattice defining the periodicity of the function. For this reason, Fourier expansions are sometimes equivalently called “plane wave expansions”.

I display an example of the usefulness of the complex exponential form of traveling sinusoidal plane waves in section 1.7 of the extracurricular part.

1.4.7 The complex exponential form of stationary sinusoidal waves

131. Since we will come across and discuss standing plane waves expressed in complex exponential form, it is convenient to mention them at this point. In point 129 we saw that the peculiar feature of a stationary plane wave is that space and time dependencies are “separated”. With the complex exponential notation, this means that the spatial part of the wave is purely real or purely imaginary, where the temporal part is a complex exponential. For instance:

$$\overbrace{A \cos(\vec{k} \cdot \vec{r})}^{\text{spatial part}} \overbrace{\exp(-i\omega t)}^{\text{temporal part}}$$

You can see that the real part of the above function is just a stationary wave like 250:

$$\begin{aligned} \Re \left(A \cos(\vec{k} \cdot \vec{r}) \exp(-i\omega t) \right) &= \Re \left(A \cos(\vec{k} \cdot \vec{r}) (\cos(\omega t) - i \sin(\omega t)) \right) \\ &= \Re \left(A \cos(\vec{k} \cdot \vec{r}) \cos(\omega t) - i A \cos(\vec{k} \cdot \vec{r}) \sin(\omega t) \right) \\ &= A \cos(\vec{k} \cdot \vec{r}) \cos(\omega t) \end{aligned} \quad (258)$$

The same holds when the spatial part is a purely imaginary sinusoidal function, for example:

$$\overbrace{i A \sin(\vec{k} \cdot \vec{r})}^{\text{spatial part}} \overbrace{\exp(-i\omega t)}^{\text{temporal part}}$$

$$\begin{aligned} \Re \left(i A \sin(\vec{k} \cdot \vec{r}) \exp(-i\omega t) \right) &= \Re \left(i A \sin(\vec{k} \cdot \vec{r}) (\cos(\omega t) - i \sin(\omega t)) \right) \\ &= \Re \left(i A \sin(\vec{k} \cdot \vec{r}) \cos(\omega t) + A \sin(\vec{k} \cdot \vec{r}) \sin(\omega t) \right) \\ &= A \sin(\vec{k} \cdot \vec{r}) \sin(\omega t) = A \cos\left(\vec{k} \cdot \vec{r} - \frac{\pi}{2}\right) \cos\left(\omega t - \frac{\pi}{2}\right) \end{aligned} \quad (259)$$

(in this case an initial phase of $-\pi/2$ is also introduced)

2 The structure of crystalline solids

132. As you will realize, the next to come topics of this course require some concepts which lie at the base of the description of the crystalline solids. For this reason, I will introduce in this section the ones that we will be needing.

I want to emphasize that I will limit the material to those parts which are strictly functional to this course (which is *not* a crystallography course).

133. I assume that you all have the notion of a crystalline solid as a system whose peculiar feature is that of being made up, at a microscopic level, by a group of atoms (or ions or molecules) which gets repeated *periodically* and (in theory) *indefinitely* in space.

134. The group of atoms which generates the whole crystal by periodic repetition along three (non coplanar) directions is called *basis*. In the simplest case (and we will be limiting ourselves to this) the basis is made by a single atom (thus, in our case, a macroscopic crystal will be in general the crystal of an element; most of the time, although not always, we will be dealing with metallic elements, like *Na*, *Ca* etc.)

135. The periodic replication in space of the basis is described in abstract terms by means of a three-dimensional lattice called *Bravais lattice* or *direct lattice*.

A replica of the basis is associated with each point of the Bravais lattice, which thus accomplishes its indefinite repetition in space. Each basis replica is also called an *image* of the basis.

When the basis is itself a 3D object (i.e. it is not a single atom/point), it is insignificant which point of the object is made coincident with a lattice point, as long as always the same point of the object is brought in coincidence with every lattice point: the resulting crystal structure will be always exactly the same.

As mentioned, the basis repeated by the points of the Bravais lattice on which the real crystalline solid is built is a group of atoms. However, and I'm saying this because we will happen to use it, the concept of a Bravais lattice is an abstract mathematical concept and any (abstract) object can actually be associated with each lattice point (for instance, the basis might be, in turn, a set of ordered lattice points, as we will see in a while).

The logic behind the process of generating an abstract bidimensional crystal is shown in figure 20.

136. You remember that we already introduced the concept of a Bravais lattice in the context of the Fourier expansion of periodic functions in multiple dimensions (p. 31). Of course, in this section we are speaking about precisely the same thing and you can realize it in the light of the following argument.

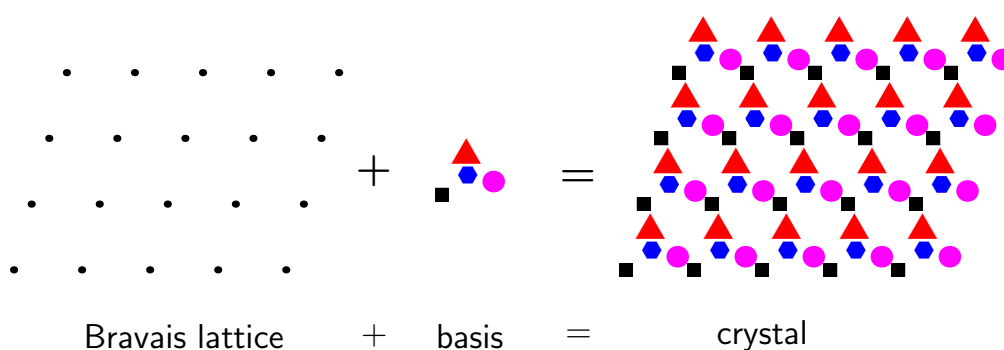


Figure 20: The periodic structure of a crystalline solid is obtained by associating a motif (the basis) to each point of a Bravais lattice

Since the atoms that make up a crystal are repeated periodically, any physical property related to the atomic position *must be a three-dimensional periodic function of the spatial coordinates* and its periodicity must be defined by the same Bravais lattice on which the crystalline structure is based. A trivial example of such a property is the electron density: it is a function of x, y, z and in a crystal it will clearly show a periodic behavior in the three dimensions (with maxima on the atomic nuclei); this periodicity must necessarily coincide with that of the crystal, that is, it must be based on the same Bravais lattice. Another example of a physical property exhibiting a periodic behavior in a crystal is the potential energy field generated by atoms (nuclei plus electrons).

Therefore, it should be clear that the Bravais lattice needed to describe a crystalline structure is also needed for the mathematical description of all those physical properties which depend on that crystalline structure.

In this part of the notes we will take up the concepts of Bravais lattice and reciprocal lattice in order to make them more formal and further explore them.

2.1 The (direct) Bravais lattice

137. There are two equivalent formal definitions of a Bravais lattice.

1. A Bravais lattice $\mathcal{R}$ is an infinite set of discrete points in space such that their *disposition and orientation* appears the same when the set is looked at from any one of its elements
2. A Bravais lattice $\mathcal{R}$ is the infinite set of points located by the $\vec{R}$ vectors which are defined by:

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \quad (260)$$

where $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are three non coplanar (that is, linearly independent) vectors and $n_1, n_2, n_3 \in \mathbb{Z}$.

The vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are called *primitive vectors* or *generators* of the lattice.

The point located by the vector $\vec{R}$ is reached by moving n_1 steps of length a_1 in the direction of $\vec{a}_1$, n_2 steps of length a_2 in the direction of $\vec{a}_2$ and n_3 steps of length a_3 in the direction of $\vec{a}_3$.

138. Remark: in general mathematical terms, a point of a Bravais lattice is represented by its three coordinates in a reference system, which can be equivalently interpreted as the components of a corresponding position vector. For this reason, with reference to Bravais lattices, I will use the words “point” or “vector” interchangeably (that is: “the points of a Bravais lattice” or “the vectors of a Bravais lattice” will mean exactly the same thing).

139. Please note: any three non coplanar vectors in $\mathbb{R}^3$ are a basis of $\mathbb{R}^3$ (in an algebraic sense) and *any* point of $\mathbb{R}^3$ can be expressed as a linear combination of them. What makes of a Bravais lattice a *lattice*, precisely, is that the coefficients of the linear combination are *integer numbers*.

140. Figure 21 shows a portion of a bidimensional Bravais lattice together with its two primitive vectors (which, in the bidimensional case, are required to be non collinear, of course).

Figure 22 shows the simplest three-dimensional Bravais lattice: the *simple cubic lattice*, in which the three generators share the same modulus and are oriented along the three cartesian axes.

141. When a basis with multiple elements is associated with the points of a Bravais lattice to make up a crystal structure, each element of the basis is related to all its replicas by all the vectors of the Bravais lattice; I mean: if you take a given reference point P of the lattice and consider a

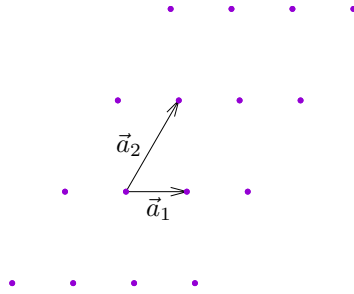


Figure 21: Bidimensional Bravais lattice generated by the two linearly independent vectors $\vec{a}_1$ e $\vec{a}_2$.

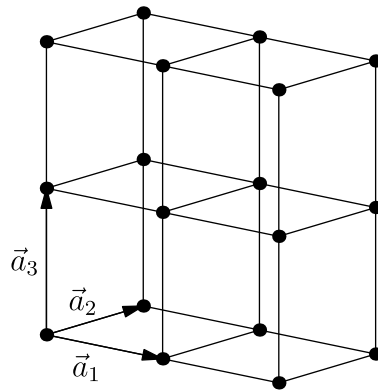


Figure 22: The simple cubic lattice.

given element E of the basis associated with this point, then all the (infinite) E replicas related to E by the translational symmetry of the lattice are reached by adding to the position vector of E all the lattice vectors. This is shown in figure 23 for a bidimensional “crystal”.

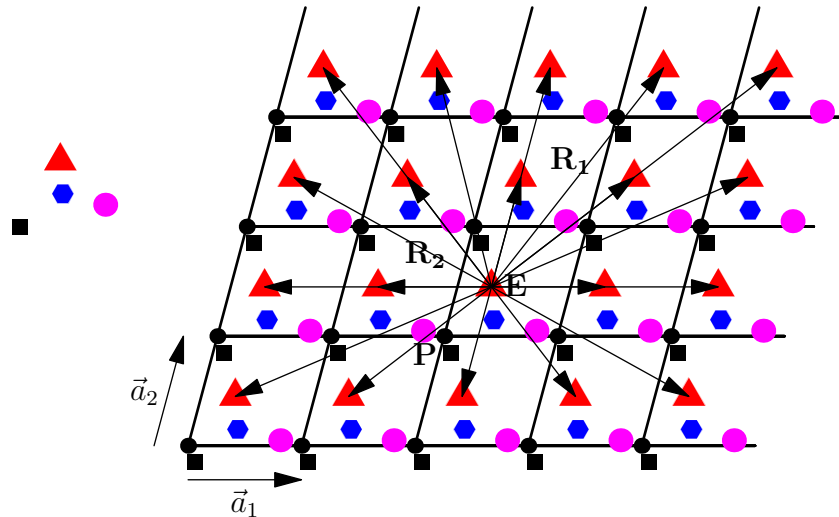


Figure 23: A basis of four elements, shown on the left for clarity, is associated with every point of a bidimensional Bravais lattice defined by the two primitive vectors $\vec{a}_1$, $\vec{a}_2$. The lattice point P is taken as reference and the basis element E of the basis associated with P is chosen. All the images of E generated by the translational symmetry of the Bravais lattice are reached by adding to the position of E all the vectors of the Bravais lattice. For example:

$$\begin{aligned}\vec{R}_1 &= \vec{a}_1 + 2\vec{a}_2 \\ \vec{R}_2 &= -2\vec{a}_1 + \vec{a}_2\end{aligned}$$

142. We will use here and there the following trivial property of a Bravais lattice: the difference (or the sum) of any two vectors of a Bravais lattice is still a vector of the Bravais lattice. The proof is immediate in the light of definition 2. Any two lattice vectors $\vec{R}_i$ and $\vec{R}_j$ are defined by:

$$\begin{aligned}\vec{R}_i &= n_{1i}\vec{a}_1 + n_{2i}\vec{a}_2 + n_{3i}\vec{a}_3 = \sum_{l=1}^3 n_{li}\vec{a}_l \quad n_{li} \in \mathbb{Z} \\ \vec{R}_j &= n_{1j}\vec{a}_1 + n_{2j}\vec{a}_2 + n_{3j}\vec{a}_3 = \sum_{l=1}^3 n_{lj}\vec{a}_l \quad n_{lj} \in \mathbb{Z}\end{aligned}$$

For their difference (or sum) we have:

$$\vec{R} = \vec{R}_i \mp \vec{R}_j = \overbrace{(n_{1i} \mp n_{1j})}^{\in \mathbb{Z}} \vec{a}_1 + \overbrace{(n_{2i} \mp n_{2j})}^{\in \mathbb{Z}} \vec{a}_2 + \overbrace{(n_{3i} \mp n_{3j})}^{\in \mathbb{Z}} \vec{a}_3$$

which is to say that $\vec{R}$ belongs to the Bravais lattice, again by virtue of definition 2.

143. Note that not every regular net of points is a Bravais lattice. The most quoted example in this regard is the so called “honeycomb lattice”, which is shown in figure 24. All the points

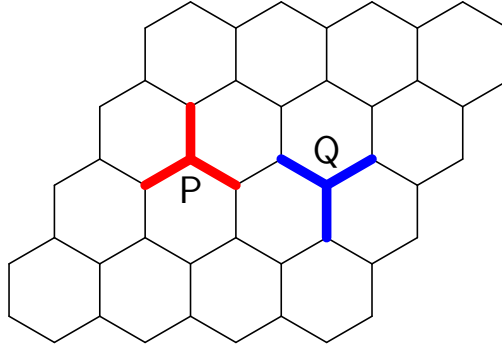


Figure 24: A regular “honeycomb” lattice of points is *not* a Bravais lattice. Both P and Q have three lattice points around them at the same distance, but the *orientation* of such lattice points is not the same in the two cases.

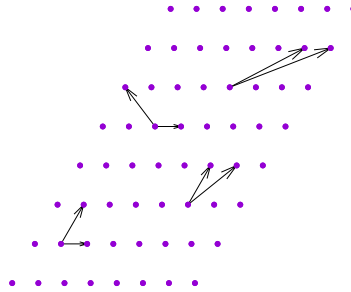


Figure 25: The choice of the primitive vectors of a Bravais lattice is not unique. In this figure four different and equivalent choices of the generators of a bidimensional lattice are shown.

of this lattice are connected to the neighboring points in the same way, but the *orientation* of these connections is not the same for every point. Refer to figure 24: point P has three nearest lattice points at the same distance: one is “up”, one is “down left” and one is “down right”; point Q is surrounded by three lattice points at the same distance as those surrounding P , but, when viewed from Q , these three points have a different orientation: one is “down”, one is “up left” and one is “up right” (i.e. the specular image of the points around P). Since it is not the same when viewed from P or Q , the “honeycomb” lattice does not satisfy definition 1 and thus is not a Bravais lattice (you can easily convince yourself that the “honeycomb” lattice does not satisfy definition 2 either).

144. The choice of the primitive vectors of a Bravais lattice is not unique (for exactly the same reason that the choice of a basis of $\mathbb{R}^2$ or $\mathbb{R}^3$ is not unique); there are infinite vector triplets that generate the same Bravais lattice. This is shown in figure 25 for a bidimensional Bravais lattice.

2.1.1 First, second, ... neighbors

145. For a fixed point P of a Bravais lattice, the points at a minimum distance from P are called *first neighbors*; those at the next minimum distance are called *second neighbors* and so on. Clearly, by definition of Bravais lattice, every point of the lattice has exactly the same first,

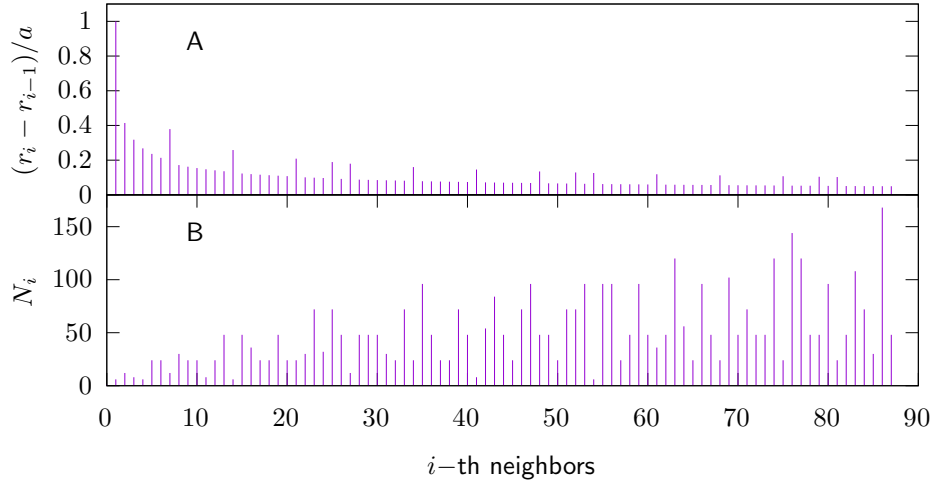


Figure 26: For a simple cubic Bravais lattice: A: difference (in units of the cell constant a) between the radii r_i and r_{i-1} of the spheres corresponding to the i -th and $(i-1)$ -th neighbors of the point at the origin; B: number of the first, second, $\dots$ i -th, $\dots$ neighbors of the point at the origin.

second, etc. neighbors, at the same distances and orientation.

All the first neighbors of a given point lie on the surface of a sphere (3D case) or on a circle (2D case), whose radius is the common distance from the considered point. The same holds for the second neighbors etc. The spheres (circles) corresponding to the first, second etc. neighbors are concentric and can be sorted on the base of their radius.

As you can easily guess, in general, the number and (common) distance of the first, second etc. neighbors depend on the type of Bravais lattice.

Moreover, the number of neighbors of a given type increases and the difference between the radii of two consecutive spheres decreases at increasing distance from the reference point. However, this behavior is not monotonic, as you can see in figure 26, which refers to a simple cubic Bravais lattice.

2.2 Primitive cell

146. As already mentioned (point 57) the three primitive vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ of a Bravais lattice define a *primitive* or *elementary cell*, which is the parallelepiped whose any three sides sharing a vertex are the three primitive vectors.

The 8 vertices of the primitive cell are obtained by combining the primitive vectors as (fig. 27):

$$n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \quad n_1, n_2, n_3 \in \{0, 1\} \quad (261)$$

The set of lengths and angles necessary and sufficient to define the elementary cell of a given Bravais lattice are usually called *cell parameters*. For instance, the primitive cell for a simple cubic lattice is a cube: the three primitive vectors share the same modulus and the angle between any pair of primitive vectors is always $\pi/2$; in this case, the cell parameters reduce to the single value of the common length of the primitive vectors (all other cell parameters are fixed).

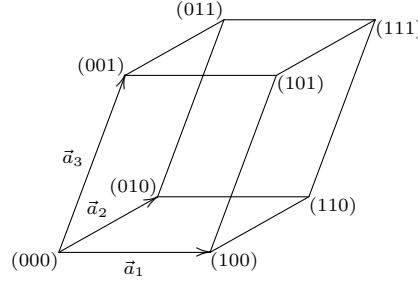


Figure 27: The parallelepiped formed by the three primitive vectors combined according to 261. For each vertex the three integer coefficients (n_1, n_2, n_3) used in the linear combination are shown. For instance, the vertex (101) is obtained with the linear combination: $1 \cdot \vec{a}_1 + 0 \cdot \vec{a}_2 + 1 \cdot \vec{a}_3$.

In the most general three-dimensional case, there will be 6 cell parameters: the three moduli of the primitive vectors and the three angles between any pair of primitive vectors:

$$\text{3D case: cell parameters: } a_1, a_2, a_3, \angle(\vec{a}_1 \vec{a}_2), \angle(\vec{a}_2 \vec{a}_3), \angle(\vec{a}_1 \vec{a}_3)$$

In the 2D case the number of cell parameters decreases to 3:

$$\text{2D case: cell parameters: } a_1, a_2, \angle(\vec{a}_1 \vec{a}_2)$$

In the 1D case the primitive cell is just a scalar interval and so there is a single cell parameter, which is the interval's amplitude a (point 6):

$$\text{1D case: cell parameters: } a$$

The primitive cell enjoys the following properties:

1. when it gets translated according to all the vectors $\vec{R}$ of the Bravais lattice it fills the whole space without either overlapping itself or leaving voids: in other words, the whole space is fully *partitioned* between the infinite primitive cells of the lattice. Every replica of the primitive cell is uniquely associated with a lattice vector $\vec{R}$; a Bravais lattice can be equivalently thought of as generated by the translation of its primitive cell according to all its infinite vectors: $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$ with $n_1, n_2, n_3 \in \mathbb{Z}$
2. the primitive cell is *semi open*: that is, the three cell faces containing the three generator vectors belong to the primitive cell, but the remaining three faces do not. Also the three lattice points $\vec{a}_1, \vec{a}_2, \vec{a}_3$, that is the points located by the tip of the primitive vectors, do not belong to the primitive cell. In a more synthetic, formal and elegant way, the characteristic of being semi open is described in mathematical symbols by defining the volume V of the primitive cell as the set of $\mathbb{R}^3$ points $\vec{v}$:

$$V = \left\{ \vec{v} \in \mathbb{R}^3 : \vec{v} = \sum_{i=1}^3 x_i \vec{a}_i : 0 \leq x_i < 1 \right\} \quad (262)$$

where the “asymmetry” of the limits for the x_i coefficients should be noted: $0 \leq x_i$ but $x_i < 1$ (please be careful not to confuse the x_i 's ($\in \mathbb{R}$) with the n_i 's ($\in \mathbb{Z}$) in eq. 261).

I have tried to make this point clearer for a bidimensional case in figure 28.

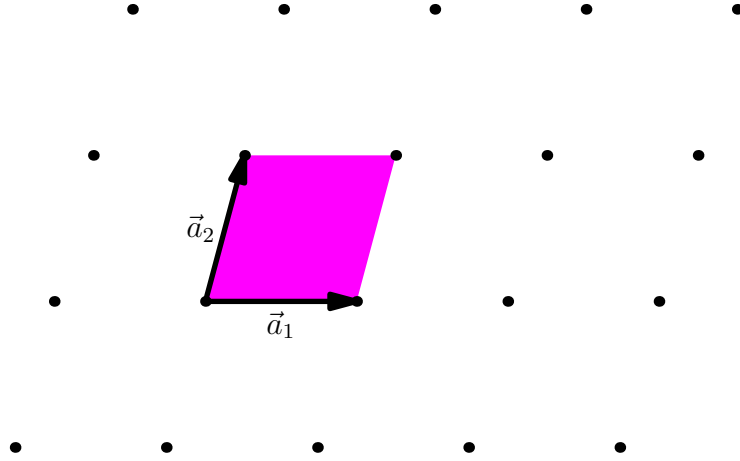


Figure 28: The *semi open* primitive cell of a bidimensional Bravais lattice: the sides corresponding to the two primitive vectors $\vec{a}_1$ and $\vec{a}_2$ belong to the area of the primitive cell; the remaining two sides, including the lattice points $\vec{a}_1$ and $\vec{a}_2$, are *not* included in the area of the primitive cell:

$$\text{area} = \left\{ \vec{r} : \vec{r} = \sum_{i=1}^2 x_i \vec{a}_i : 0 \leq x_i < 1 \right\}$$

This ensures that translating the primitive cell according to all the lattice vectors fills the whole plane without either *overlapping itself* or leaving voids.

Realize that being semi open is a necessary condition for the primitive cell to enjoy property 1 above.

3. once built as per eq. 261, the primitive cell can be translated (but *not* rotated!) by any vector (not necessarily a vector of the Bravais lattice), while still enjoying property 1. Note that this (of which I do not give any formal proof) is the three-dimensional analog of what we already observed for the 1D case at point 6.
4. a direct consequence of being semi open is that any primitive cell contains always one and only one lattice point (refer to fig. 28); you can realize this in an equivalent way if you think of appropriately translating the primitive cell (thanks to property 3) such that there are no lattice points on its faces or sides or vertices. Yet another way to see this is that of assigning to a given primitive cell the lattice points on its “borders” taking into account that those lattice points are shared with the neighboring cells:

- ⇒ a lattice point on a face will be counted for 1/2 only, since it is shared between 2 neighboring cells
- ⇒ a lattice point on a side will be counted for 1/4 only, being shared between 4 cells
- ⇒ a lattice point on a vertex will be counted for 1/8 only, being shared between 8 cells

(obviously, in the case of a bidimensional lattice, which I will use very often because it is simpler to visualize and draw, the primitive cell is a parallelogram and thus the fractions to be considered are: 1/2 for a lattice point on a side and 1/4 for a lattice point on a vertex; there are no faces in this case)

In figure 29 these two methods for counting the number of lattice points included in a primitive cell of a bidimensional lattice are shown.

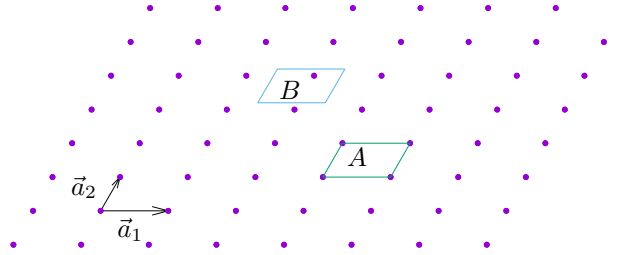


Figure 29: The primitive vectors $\vec{a}_1$ and $\vec{a}_2$ of the shown Bravais lattice define a primitive cell of which A and B are two identical replicas. The number of lattice points contained in cell A is obtained by considering that each of the 4 points at the vertices is shared between 4 cells and thus counts for $1/4$ only: n. of points = $4 \times 1/4 = 1$. The cell B has been translated by $0.4\vec{a}_1 + 0.2\vec{a}_2$ such that it has no lattice points on its sides or vertices: this way it is readily seen that it contains a single lattice point.

5. all the infinite possible primitive cells of a Bravais lattice share the same volume. You can convince yourself in the following way (this proof is not mathematically rigorous: you might be interested in a more formal derivation which I present in section 2.1 of the extracurricular part).

The density of lattice points per unit volume of a Bravais lattice is given by:

$$\rho_p = \frac{N}{V} \quad (263)$$

where N is the number of lattice points contained in a portion of the lattice of volume V . Now: *the periodicity of the lattice* ensures a direct proportionality between N and V : a portion of lattice of double volume must contain a double number of lattice points. Note that this would not be the case for an infinite, *but not periodic* set of points. (Actually, this is a weak point: even for a Bravais lattice, in general, the number of points contained in a given volume depends on the *shape* of that volume; the numbers of points corresponding to two equal volumes of different shapes might actually be different; however, if in eq. 263 you assume to always consider volumes of the same shape, then it is true that N and V are directly proportional, and this is due to the periodicity of the Bravais lattice).

So: if you take for good eq. 263, the direct proportionality between N and V means:

$$N = \alpha V \quad (264)$$

with α the proportionality constant.

By substituting above we get:

$$\rho_p = \frac{\alpha V}{V} = \alpha \quad (265)$$

that is: the density of lattice points per unit volume of a Bravais lattice is constant.

If you now consider *any* primitive cell of volume v and keep in mind that it must contain one and only one lattice point (point 4 above), then:

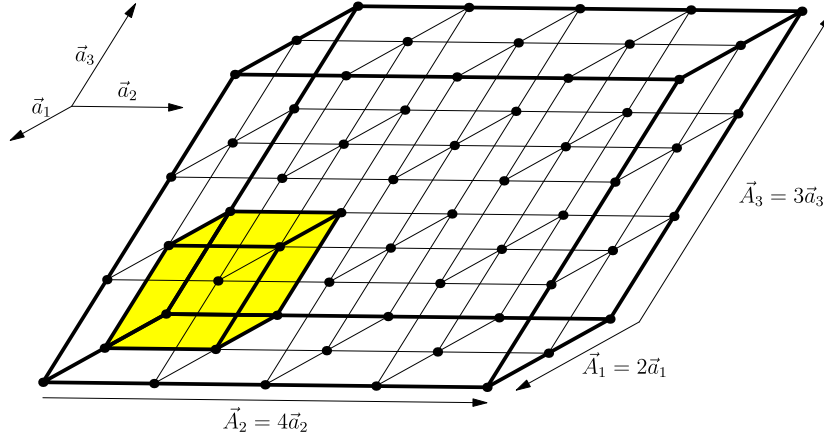


Figure 30: An example of a $2 \times 4 \times 3$ supercell for the 3D case. I have highlighted the faces of the primitive cell; the edges of both the primitive cell and the supercell are evidenced with a thicker line.

$$\rho_p = \alpha = \frac{[\text{n. of points contained in the volume } v]}{v} = \frac{1}{v} \implies v = \frac{1}{\alpha} = \text{constant} \quad (266)$$

that is: as advertised, the volume of any primitive cell is always the same.

6. since the primitive cell contains a single lattice point, there is a bijective correspondence between primitive cells and lattice points: every vector $\vec{R}$ of a Bravais lattice locates one and only one primitive cell and, correspondingly, every primitive cell locates one and only one lattice point (the one contained in it) (I already mentioned this property in previous point 1)

2.3 Supercells

147. In some contexts it is convenient to define and use a *non primitive* cell obtained, in the simplest case, by “adding together” n_1 consecutive primitive cells along the direction of $\vec{a}_1$, n_2 consecutive primitive cells along the direction of $\vec{a}_2$ and n_3 consecutive primitive cells along the direction of $\vec{a}_3$. We will call “ $n_1 \times n_2 \times n_3$ supercell” (or *unit cell*) such non primitive cell (I already mentioned this type of simple supercell for the 1D case, at point 6).

An example of this simple type of supercell for the 3D case is shown in figure 30.

Of course, a supercell contains more than one lattice point; in particular, since it is made up by $N = n_1 n_2 n_3$ primitive cells, each containing a single lattice point, a $n_1 \times n_2 \times n_3$ supercell will contain N lattice points.

It is easily realized that the three vectors defining a supercell (of the simple type we are dealing with here) must be integer multiples of the primitive vectors which define the primitive cell from which the supercell was derived. In particular, the vectors $\vec{A}_1$, $\vec{A}_2$, $\vec{A}_3$ which define a $n_1 \times n_2 \times n_3$ supercell are related to the primitive vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ by:

$$\vec{A}_1 = n_1 \vec{a}_1 \quad (267)$$

$$\vec{A}_2 = n_2 \vec{a}_2 \quad n_1, n_2, n_3 \in \mathbb{N} \quad (268)$$

$$\vec{A}_3 = n_3 \vec{a}_3 \quad (269)$$

As already noted, the supercell described in this section is the simplest possible: eqs. 267–269 are just a special case of a general “recipe” for constructing a supercell by combining the primitive vectors which I will briefly present in section 2.5.1.

2.3.1 Commensurate lattices

148. Trivially, being integer multiples of the $\vec{a}_j$ ’s, the vectors $\vec{A}_i$ defined by eqs. 267–269 are linearly independent and thus define themselves a Bravais lattice of which the $n_1 \times n_2 \times n_3$ supercell is the primitive cell.

As you can easily realize, the Bravais lattice defined by the $\vec{A}_i$ ’s and the original Bravais lattice defined by the $\vec{a}_j$ ’s are closely related: we say that the two lattices and the corresponding two primitive cells are *commensurate*.

Commensurate lattices enjoy some very intuitive properties and since this concept will be of crucial importance for us in the following (point 299 and, in general, section 4), we present and discuss some of these properties here (these properties are really very simple, so I will skip any formal proof of them).

149. Before presenting the properties, let’s introduce a notation aimed at improving readability and syntheticity of the text to follow:

- $\mathcal{R}_S$ the original Bravais lattice, defined by the primitive vectors $\vec{a}_j$. The subscript S stands for *small*, since $\mathcal{R}_S$ has the smaller primitive cell.
- $\mathcal{C}_S$ the primitive cell of $\mathcal{R}_S$
- $\mathcal{R}_B$ the Bravais lattice defined by the primitive vectors $\vec{A}_j = n_j \vec{a}_j$. The subscript B stands for *big*, since $\mathcal{R}_B$ has the larger primitive cell.
- $\mathcal{C}_B$ the primitive cell of $\mathcal{R}_B$

(Note: for reasons that will become clear in the following, I will use a different notation for these lattices and primitive cells later on; in particular, the indexes will change as: $S \rightarrow \mu$ and $B \rightarrow M$, where μ will stand for *microscopic* and M will stand for *macroscopic*)

150. Let’s also clarify the meaning of the adjective “commensurate” in our context.

For all what we will need in this course, two Bravais lattices (and the two corresponding primitive cells) are commensurate if one is obtained by scaling the other *an integer number of times* along each primitive direction.

Note: the crucial keyword here is “integer”.

With reference to eqs. 267–269 it should be clear that $\mathcal{R}_B$ is obtained from $\mathcal{R}_S$ in exactly this way.

Two commensurate primitive cells have strictly related parameters (point 146): the directions of the primitive vectors are the same (thus the three angles between any pair of primitive vectors are the same) and the ratio of the moduli of corresponding primitive vectors is an integer number: $A_i/a_i = n_i$.

151. And now for the properties enjoyed by the two commensurate Bravais lattices $\mathcal{R}_S$ and $\mathcal{R}_B$:

- a. As already noted, $N = n_1 n_2 n_3$ lattice points of $\mathcal{R}_S$ can be fitted in the primitive cell of $\mathcal{R}_B$ (which is a $n_1 \times n_2 \times n_3$ supercell of $\mathcal{C}_S$). Since with each point of $\mathcal{R}_S$ is associated one $\mathcal{C}_S$ cell, the $\mathcal{C}_B$ cell contains exactly $N = n_1 n_2 n_3$ $\mathcal{C}_S$ cells: see also figure 30.

- b. Letting V and v be the volumes of $\mathcal{C}_B$ and $\mathcal{C}_S$, respectively, from the above it trivially follows:

$$V = Nv \quad (270)$$

- c. All the vectors of $\mathcal{R}_B$ are also vectors of $\mathcal{R}_S$, while the opposite is not true; i.e. there are vectors of $\mathcal{R}_S$ which are *not* vectors of $\mathcal{R}_B$:

$$\vec{R} \in \mathcal{R}_B \implies \vec{R} \in \mathcal{R}_S \quad (271)$$

but:

$$\exists \vec{R} \in \mathcal{R}_S : \vec{R} \notin \mathcal{R}_B \quad (272)$$

This is shown for the 2D case in fig. 31.

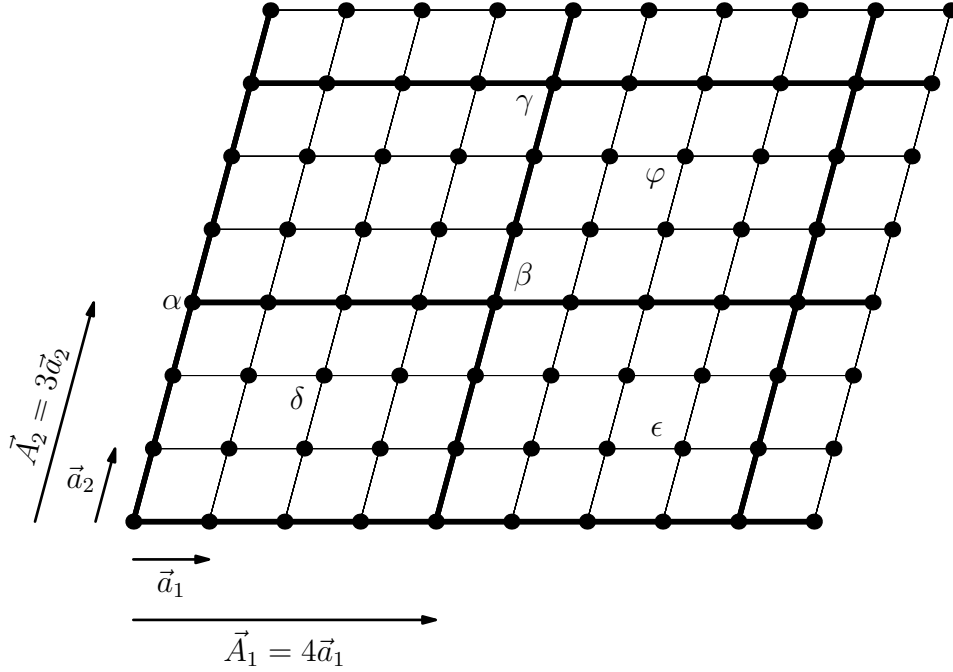


Figure 31: A portion of two 2D commensurate Bravais lattices: $\mathcal{R}_S$ (primitive vectors: $\vec{a}_1, \vec{a}_2$) and $\mathcal{R}_B$ (primitive vectors: $\vec{A}_1 = 4\vec{a}_1, \vec{A}_2 = 3\vec{a}_2$). The primitive cells of $\mathcal{R}_B$ are evidenced with a thicker line.

The points α, β, γ belong to both $\mathcal{R}_S$ and $\mathcal{R}_B$; the points δ, ϵ, ϕ belong to $\mathcal{R}_S$, but not to $\mathcal{R}_B$.

You can think of $\mathcal{R}_B$ as being “immersed” into $\mathcal{R}_S$ or, in math jargon:

$$\mathcal{R}_B \subset \mathcal{R}_S \quad (273)$$

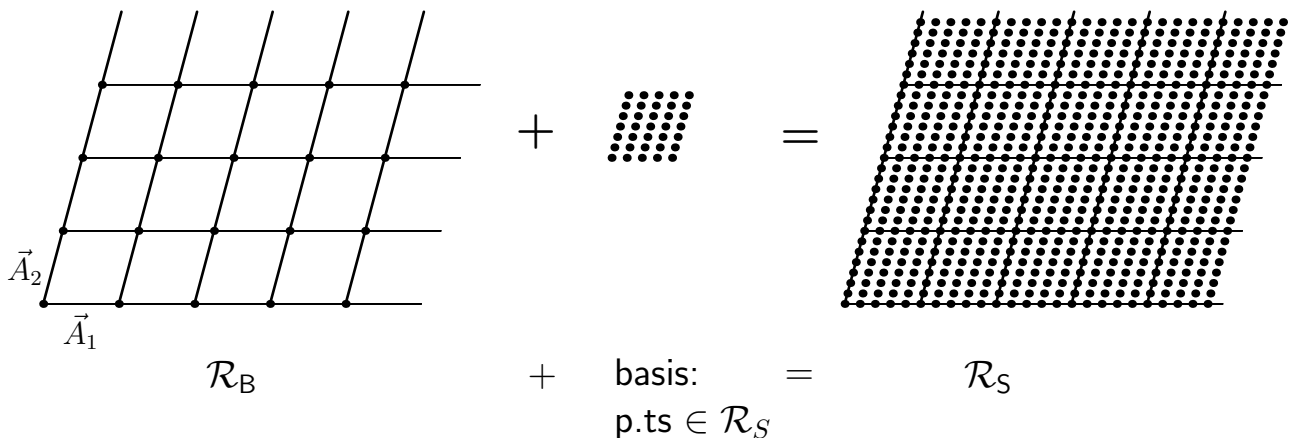


Figure 32: The $\mathcal{R}_B$ Bravais lattice is generated by $\vec{A}_1 = 5\vec{a}_1$ and $\vec{A}_2 = 7\vec{a}_2$ ($\vec{a}_1$ and $\vec{a}_2$ are not shown). Thus the primitive cell of $\mathcal{R}_B$ contains $5 \times 7 = 35$ points of $\mathcal{R}_S$. These can be thought of as the basis (point 135) associated with each $\mathcal{R}_B$ point. The translation of this basis according to all the points of $\mathcal{R}_B$ generates the original $\mathcal{R}_S$ lattice. Compare this with figure 20.

- d. In terms of number of lattice points per unit volume, $\mathcal{R}_S$ is “denser” than $\mathcal{R}_B$ because, as said above, the points of $\mathcal{R}_B$ are a (strict) subset of the points of $\mathcal{R}_S$.

However, $\mathcal{R}_S$ can be completely recovered from $\mathcal{R}_B$ by replicating $\mathcal{C}_B$ together with its content of $\mathcal{R}_S$ points according to all the vectors of $\mathcal{R}_B$. In other words: if we consider the $\mathcal{R}_S$ points contained within a primitive cell of $\mathcal{R}_B$ as the basis (point 135) associated with each $\mathcal{R}_B$ point, then by replicating this basis on all the infinite points of $\mathcal{R}_B$ we obtain $\mathcal{R}_S$ (this was the intended meaning of the statement I had made in point 135 and maybe that time it might have sounded a little “smoky”).

The exact meaning of this statement should be apparent in figure 32 for a bidimensional lattice.

- e. Since $\mathcal{C}_B$ contains an integer number of $\mathcal{C}_S$ cells, if a function is periodic on $\mathcal{R}_S$, it will be also periodic on $\mathcal{R}_B$ while, of course, the opposite is not true in general. This is shown in figure 33 for a function of two variables.
- f. This is the most important (for us) property of two commensurate lattices, and perhaps the less obvious/intuitive.

Claim: the infinite set of points of the small lattice ($\mathcal{R}_S$, the “denser” one) can be partitioned into a finite number of (infinite) subsets.

To see how this is possible, let’s concentrate on a given primitive cell $\mathcal{C}_B$ of $\mathcal{R}_B$ (the larger one, the less “dense”).

As we saw, $\mathcal{C}_B$ is a (simple) supercell of $\mathcal{C}_S$ and contains $N = n_1 n_2 n_3$ lattice points of $\mathcal{R}_S$ (the n_j ’s are the integer factors by which $\mathcal{R}_S$ was scaled along the three primitive directions to obtain $\mathcal{R}_B$).

Based on property d. above, we can regard the N lattice points of $\mathcal{R}_S$ contained in $\mathcal{C}_B$ as the basis associated with every $\mathcal{R}_B$ point.

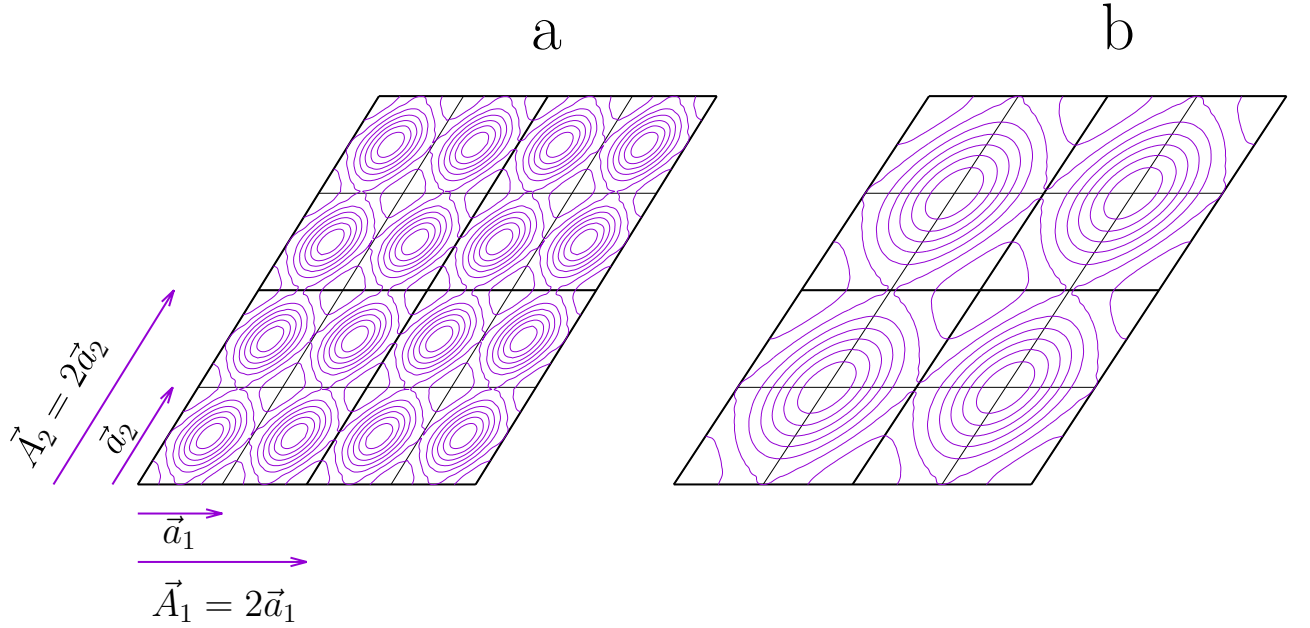


Figure 33: In this figure I have represented two bidimensional commensurate lattices: $\mathcal{R}_S$, defined by the primitive lattice vectors $\vec{a}_1, \vec{a}_2$ and $\mathcal{R}_B$, defined by primitive lattice vectors $\vec{A}_1 = 2\vec{a}_1, \vec{A}_2 = 2\vec{a}_2$ (the cells of $\mathcal{R}_B$ are drawn with a thicker line).

a: isoline plot of a function (of two variables) which is periodic on $\mathcal{R}_S$: the function is also periodic on $\mathcal{R}_B$. b: isoline plot of a function which is periodic on $\mathcal{R}_B$: the function is *not* periodic on $\mathcal{R}_S$.

Now: consider one of the $\mathcal{R}_S$ points inside $\mathcal{C}_B$. Being an element of the basis, this point will have infinite images which are obtained by adding to it all the vectors of $\mathcal{R}_B$ (point 141). Trivially, the considered point plus all its images constitute a *subset* of the points of $\mathcal{R}_S$ (the number of elements of this subset is clearly infinite, for the number of $\mathcal{R}_B$ vectors is infinite).

Of course, exactly the same argument can be applied to all the N basis points; the end result is that we can build N subsets of $\mathcal{R}_S$, indexed by the $\mathcal{R}_S$ points inside a given primitive cell of $\mathcal{R}_B$; each subset is made up by an $\mathcal{R}_S$ point inside $\mathcal{C}_B$ plus all its infinite images.

Figure 34 illustrates this argument for the 2D case.

If we call:

- $\vec{r}_j$ the j -th point of $\mathcal{R}_S$ inside $\mathcal{C}_B$ ($1 \leq j \leq N$)
- $\vec{r}$ the generic point of $\mathcal{R}_S$
- $\vec{R}$ the generic point of $\mathcal{R}_B$

then the subset $\mathcal{S}_j$ of $\mathcal{R}_S$ points corresponding to $\vec{r}_j$ is mathematically defined as:

$$\mathcal{S}_j = \left\{ \vec{r} : \vec{r} = \vec{r}_j + \vec{R}, \vec{r}_j \in \mathcal{C}_B, \vec{R} \in \mathcal{R}_B \right\} \quad (274)$$

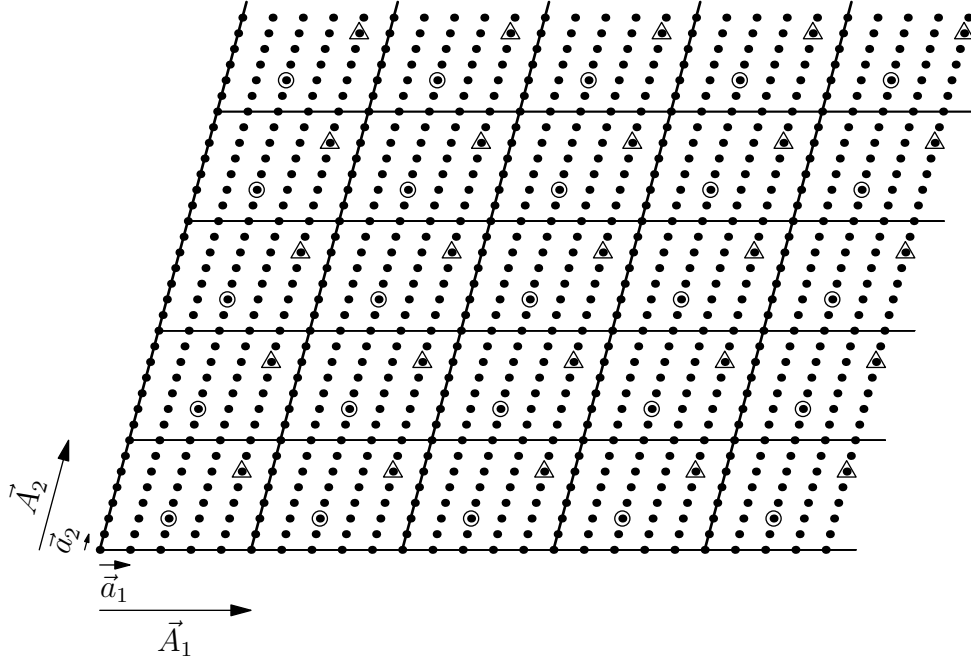


Figure 34: Two commensurate lattices: $\mathcal{R}_S$ (primitive vectors $\vec{a}_1, \vec{a}_2$) and $\mathcal{R}_B$ (primitive vectors $\vec{A}_1 = 5\vec{a}_1, \vec{A}_2 = 7\vec{a}_2$). Each primitive cell of $\mathcal{R}_B$ is a 5×7 supercell of the primitive cell of $\mathcal{R}_S$ and thus contains $5 \times 7 = 35$ points of $\mathcal{R}_S$. Take any primitive cell of $\mathcal{R}_B$ (for instance the one in the center of the picture): the $\mathcal{R}_S$ point marked with a circle identifies an infinite subset of the $\mathcal{R}_S$'s points made up by itself plus all its infinite replicas (images), also marked with a circle. Another $\mathcal{R}_S$ point inside the same primitive cell of $\mathcal{R}_B$, marked with a triangle, will identify another infinite subset of the $\mathcal{R}_S$'s points made up by itself plus all its infinite replicas (images), also marked with a triangle.

This holds for all the $\mathcal{R}_S$ points inside a given primitive cell of $\mathcal{R}_B$. So: the infinite points of $\mathcal{R}_S$ can be partitioned into 35 infinite subsets, indexed by the $\mathcal{R}_S$ points inside a given primitive cell of $\mathcal{R}_B$.

There will be N such subsets, one for each point of $\mathcal{R}_S$ inside $\mathcal{C}_B$. It should be clear that the N subsets so defined do constitute a *partition* of (all the points of) $\mathcal{R}_S$, ie, mathematically:

$$\bigcup_{j=1}^N \mathcal{S}_j = \mathcal{R}_S$$

$$\mathcal{S}_i \cap \mathcal{S}_j = \emptyset, \forall i \neq j$$

(I will not prove this, but just ask yourself: “Can a point of $\mathcal{R}_S$ exist such that it does not belong to any of the subsets $\mathcal{S}_j$?” and “Can a point of $\mathcal{R}_S$ exist such that it belongs to two distinct subsets $\mathcal{S}_j$ at the same time?”; you should be able to easily give a convincing answer to these questions)

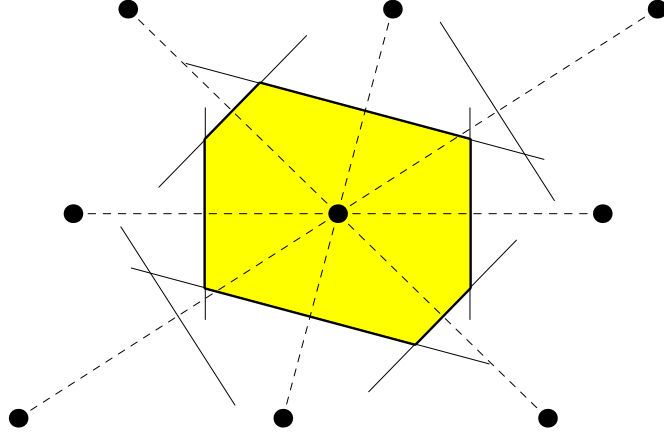


Figure 35: The construction of the Wigner–Seitz cell for a bidimensional lattice. The black dots are 9 points of the lattice; the central point is connected to the peripheral dots (its first and second neighbors) by the dashed segments; for each segment, a straight line is drawn orthogonal to it and passing through its midpoint: the polygon of minimal area delimited by the lines is the Wigner–Seitz cell (in yellow).

Since we will make use of it, it is worth making an additional remark regarding this property: for any pair of points of $\mathcal{R}_S$ belonging to the *same* subset $\mathcal{S}_j$ there always exists one and only one vector $\vec{R}$ of $\mathcal{R}_B$ connecting them, i.e.:

$$\vec{r}_i \in \mathcal{S}_j, \vec{r}_k \in \mathcal{S}_j \implies \exists! \vec{R} \in \mathcal{R}_B : \vec{r}_i - \vec{r}_k = \vec{R} \quad \forall i, k \quad (275)$$

Also this claim is very easy to prove: just think that all the elements of the subset $\mathcal{S}_j$ are obtained by adding all the vectors of $\mathcal{R}_B$ to one point of $\mathcal{R}_S$ inside $\mathcal{C}_B$ and that the difference of any two vectors of a Bravais lattice is still a vector of the lattice (point 142).

Of course, also the opposite does hold: given any vector $\vec{R} \in \mathcal{R}_B$, there always exist a pair of vectors belonging to the *same* subset $\mathcal{S}_j$ such that their difference is equal to $\vec{R}$:

$$\vec{R} \in \mathcal{R}_B \implies \exists! \vec{r}_i \in \mathcal{S}_j, \vec{r}_k \in \mathcal{S}_j : \vec{r}_i - \vec{r}_k = \vec{R} \quad (276)$$

Note that the above is true only when the pair of points of $\mathcal{R}_S$ belongs to the *same* subset $\mathcal{S}_j$: if the two points belong to *different* subsets, then no vector $\vec{R}$ of $\mathcal{R}_B$ connecting them can be found.

2.4 Wigner–Seitz (primitive) cell

152. We have already noted that the choice of the primitive vectors of a Bravais lattice is not unique (point 144).

However, there is a procedure to generate a (call it) “standard” primitive cell, known as *Wigner–Seitz cell*.

The procedure is shown in figure 35 for a bidimensional lattice.

Basically, you choose a lattice point, connect it with all its first, second, . . . neighbors and draw straight lines that (i) are orthogonal to each connecting segment and (ii) intersect it at the midpoint.

The polygon of minimal area enclosed by the straight lines is the Wigner–Seitz primitive cell.

For a 3D lattice the procedure is exactly the same, with due replacement of terms: you connect a given lattice point with all its first, second, . . . neighbors and consider the planes (instead of straight lines) that (i) are orthogonal to each connecting segment and (ii) intersect it at the midpoint. The polyhedron (instead of polygon) of minimal volume (instead of area) enclosed by the planes is the Wigner–Seitz primitive cell.

It should be clear that the Wigner–Seitz cell is a primitive cell “by construction”: it obviously contains a single lattice point; moreover, each side (in the 2D case) or face (in the 3D case) is shared with the side or face of the cell centered on a neighboring lattice point (refer to figure 35): this ensures that its periodic repetition will cover the whole (2D or 3D) space with no overlapping or gaps, that is: it is a primitive cell according to property 1 on p. 88.

An equivalent definition of the Wigner–Seitz cell is that it is the space region whose points are closer to a given lattice point than to any other lattice point (a bit of thinking should make you realize this).

2.5 Classification of Bravais lattices

153. All possible Bravais lattices can be classified on the basis of their symmetry.

I will present this argument only superficially, since in this course we will almost never use this classification (except in an extremely intuitive and informal way). However, keep in mind that the symmetry of Bravais lattices is of paramount importance in crystallography.

For a Bravais lattice, a symmetry operation is defined as a transform of the lattice in itself. All the symmetry operations for a Bravais lattice can always be decomposed into a lattice translation, that is a translation by any lattice vector $\vec{R}$, followed by a symmetry operation (rotation, reflection or inversion) which leaves a lattice point unmoved.

When all the possible symmetry operations for a given Bravais lattice are taken into account, it can be shown (in a non trivial way) that there can be only 14 groups of such operations that transform a given lattice into itself: any Bravais lattice will be turned into itself by one and only one of these groups of symmetry operations. Thus, the 14 groups of symmetry operations define as many “categories” of Bravais lattices, which exhaust all the possibilities. Any Bravais lattice can be assigned to one and only one of these 14 “categories”. Each category can be represented by a “prototype” lattice which enjoys all the symmetry operations of the group.

The above means that there are only 14 distinct “prototypes” of Bravais lattices, and they can be identified on the basis of their primitive cell and its cell parameters (point 146).

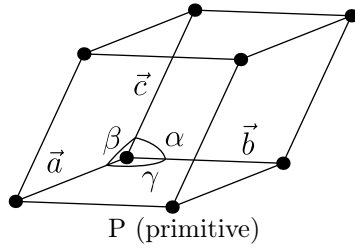
Usually, by “Bravais lattice” is meant both a particular Bravais lattice and any of the 14 lattice prototypes, the context being unequivocal most of the time.

In figures 36 and 37 I have shown the primitive cells originating the 14 distinct Bravais lattice prototypes together with the corresponding cell parameters based on which the lattices are classified (actually, you can very easily realize that some of the cells shown are *not* primitive: more on this in a while).

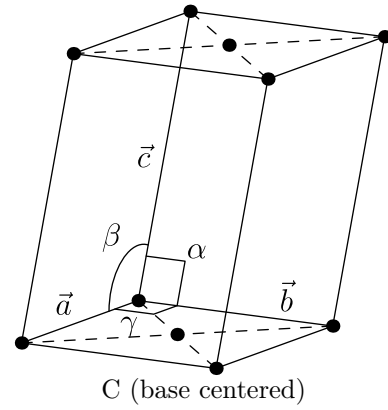
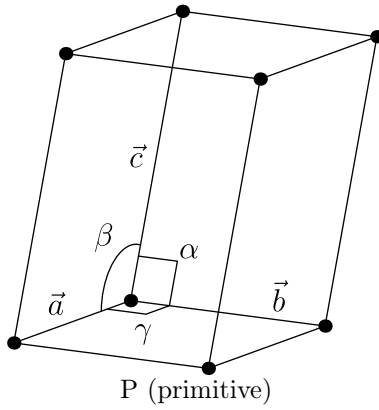
154. It is worth noting that, as you can see from the figures, the particular values of the cell parameters do not matter; it is their *mutual relationships* that define a particular type of Bravais lattice.

For example, what classifies a Bravais lattice as “rhombohedral” (fig. 37) is that its three cell vectors share a common modulus and make one same angle when taken in pairs: the particular values of that modulus and that angle do not have any importance.

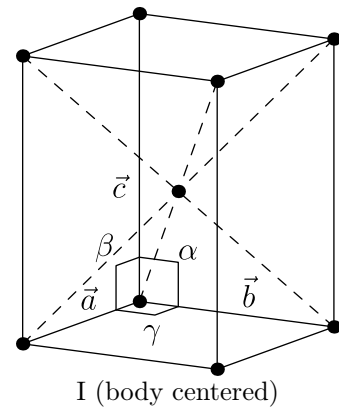
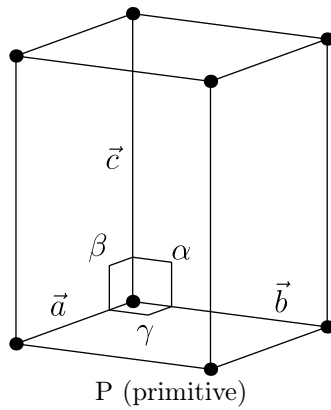
triclinic
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma$



monoclinic
 $a \neq b \neq c$
 $\alpha = \gamma = \frac{\pi}{2} \neq \beta$



tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = \frac{\pi}{2}$



orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = \frac{\pi}{2}$

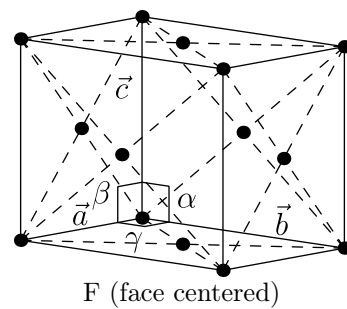
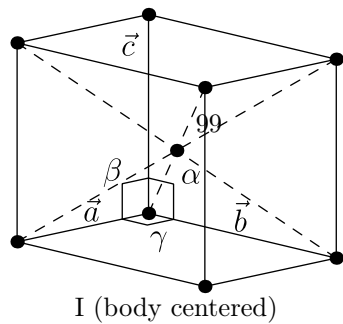
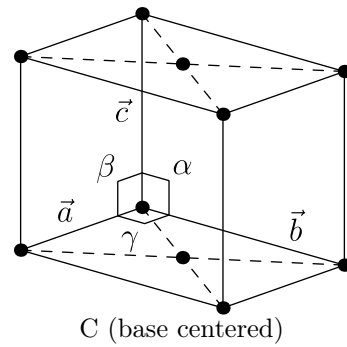
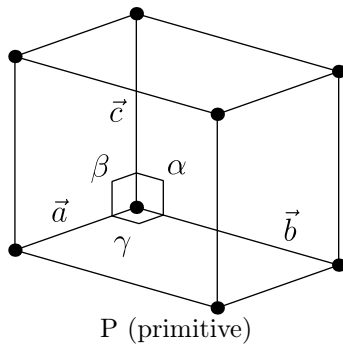
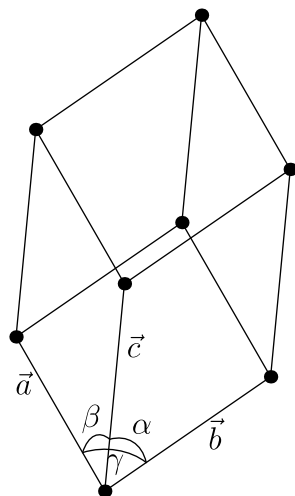


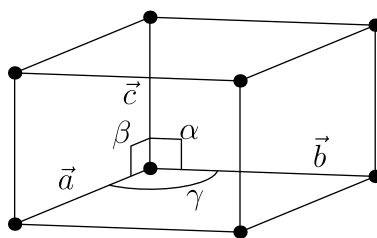
Figure 36: The 14 Bravais lattices (continued in figure 37)

rhombohedral
 $a = b = c$
 $\alpha = \beta = \gamma$
 $\neq \frac{\pi}{2}, \frac{\pi}{3}, \arccos\left(-\frac{1}{3}\right)$



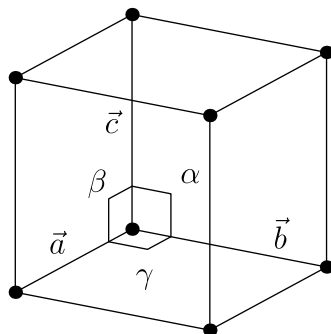
P (primitive)

hexagonal
 $a = b \neq c$
 $\alpha = \beta = \frac{\pi}{2} \quad \gamma = \frac{2}{3}\pi$

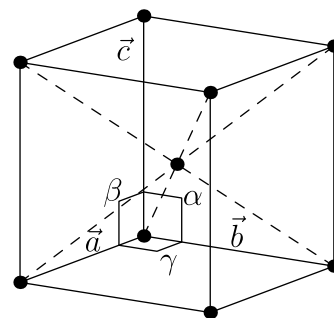


P (primitive)

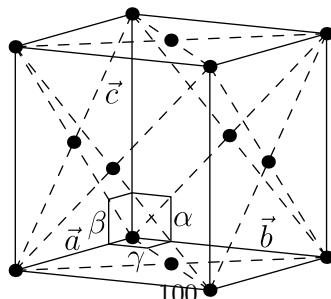
cubic
 $a = b = c$
 $\alpha = \beta = \gamma = \frac{\pi}{2}$



P (primitive)



I (body centered)



F (face centered)

Figure 37: (continuing from figure 36)

2.5.1 Conventional cell

155. You may have noticed that in figures 36 and 37, for some lattices, e.g. the orthorhombic lattice in fig. 36, multiple cells (labelled with uppercase letters P,C,I,F) are drawn. The reason is the following.

For the purpose of classification, it may happen that a given lattice enjoys a number of symmetry elements *greater* than that of any of its primitive cells (an example is the face centered cubic lattice (F), which I will briefly discuss in a while). When this is the case, it is customary to represent the lattice with a so called *conventional cell*, which is built such that it exhibits the complete symmetry of the lattice. The conventional cell is not primitive (for example, you can easily realize that the body centered cell for the tetragonal lattice in figure 36 contains 2 lattice points and so cannot be a primitive cell).

A conventional cell is a supercell (so it contains more than 1 lattice point and generates the whole lattice by translation). However, a conventional cell is obtained in a more complex (and general) way than what we have discussed at point 147. The conventional cell vectors $\vec{A}_j$ are obtained by a linear combination of the primitive vectors $\vec{a}_i$ according to:

$$\vec{A}_1 = c_{11}\vec{a}_1 + c_{12}\vec{a}_2 + c_{13}\vec{a}_3 \quad (277)$$

$$\vec{A}_2 = c_{21}\vec{a}_1 + c_{22}\vec{a}_2 + c_{23}\vec{a}_3 \quad (278)$$

$$\vec{A}_3 = c_{31}\vec{a}_1 + c_{32}\vec{a}_2 + c_{33}\vec{a}_3 \quad (279)$$

or, in matrix form:

$$\begin{pmatrix} \vec{A}_1 \\ \vec{A}_2 \\ \vec{A}_3 \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix} \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix}$$

where the c_{ij} 's are scalar factors.

Note that eqs. 267–269 are just a particular case of 277–279, with:

$$c_{ij} = \delta_{ij}n_i \quad n_i \in \mathbb{N} \quad (280)$$

(δ_{ij} is the Kronecker delta)

In figure 38 the primitive and conventional cells for the face centered cubic Bravais lattice are shown.

The primitive cell is a rhombohedron (a polyhedron made up by 6 identical rhombic faces); this cell does *not* enjoy all the symmetry operations of the Bravais lattice which it itself generates (this may sound counter-intuitive, but it is just so).

On the other hand, the conventional cell is a cube and has the same (higher) symmetry of the lattice (please note that the primitive rhombohedral cell and the conventional (super)cell generate exactly the *same* face centered cubic Bravais lattice); the conventional cell contains 4 lattice points: there are 8 points at the vertices (each counting for 1/8) and 6 points at the center of the 6 cube faces (each counting for 1/2).

(Note also that the rhombohedral primitive cell for the face centered cubic Bravais lattice is nothing but the primitive cell of a rhombohedral lattice, fig 37, in which: $\alpha = \beta = \gamma = \pi/3$. This is the reason why, in figure 37, the common value of the angles α , β , γ for the rhombohedral lattice cannot be $\pi/3$. The values $\pi/2$ and $\arccos(-1/3)$ of the angles for the same rhombohedral lattice are forbidden for similar reasons: if $\alpha = \beta = \gamma = \pi/2$ then, trivially, a primitive (P) cubic

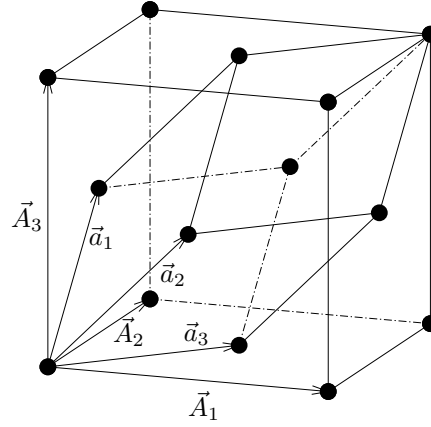


Figure 38: The relation between the primitive cell (defined by the $\vec{a}_i$ vectors) and the conventional cell (defined by the $\vec{A}_i$ vectors) for the face centered cubic Bravais lattice.

lattice is obtained; while if $\alpha = \beta = \gamma = \arccos(-1/3)$ then (less trivially) a body centered (I) cubic lattice is generated).

Still discussing the example of the face centered cubic lattice, letting a the side of the conventional cubic (super)cell, the primitive vectors have cartesian components (refer to figure 38):

$$\vec{a}_1 = a(0, 1/2, 1/2) \quad (281)$$

$$\vec{a}_2 = a(1/2, 0, 1/2) \quad (282)$$

$$\vec{a}_3 = a(1/2, 1/2, 0) \quad (283)$$

while for the vectors defining the conventional cell:

$$\vec{A}_1 = a(1, 0, 0) \quad (284)$$

$$\vec{A}_2 = a(0, 1, 0) \quad (285)$$

$$\vec{A}_3 = a(0, 0, 1) \quad (286)$$

The two vector triplets are related by the transformation:

$$\begin{pmatrix} \vec{A}_1 \\ \vec{A}_2 \\ \vec{A}_3 \end{pmatrix} = \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix} \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix} \quad (287)$$

where the matrix elements on the RHS are the c_{ij} 's of eqs. 277–279.

All the non primitive lattices (i.e. not of type (P)) in figures 36 and 37 are represented with conventional cells.

2.6 The reciprocal lattice

156. Any crystal structure is defined by a Bravais lattice; this latter, in turn, defines a reciprocal lattice through eqs. 159. The points of this reciprocal lattice identify the wave vectors of the Fourier expansion of any function (electron density, potential energy etc.) which is periodic on the Bravais lattice (eqs. 126 and 153).

The reciprocal lattice enjoys many other properties and in this part we will see some of them.

2.6.1 The reciprocal lattice is itself a Bravais lattice

157. The proof follows immediately from the definition of reciprocal lattice (eq. 159): since the primitive vectors of the direct lattice are not coplanar (by hypothesis) and the primitive vectors of the reciprocal lattice are orthogonal to the three planes identified by the primitive vectors of the direct lattice taken in pairs (point 89), also the primitive vectors of the reciprocal lattice are not coplanar (i.e. they are linearly independent).

Thus, the reciprocal lattice satisfies the definition 2 on p. 83 and is a Bravais lattice.

2.6.2 The reciprocal lattice of the reciprocal lattice is the direct lattice

(Note: this is not a tongue twister)

Since we have just seen above that the reciprocal lattice of a given Bravais lattice is itself a Bravais lattice, it makes sense to ask ourselves which is the reciprocal lattice of the reciprocal lattice.

Well, given $\mathcal{R}$ a Bravais lattice and $\mathcal{R}^*$ its reciprocal lattice, the following holds true:

$$(\mathcal{R}^*)^* = \mathcal{R} \quad (288)$$

that is: the reciprocal lattice of $\mathcal{R}^*$ is the Bravais lattice of which $\mathcal{R}^*$ is reciprocal.

The proof goes like this.

Based on the definition of reciprocal lattice 197, the vectors $\vec{G}$ of $(\mathcal{R}^*)^*$ must satisfy the condition:

$$\vec{G} \cdot \vec{k} = n(2\pi) \quad n \in \mathbb{Z} \quad \forall \vec{k} \in \mathcal{R}^* \quad (289)$$

Now: it is certainly true that every vector $\vec{G} \in \mathcal{R}$ does satisfy condition 289 because $\mathcal{R}^*$ is the reciprocal of $\mathcal{R}$.

Thus, all the vectors of $\mathcal{R}$ are also vectors of $(\mathcal{R}^*)^*$, that is:

$$\vec{G} \in \mathcal{R} \implies \vec{G} \in (\mathcal{R}^*)^* \quad (290)$$

On the other hand, no any other vector $\vec{v}$ of the direct (continuous) space $\mathbb{R}^3$ (thus: $v \notin \mathcal{R}$) can belong to $(\mathcal{R}^*)^*$. In fact, if it were so, since the primitive vectors of $\mathcal{R}$ make up a basis (in an algebraic sense) of the direct space $\mathbb{R}^3$, $\vec{v}$ should be of type:

$$\vec{v} = x_1 \vec{a}_1 + x_2 \vec{a}_2 + x_3 \vec{a}_3 \quad (291)$$

with at least one non-integer coefficient (because $v \notin \mathcal{R}$). But then, with an argument identical to that in section 1.3.4, letting j be the index for which x_j is not integer and taking $\vec{k} = \vec{b}_j$, we would have:

$$\vec{v} \cdot \vec{k} = \left(x_j \vec{a}_j + \sum_{i \neq j} x_i \vec{a}_i \right) \cdot \vec{b}_j = 2\pi x_j \quad \text{with } x_j \notin \mathbb{Z} \quad (292)$$

and thus 289 (which must hold for *any* $\vec{k}$ vector) would not be satisfied.

In conclusion: all vectors of $\mathcal{R}$ belong to $(\mathcal{R}^*)^*$, no any other vector can be part of $(\mathcal{R}^*)^*$, and thus $(\mathcal{R}^*)^* \equiv \mathcal{R}$:

$$\left. \begin{array}{l} \vec{G} \in \mathcal{R} \implies \vec{G} \in (\mathcal{R}^*)^* \\ \vec{v} \notin \mathcal{R} \implies \vec{v} \notin (\mathcal{R}^*)^* \end{array} \right\} \implies (\mathcal{R}^*)^* \equiv \mathcal{R} \quad (293)$$

2.6.3 Volume of direct cell vs volume of reciprocal cell

158. The volume v of the primitive cell of the direct lattice $\mathcal{R}$ and the volume v^* of the primitive cell of the reciprocal lattice $\mathcal{R}^*$ are related by:

$$v^* = \frac{(2\pi)^3}{v} \quad (294)$$

(look: another reciprocity relation)

The proof of this property relies on the knowledge of an identity of vector algebra about the so called quadruple scalar product. The identity (which we take as such without proof) is:

$$(\vec{a} \times \vec{b}) \cdot (\vec{q} \times \vec{r}) = (\vec{a} \cdot \vec{q})(\vec{b} \cdot \vec{r}) - (\vec{a} \cdot \vec{r})(\vec{b} \cdot \vec{q}) \quad (295)$$

Then: the volume of the reciprocal cell is (review point 89):

$$v^* = \left| \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) \right| \quad (296)$$

where the $\vec{b}_i$'s are the primitive vectors of $\mathcal{R}^*$.

We now write $\vec{b}_1$ as a function of the primitive vectors of $\mathcal{R}$ (eq. 159), use property 295 and the orthogonality relations 135:

$$= \left| \overbrace{2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}}^{\vec{b}_1} \cdot (\vec{b}_2 \times \vec{b}_3) \right| \quad (297)$$

$$= \left| 2\pi \frac{\overbrace{(\vec{a}_2 \cdot \vec{b}_2)}^{=2\pi} \overbrace{(\vec{a}_3 \cdot \vec{b}_3)}^{=2\pi} - \overbrace{(\vec{a}_2 \cdot \vec{b}_3)}^{=0} \overbrace{(\vec{a}_3 \cdot \vec{b}_2)}^{=0}}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \right| \quad (298)$$

$$= \frac{(2\pi)^3}{|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|} = \frac{(2\pi)^3}{v} \quad (299)$$

159. In the bidimensional case, as you might expect, the relation becomes:

$$A^* = \frac{(2\pi)^2}{A} \quad (300)$$

where A^* and A are the area of the primitive cell of $\mathcal{R}^*$ and the area of the primitive cell of $\mathcal{R}$, respectively.

Proving the above result is simpler than the 3D case.

Since $\vec{b}_1$ and $\vec{b}_2$ are orthogonal to $\vec{a}_2$ and $\vec{a}_1$, respectively, the angle θ (always assumed $< \pi$, point 86) between $\vec{b}_1$ and $\vec{b}_2$ is equal to that between $\vec{a}_1$ and $\vec{a}_2$.

Then:

$$A^* = b_1 b_2 \sin(\theta) \quad (301)$$

Replace b_1 and b_2 with 181 and 182, respectively:

$$A^* = 2\pi \frac{a_2}{A} 2\pi \frac{a_1}{A} \sin(\theta) = \frac{(2\pi)^2}{A^2} \overbrace{a_1 a_2 \sin(\theta)}^{=A} = \frac{(2\pi)^2}{A} \quad (302)$$

160. Finally, for the monodimensional case, we already saw that the relation is (not surprisingly):

$$a^* = \frac{2\pi}{a} \quad (303)$$

where a^* and a are the lengths of the reciprocal and direct “primitive cells”, respectively (point 47).

2.6.4 Brillouin zones

We now define the so called *Brillouin zones*, since they will play a central role in the following.

161. You can view the Brillouin zones as a sort of generalization of the Wigner–Seitz cell (point 152). Traditionally, they are always associated with the reciprocal lattice but, as you will see in a while, the procedure for their definition and construction can be applied to any Bravais lattice (be it direct or reciprocal).

We speak about “zones” (plural) because their number is infinite.

The first Brillouin zone of the reciprocal lattice is simply its Wigner–Seitz cell. That is: if you build the Wigner–Seitz primitive cell for the reciprocal lattice (using the procedure outlined at point 152), then you have obtained the first Brillouin zone.

162. The second, third ... Brillouin zones are obtained in the same way as the first, by continuing to connecting the central point taken as a reference with the points that are around it and tracing planes (3D case) or lines (2D case) which are orthogonal to the connecting segments and intersect them at the midpoint.

The regions of the reciprocal lattice so delimited can be sorted based on their volume (3D case) or area (2D case).

Be:

$$V_1 \ V_2 \ V_3 \dots$$

these ordered volumes (areas).

The region of smallest volume (area) is, as said above, the first Brillouin zone.

For the following zones, refer to figure 39 which shows the procedure for a bidimensional lattice. The second Brillouin zone is the region of volume (area) V_2 in which, however, V_1 is not included: that is, the region corresponding to V_1 is *not* part of the second Brillouin zone.

The third Brillouin zone is the region of volume (area) V_3 , from which the regions corresponding to V_1 and V_2 are excluded.

And so on and so forth.

As I mentioned above (and as it should be clear) this procedure would work unchanged also for the direct lattice; however, as you will see, only the Brillouin zones of the reciprocal lattice are relevant for their applications.

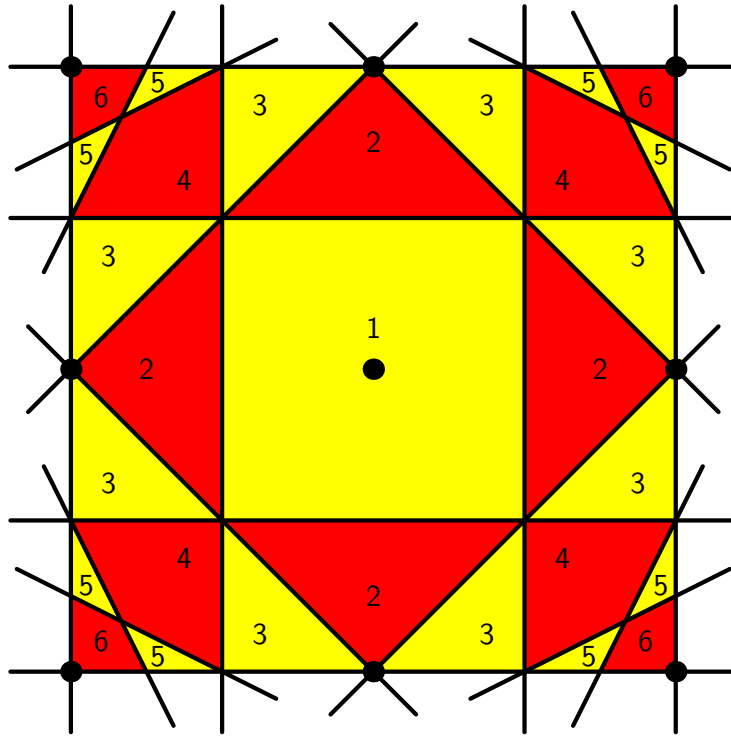


Figure 39: The construction of the first 6 Brillouin zones for a square (bidimensional) lattice. I have numbered the consecutive zones starting from the first. The lattice points are the black dots. Only the first 3 zones are completely contained in the figure; for the other three (fourth, fifth and sixth Brillouin zones) there are additional portions not shown in the figure.

You can find an “exaggerated” and colorful representation of a long succession of Brillouin zones for some bidimensional lattices at the web site of reference 11.

At the site web of this course I have created an interactive page which allows you to visualize both the direct and reciprocal cell, the Wigner–Seitz cell and the first Brillouin zone for an arbitrary threedimensional lattice.¹²

163. Since we will happen to consider the Brillouin zones for a monodimensional reciprocal “lattice”, let’s present them here (refer to figure 40).

The monodimensional case is very simple: the procedure is always the same, but the first, second, third . . . neighbors are found most easily.

The first neighbors of the origin, P_0 , are the point to the left (P_{-1}) and the point to the right (P_1), both at a distance of $2\pi/a$ from the origin (a is the length of the direct primitive cell (interval), point 47). Hence, the first Brillouin zone is the interval of the reciprocal axis delimited by the midpoint of the segment $P_{-1} - P_0$ and the midpoint of the segment $P_0 - P_1$, that is $[-\pi/a, \pi/a]$. The second neighbors of P_0 are P_{-2} and P_2 , at distances of $4\pi/a$ in the negative and positive directions, respectively: the second Brillouin zone is made up by the intervals $[-2\pi/a, -\pi/a]$ and $[\pi/a, 2\pi/a]$; note: as already mentioned, the first Brillouin zone is *not* included into the second one.

And so on and so forth.

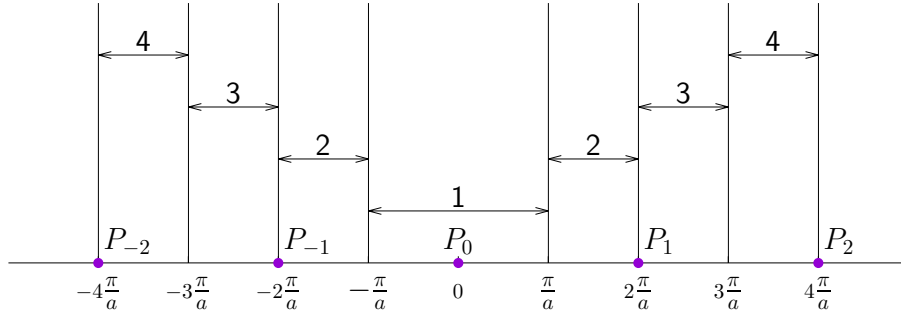


Figure 40: The first 4 Brillouin zones for a monodimensional reciprocal lattice (a is the length of the direct primitive cell, which in the 1D case is just an interval on the abscissa).

The boundaries separating the Brillouin zones (which are just points in the 1D case) are defined by:

$$n \frac{\pi}{a} \quad n \in \mathbb{Z} - \{0\} \quad (304)$$

2.6.5 Lattice planes and reciprocal vectors

164. For a given Bravais lattice, a plane defined by three non-collinear lattice points is called a *lattice plane*.

- Due to the translational symmetry of a Bravais lattice, a lattice plane contains an infinite number of lattice points (which, in turn, constitute a bidimensional lattice): you can convince yourself by drawing three non-collinear lattice points and reproducing around each of them the lattice points as “seen” by the remaining two, with the same orientation (based on the definition 1 of a Bravais lattice on p. 83); if you do this recursively, you will obtain an infinitely extended lattice plane. Alternatively, you can just think that three non-collinear lattice points always define (by their differences) two non-parallel (and thus linearly independent) lattice vectors: if you take linear combinations (with integer coefficients) of these two lattice vectors, you will end up with an infinite number of *coplanar* lattice points.
- Still due to the symmetry of a Bravais lattice, given a single lattice plane, there exist infinite lattice planes which are parallel to it and with a common interplanar spacing. Given a single lattice plane, consider the lattice point not belonging to the plane and at the minimum distance from it: if you reproduce around this point the environment of any point of the original plane (this environment must be always the same, by definition of Bravais lattice), then you obviously end up with a second infinite lattice plane which is parallel to the original one. Then, if you iterate this procedure, you will get an infinite set of lattice planes parallel to the original plane and with a common interplanar spacing.

The infinite set of identical, parallel and equispaced planes obtained as per above is called *family*. You should easily realize that the planes of a given family do constitute a *partition* of the Bravais lattice, that is: all the lattice points are contained in one plane or the other and, trivially, a given lattice point cannot belong to two lattice planes at the same time.

In figure 41 I have shown three different plane families for the simple cubic Bravais lattice.

165. From the above it should be evident that, for a given Bravais lattice, there is an infinite number of plane families, differing for their orientation.

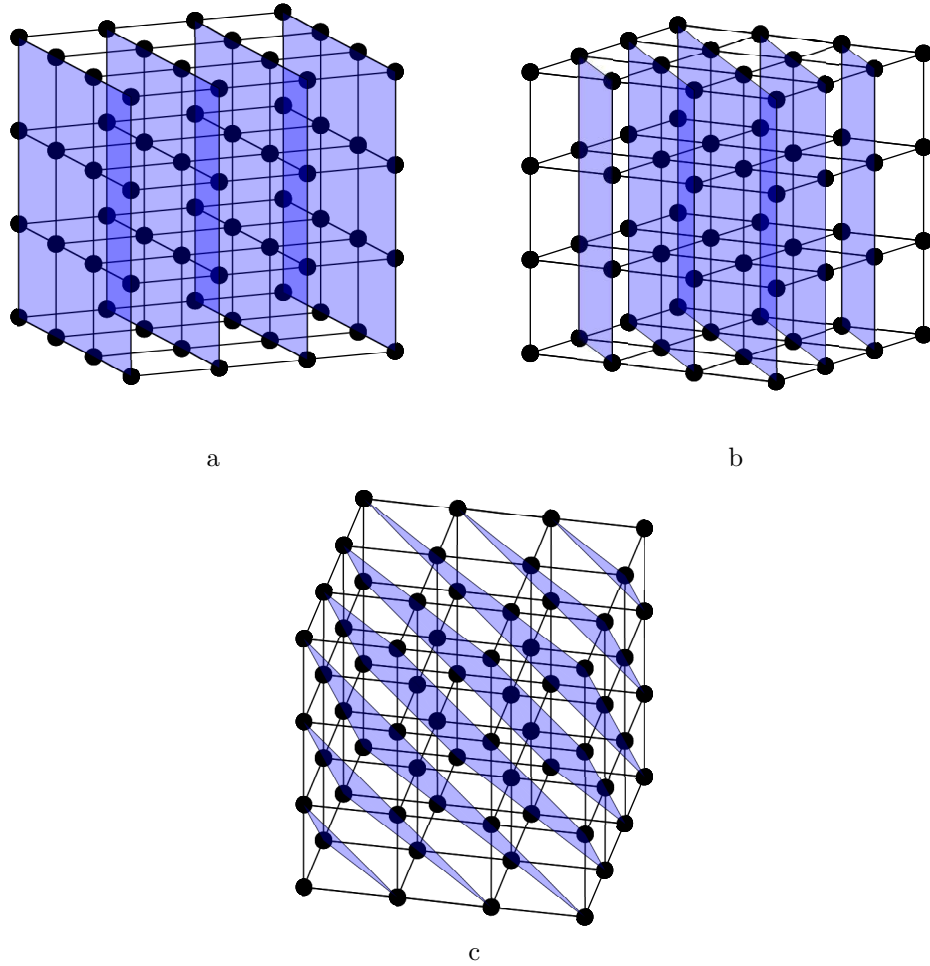


Figure 41: Three (among the infinite) possible families of lattice planes for the simple cubic Bravais lattice. a: the planes of the family are parallel to a face of the primitive cell; b: the planes of the family do section the primitive cell orthogonally to the “horizontal” face, along its diagonal; c: the planes of the family are parallel to the plane defined by the three lattice points corresponding to the three primitive vectors of the Bravais lattice.

All these infinite families are classified by the reciprocal lattice vectors, on the basis of the following theorem.

Claim:

For each family of lattice planes equispaced at the distance d there exist reciprocal vectors which are orthogonal to the planes of the family (and thus parallel to each other) and the modulus of the shortest of these reciprocal vectors is $k = 2\pi/d$.

The viceversa also holds: for a given reciprocal vector $\vec{k}$ of minimal modulus among all the vectors parallel to it there exists a family of lattice planes orthogonal to $\vec{k}$ and equispaced at the distance $d = 2\pi/k$.

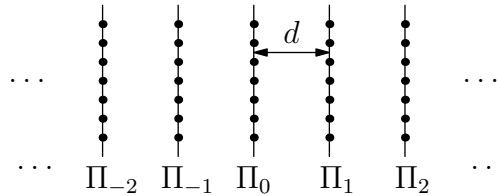
166. The outline of the proof of the first part is as follows.

- We consider a plane wave traveling in the direction orthogonal to the plane family and having a wavelength equal to the spacing of the lattice planes.
- We then realize that the wave vector of this plane wave is such that its scalar product with all the direct lattice points is equal to an integer multiple of 2π : as seen on p. 101, this is a necessary and sufficient condition for the wave vector being a reciprocal lattice point.
- Eventually, we prove that the wave vector is also the shortest reciprocal lattice vector orthogonal to the plane family.

167. And now for the actual demonstration of the first part of the theorem.

Let's use the following notation:

$\mathcal{R}$	the direct lattice
$\mathcal{R}^*$	the reciprocal lattice
$\vec{R}$	a generic direct vector
$\mathcal{F}_\Pi$	the family of lattice planes
$\Pi_j, j \in \mathbb{Z}$	the j -th plane of $\mathcal{F}_\Pi$; the index j is defined as per the following figure:



where Π_0 is the plane of $\mathcal{F}_\Pi$ passing through the origin. In this regard, note that since any family of lattice planes contains *all* the points of $\mathcal{R}$ (point 164 on p. 107), there will certainly be one (and only one) plane of the family passing through the origin (there is always a lattice point at the origin: $\vec{R} = 0\vec{a}_1 + 0\vec{a}_2 + 0\vec{a}_3$).

$\vec{n}$ the versor orthogonal to $\mathcal{F}_\Pi$

1. We consider the plane waveⁱ:

ⁱQuite often by “plane wave” I will actually mean only the spatial part of a plane wave. Of course, in those cases it is understood that the complete plane wave is the spatial part multiplied by the corresponding temporal part:

$$\Re \left(\exp \left(i \vec{k} \cdot \vec{r} \right) \exp \left(-i \omega t \right) \right) = \Re \left(\exp \left(i \left(\vec{k} \cdot \vec{r} - \omega t \right) \right) \right) = \cos \left(\vec{k} \cdot \vec{r} - \omega t \right)$$

$$\exp\left(i\vec{k} \cdot \vec{r}\right) \quad (305)$$

with wave vector:

$$\vec{k} = \frac{2\pi}{d} \vec{n} \quad (306)$$

and, thus, wave length:

$$\lambda = \frac{2\pi}{k} = d \quad (307)$$

(please, review the section about plane waves)

Clearly, for this plane wave the following statements hold true:

- (a) it is traveling in the direction of $\vec{n}$ (that is: the wave vector $\vec{k}$ is orthogonal to the Π_j 's)
 - (b) the lattice planes of the family are contained into its wave fronts, since they are orthogonal to $\vec{n}$
 - (c) it takes the same value on all the Π_j 's, because their spacing is equal to the wave length λ in the direction of $\vec{n}$ (point 124)
2. Now focus on Π_0 , that is: the plane of $\mathcal{F}_{\Pi}$ passing through the origin.
For all the lattice points of Π_0 , the following holds true:

$$\exp\left(i\vec{k} \cdot \vec{R}\right) = 1 \quad \forall \vec{R} \in \Pi_0 \quad (308)$$

because all the vectors $\vec{R} \in \Pi_0$ are orthogonal to $\vec{k}$ (realize this!).

3. But then it must be:

$$\exp\left(i\vec{k} \cdot \vec{R}\right) = 1 \quad (309)$$

not only for the lattice points of Π_0 , but for the lattice points of *all the* Π_j 's (point 1c above):

$$\exp\left(i\vec{k} \cdot \vec{R}\right) = 1 \quad \forall \vec{R} \in \Pi_j, \quad j \in \mathbb{Z} \quad (310)$$

4. And this is equivalent to say:

$$\exp\left(i\vec{k} \cdot \vec{R}\right) = 1 \quad \forall \vec{R} \in \mathcal{R} \quad (311)$$

because the Π_j 's contain all the vectors of $\mathcal{R}$ (the important thing to note here is the “ $\forall \vec{R} \in \mathcal{R}$ ” in 311).

5. But 311 implies:

$$\vec{k} \cdot \vec{R} = 2\pi n \quad n \in \mathbb{Z} \quad \forall \vec{R} \in \mathcal{R} \quad (312)$$

and thus $\vec{k} \in \mathcal{R}^*$ based on the definition on p. 62.

Hence, it remains proved that for the given family of lattice planes there always exists a reciprocal vector orthogonal to them.

6. We still have to prove that $\vec{k}$ is the shortest of all $\mathcal{R}^*$ vectors orthogonal to the planes of the family.

The proof is obtained by contradiction.

If it existed a vector $\vec{k}' \in \mathcal{R}^*$ with modulus $k' < k$ and orthogonal to the Π_j 's (so, parallel to $\vec{k}$), then the plane wave:

$$\exp(i\vec{k}' \cdot \vec{r})$$

would still travel in the direction of $\vec{n}$, but its wave length would be:

$$\lambda' = 2\pi/k' > 2\pi/k = d \quad (313)$$

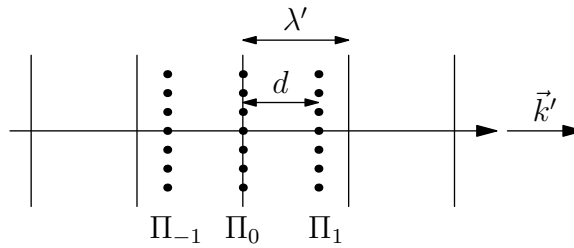
By considering again Π_0 , it would still hold that:

$$\exp(i\vec{k}' \cdot \vec{R}) = 1 \quad \forall \vec{R} \in \Pi_0$$

7. Call $\mathcal{F}'_{WF}$ the (infinite) sequence of wave fronts, equispaced by the wave length λ' , on which the plane wave takes the unit value.

Since now the wave length of the plane wave would be *greater* than the spacing of the family planes (eq. 313), there would certainly be at least one lattice plane *not* contained in $\mathcal{F}'_{WF}$.

For example, this would be the case for Π_{-1} and Π_1 , parallel to Π_0 and nearest to it, thus at a distance $d < \lambda'$ from Π_0 :



8. Clearly, since $\Pi_{-1} \notin \mathcal{F}'_{WF}$ and $\Pi_1 \notin \mathcal{F}'_{WF}$ it would hold that:

$$\exp(i\vec{k}' \cdot \vec{R}) \neq 1 \quad \forall \vec{R} \in \Pi_1, \forall \vec{R} \in \Pi_{-1}$$

or:

$$\exists \vec{R} \in \mathcal{R} : \vec{k}' \cdot \vec{R} \neq 2\pi n \quad n \in \mathbb{Z} \quad (314)$$

But this is a sufficient condition for:

$$\vec{k}' \notin \mathcal{R}^* \quad (315)$$

(based on the definition on p. 62).

9. Note that one might argue that there might be wave fronts *not belonging* to the $\mathcal{F}'_{WF}$ sequence on which, however, the plane wave still takes the unit value: the Π_{-1} and Π_1 lattice planes might then be contained in these wave fronts and thus satisfy:

$$\exp(i\vec{k}' \cdot \vec{R}) = 1 \quad \forall \vec{R} \in \Pi_1 \quad \forall \vec{R} \in \Pi_{-1} \quad (316)$$

anyway. But this is impossible and I show you the reason why in section 2.2 of the extracurricular part.

10. In summary, we have arrived at the following contradiction: if it existed a vector $\vec{k}'$ of $\mathcal{R}^*$ being parallel and shorter than $\vec{k}$, it could not be a vector of $\mathcal{R}^*$:

$$k' < k, \vec{k}' \in \mathcal{R}^* \implies \vec{k}' \notin \mathcal{R}^* \quad \text{contradiction!} \quad (317)$$

The first part of the theorem is fully proved.

168. The outline of the proof of the second part is as follows.

- We take a reciprocal lattice vector $\vec{k}$ such that it has the minimum length among all the reciprocal lattice vectors sharing the same direction.
- Similarly to the first part, we then consider a plane wave having that reciprocal lattice vector as its wave vector.
- The wave vector being at the same time a reciprocal lattice vector (by hypothesis) will allow us to establish that all the direct lattice points are contained in the wave fronts of the plane wave characterized by a unit isovalue; but this is just an equivalent way of saying that there exists a family of lattice planes (namely, those contained in the wave fronts of the plane wave with unit isovalue) which is orthogonal to the considered reciprocal lattice vector.
- Finally, we also prove that the spacing of the planes of this family is equal to $2\pi/k$.

169. Here goes the detailed proof of the second part of the theorem.

1. Let's take the vector $\vec{k} \in \mathcal{R}^*$ such that it has the minimum modulus among all the $\mathcal{R}^*$ vectors parallel to it and let's consider the plane wave:

$$\exp(i\vec{k} \cdot \vec{r}) \quad (318)$$

Let $\mathcal{F}_{WF}$ be the (infinite) sequence of wave fronts W_j on which the plane wave takes the unit value:

$$\mathcal{F}_{WF} = \left\{ W_j : \exp(i\vec{k} \cdot \vec{r}) = 1 \quad \forall \vec{r} \in W_j, \quad j \in \mathbb{Z} \right\} \quad (319)$$

(W_0 is the wave front passing through the origin, $j > 0$ indexes the wave fronts away from the origin in a given direction, $j < 0$ indexes the wave fronts away from the origin in the opposite direction)

2. All the W_j 's are:

- orthogonal to $\vec{k}$
- equispaced at a distance equal to the wavelength $d = 2\pi/k$

3. Since $\vec{k} \in \mathcal{R}^*$, it enjoys:

$$\vec{k} \cdot \vec{R} = 2\pi n \quad n \in \mathbb{Z} \quad \forall \vec{R} \in \mathcal{R} \quad (320)$$

based on the definition of p. 62.

The above is equivalent to:

$$\exp(i\vec{k} \cdot \vec{R}) = 1 \quad \forall \vec{R} \in \mathcal{R} \quad (321)$$

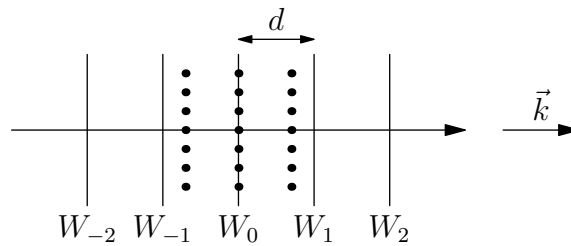
and this means that *all* the points $\vec{R} \in \mathcal{R}$ are contained in the wave fronts defined by 319:

$$\forall \vec{R} \in \mathcal{R} \quad \exists j : \vec{R} \in W_j \quad (322)$$

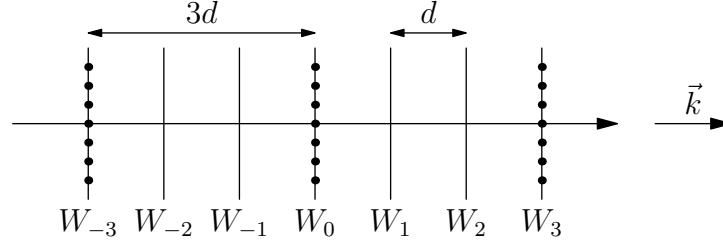
Thus: it remains proved that there exists a family of lattice planes orthogonal to $\vec{k}$ and that, at the same time, are contained in the fronts of the $\mathcal{F}_{WF}$ sequence.

4. This does not yet establish that the spacing of the lattice planes is equal to d .

For sure, the spacing cannot be $< d$, because otherwise, and contrary to what we have just established in point 3 above, there would be lattice points *not* contained in any of the W_j 's; for example, those lattice points belonging to the planes nearest to the origin, but not containing the origin itself, as already seen in the first part of the theorem:



5. However, the spacing of the lattice planes might be an integer multiple of d . For example, if the direct lattice points were contained only in a wave front every three, the spacing of the lattice planes would be equal to $3d$:



6. That the spacing of the lattice planes is precisely equal to d is proved once again by contradiction.

If the spacing of the lattice planes was $d' > d$, then, based on the first part of theorem, there would exist a vector $\vec{k}' \in \mathcal{R}^*$ orthogonal to the family of lattice planes (thus parallel to $\vec{k}$) having modulus $k' = 2\pi/d' < 2\pi/d = k$; but this is impossible (contradiction!) because, by hypothesis, $\vec{k}$ is the *shortest* among all the $\mathcal{R}^*$ vectors parallel to it:

$$d' > d \implies \exists \vec{k}' \in \mathcal{R}^* : k' < \overbrace{k}^{\text{by hyp}} \leq k' \quad \text{contradiction!} \quad (323)$$

170. You can easily verify the validity of this theorem in the trivial case of a simple cubic lattice. Take the family of planes which are parallel to one of the faces of the cubic primitive cell, for instance the one identified by the primitive vectors $\vec{a}_1, \vec{a}_2$. Obviously, the spacing of such planes is equal to the cell constant a (a is the common modulus of the three primitive vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$). On p. 59 we have seen that the reciprocal of a simple cubic lattice is itself a simple cubic lattice; the reciprocal primitive vector $\vec{b}_3$ is orthogonal to the plane defined by $\vec{a}_1, \vec{a}_2$, its length is $2\pi/a$ and, trivially, it is the shortest among all the reciprocal vectors parallel to it. So, it is just true that for the chosen family of lattice planes there exist (infinite) reciprocal vectors orthogonal to it and the shortest of such reciprocal vectors has length equal to 2π divided by the spacing of the lattice planes (that is: a).

2.6.6 Miller indices

171. The previous theorem offers an elegant way of defining the orientation of a lattice plane. In general, from a purely mathematical point, the orientation of a plane in space is completely defined by giving a vector orthogonal to it.

The general formulation of the equation of a plane in vector notation is obtained very easily making reference to figure 42.

Let $\vec{v} = (v_1, v_2, v_3)$ be a versor orthogonal to the plane Π and $\vec{p} = (p_1, p_2, p_3) \in \Pi$ any fixed point of Π . Then, for all points $\vec{r} = (x, y, z)$ of Π it must hold:

$$(\vec{r} - \vec{p}) \cdot \vec{v} = 0 \quad \forall \vec{r} \in \Pi \quad (324)$$

or:

$$\vec{r} \cdot \vec{v} = \vec{p} \cdot \vec{v} \quad (325)$$

Thus, the equation of the plane in vector notation is:

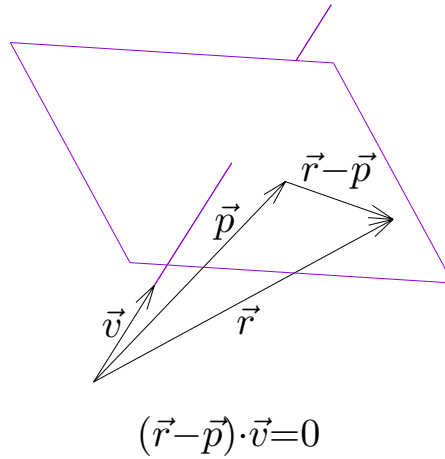


Figure 42: The condition of belonging of point $\vec{r}$ to the plane through $\vec{p}$ and having normal $\vec{v}$.

$$\vec{r} \cdot \vec{v} = C \quad (326)$$

where the constant $C = \vec{p} \cdot \vec{v}$ (which depends only upon the cartesian coordinates of the vector $\vec{v}$ and the fixed point $\vec{p}$) is the distance of the plane from the origin. In fact, since $\vec{v}$ is of unit length, $C = \vec{p} \cdot \vec{v}$ is the modulus of the projection of the vector $\vec{p}$ along the direction of $\vec{v}$ (refer to figure 42). For example, it will be $C = 0$ for a plane through the origin, because in this case any fixed vector $\vec{p} \in \Pi$ is orthogonal to $\vec{v}$.

172. Note that 326 is nothing but the cartesian equation of a plane that you all should already know:

$$\begin{aligned} \vec{r} \cdot \vec{v} &= C \\ v_1x + v_2y + v_3z &= C \end{aligned}$$

that is:

$$ax + by + cz = d$$

with:

$$\begin{aligned} a &= v_1 \\ b &= v_2 \\ c &= v_3 \\ d &= C = v_1p_1 + v_2p_2 + v_3p_3 \end{aligned}$$

173. Thanks to what we have seen in the previous section 2.6.5 (p. 107), it is possible to identify a given family of lattice planes with a reciprocal vector orthogonal to it (notice that all the planes of the family are parallel to each other: thus the direction of the reciprocal vector fixes the orientation of the family as a whole). Since there are infinite reciprocal vectors parallel to each other and orthogonal to a given family of lattice planes (if $\vec{v} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$ is orthogonal to the planes of the family, the same will hold for the infinite set of reciprocal vectors parallel to it and given by $Nm_1\vec{b}_1 + Nm_2\vec{b}_2 + Nm_3\vec{b}_3$, with $N \in \mathbb{Z}$ any integer constant), in order to make the correspondence unique the shortest reciprocal vector is taken. This vector will be of the form:

$$h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 \quad (327)$$

where the $\vec{b}_i$'s are the reciprocal primitive vectors and $h, k, l \in \mathbb{Z}$.

Thus, a given plane family will be uniquely identified by the three integers h, k, l , which are called *the Miller indices* of the family.

As for the notation, the plane family is represented by its Miller indices within parentheses: (hkl) . If an index is negative, the minus sign is placed above it, like in $(1\bar{2}2)$.

Note that since the reciprocal vector identifying the family of lattice planes is the shortest one, the three integers h, k, l cannot share a common divisor (different from 1) (if it was $(h, k, l) = (nh', nk', nl')$, $n \neq 1$, then the reciprocal vector $h'\vec{b}_1 + k'\vec{b}_2 + l'\vec{b}_3$ would be orthogonal to the same family and *shorter* than the vector $h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$).

Note also that the three integers h, k, l , and thus the label of a given family, depend upon the particular triplet of primitive vectors that were chosen to define the reciprocal lattice (eq. 327 and point 144); in other words: it is always possible to select two different triplets of reciprocal primitive vectors such that a given family of lattice planes having Miller indices, say, (122) with respect to the first triplet, will have Miller indices $(\bar{3}21)$ with respect to the second one.

2.6.7 The geometric interpretation of the Miller indices

174. It is possible to quickly visualize the orientation of the lattice planes represented by a given triplet of Miller indices thanks to a simple geometric interpretation of them.

The (hkl) lattice planes are orthogonal to the reciprocal vector $\vec{K} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$.

Take any plane of the family different from the one through the origin.

Such plane will be contained in the *continuous* plane defined by:

$$\frac{\vec{K}}{K} \cdot \vec{r} = C' \implies \vec{K} \cdot \vec{r} = C \text{ with } C = KC' \quad (328)$$

where $C \neq 0$ is an appropriate constant (review eq. 326) (K is the modulus of $\vec{K}$ and thus $\vec{K}/K$ is the versor in the direction of $\vec{K}$).

Let $x_1\vec{a}_1, x_2\vec{a}_2, x_3\vec{a}_3$ be the intersections of this plane with the axes corresponding to the direct primitive vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ (refer to figure 43).

Please note that the just mentioned intersections are expressed in units of the modulus of the corresponding primitive vector. That is to say: x_1 is the number of a_1 units (a_1 is the modulus of $\vec{a}_1$), x_2 is the number of a_2 units and x_3 is the number of a_3 units. To further clarify: if the intersection expressed in $\text{\AA}$ along the $\vec{a}_1$ direction was $4.5 \text{ \AA}$ and the modulus of $\vec{a}_1$ was $1.5 \text{ \AA}$, then it would be $x_1 = 3$.

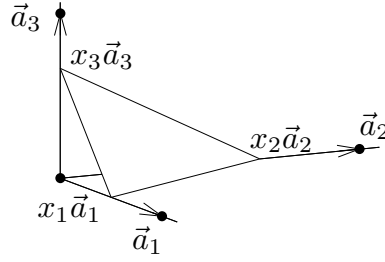


Figure 43: A lattice plane of the (hkl) family intersects the axes identified by the direct primitive vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ at points $x_1\vec{a}_1$, $x_2\vec{a}_2$, $x_3\vec{a}_3$, respectively.

Clearly, the three vectors $x_i\vec{a}_i$ do satisfy the condition for belonging to the plane. Whence, taking $x_1\vec{a}_1$ as an example, we have:

$$\begin{aligned} \vec{K} \cdot x_1\vec{a}_1 &= C \\ (h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) \cdot x_1\vec{a}_1 &= C \\ 2\pi hx_1 &= C \\ x_1 &= \frac{C}{2\pi} \frac{1}{h} \end{aligned}$$

(in the penultimate step I have taken advantage of the orthogonality conditions 135)
Finally:

$$x_1 = \frac{C}{2\pi} \frac{1}{h} \quad (329)$$

$$x_2 = \frac{C}{2\pi} \frac{1}{k} \quad (330)$$

$$x_3 = \frac{C}{2\pi} \frac{1}{l} \quad (331)$$

from which (taking the ratio of the equalities side by side):

$$\frac{x_1}{x_2} = \frac{\frac{1}{h}}{\frac{1}{k}}, \quad \frac{x_1}{x_3} = \frac{\frac{1}{h}}{\frac{1}{l}}, \quad \frac{x_2}{x_3} = \frac{\frac{1}{k}}{\frac{1}{l}}$$

or, more synthetically:

$$x_1 : x_2 : x_3 = \frac{1}{h} : \frac{1}{k} : \frac{1}{l} \quad (332)$$

That is to say: the intersections (each expressed in units of the modulus of the corresponding direct primitive vector) of any plane (not passing through the origin) of a given family with the axes identified by the direct primitive vectors are in the same ratio as the inverse of the Miller indices of that family.

So, for example, the intersections of a generic plane of the family (111) with the axes $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ will be given, in units of the corresponding direct primitive vectors, by equal numbers, that is they will be in the ratio:

$$x_1 : x_2 : x_3 = 1 : 1 : 1 \quad (333)$$

This means that the planes of the family will pass through the lattice points $\{\vec{a}_1, \vec{a}_2, \vec{a}_3\}$, $\{2\vec{a}_1, 2\vec{a}_2, 2\vec{a}_3\}$, $\{-\vec{a}_1, -\vec{a}_2, -\vec{a}_3\}$, ...

Similarly, for a generic plane of the family (12 $\bar{3}$) the intersections with the axes $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ will be expressed, in units of the corresponding direct primitive vectors, by numbers standing in the ratio:

$$x_1 : x_2 : x_3 = 1 : \frac{1}{2} : -\frac{1}{3} = 6 : 3 : -2 \quad (334)$$

So, in this case, the planes of the family pass through the lattice points $\{6\vec{a}_1, 3\vec{a}_2, -2\vec{a}_3\}$, $\{12\vec{a}_1, 6\vec{a}_2, -4\vec{a}_3\}$, $\{-6\vec{a}_1, -3\vec{a}_2, 2\vec{a}_3\}$, ...

Some planes with their Miller indices and their intersections with the axes of the direct lattice are shown in figure 44.

Note that if a Miller index is null, the corresponding intersection is infinite, that is: the plane is parallel to the corresponding axis.

175. Since we have introduced the notation for the lattice planes (and even if this is not related with the reciprocal lattice), I mention here also the notation used for specifying a direction in the direct lattice.

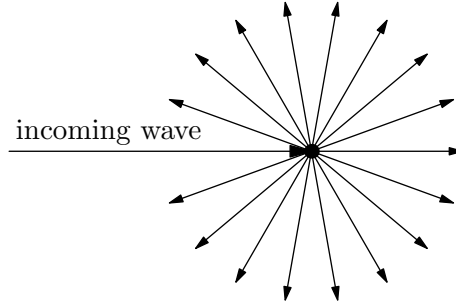
The direction defined by the direct vector:

$$n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \quad (335)$$

is expressed with the three integer numbers n_1 , n_2 , n_3 between square brackets, in order to distinguish it from the notation used for the lattice planes. For example: [120] or [12 $\bar{3}$].

2.7 Outline of diffraction theory

176. By *diffraction* it is generally meant the interaction of a wave with an obstacle (or a slit) that makes the latter to behave as a (secondary) source of the wave itself.



In other words, all works as if the obstacle “hit” by the wave re-emits it in turn in all directions. The process by which this happens is generally called *scattering*.

In the following we will make two main assumptions about a scattering process:

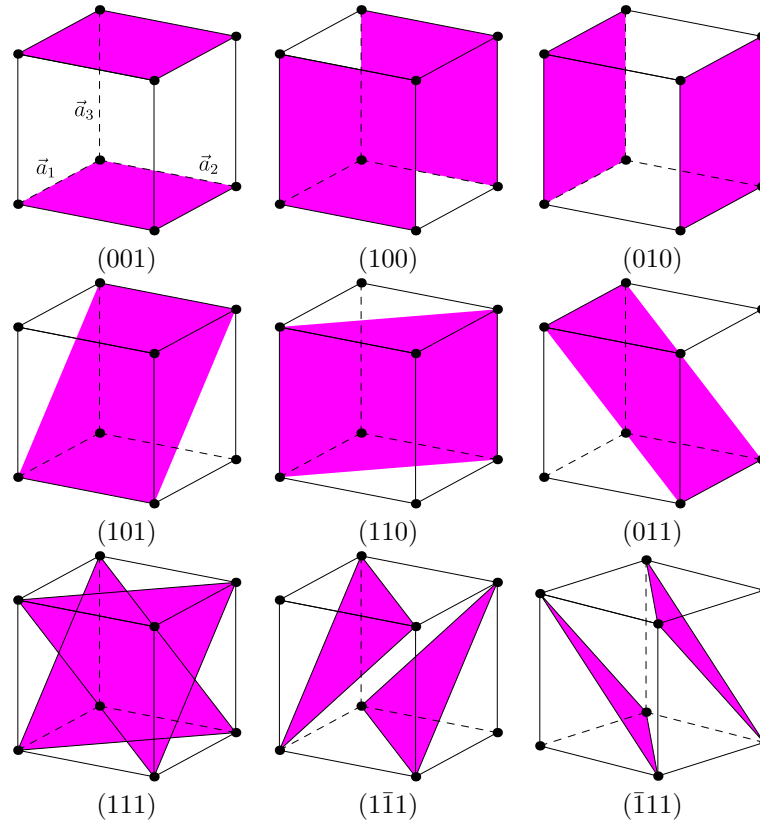
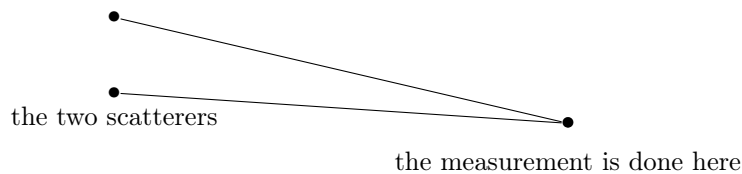


Figure 44: Some examples of lattice planes and corresponding Miller indices. For each family I have drawn only the portion of one or more planes which is inside the volume of the primitive cell (for the families (001) , (100) , (010) , (111) , $(1\bar{1}1)$, $(\bar{1}11)$ the primitive cell contains portions of two consecutive planes).

- we will assume that the scattering process is *elastic*: this means that the interaction of the wave with the scatterer (that is the point obstacle) does not change the energy transported by the wave. The main consequence of this is that the wave generated by the scatterer has the same wave length as the original incoming wave. Restricting ourselves to the case of electromagnetic waves (which is what we will consider here), you can realize this by recalling that the energy of a photon is related to its wave length by the Plank–Einstein relation: $E = h\nu = hc/\lambda$, where h is the Plank constant and c the light velocity. Note that not always the scattering processes are, or can be assumed to be, elastic
- we will assume that the scattering process does not change the phase of the wave; or that it changes it, but by a constant, definite amount. Also this aspect of a scattering process is not granted in general

177. When a plane wave impinges on two obstacles (which we will assume to be point-like for simplicity), each of them becomes a secondary source. The waves re-emitted by the two scatterers will give *interference*. The latter consists in the following: if one measures the variation of the physical quantity represented by the waves diffracted by the two scatterers at the same point in space, the result of the measurement is due to the interaction of the waves coming from the scatterers and this interaction, in turn, will depend upon the distance and relative position of the point where the measurement is being done with respect to that of the two scatterers.



Interference is a direct consequence of the so called *superposition principle*, according to which if two or more waves travel through the same point in space the time variation of the quantity represented by those waves at that point is the sum of the time variations due to each component wave. In other words, the amplitude of the resulting wave at the considered point is, at each instant, the sum of the amplitudes of the waves passing through it.

178. In turn, the resulting amplitude at the given point depends upon the relative phase of the two component waves.

If the component waves (which, for simplicity, we assume having the same maximum amplitude A) reach the same point *in phase*, that is at the given point the phases of the two waves differ by an integer multiple of 2π , then a so called *constructive interference* takes place: the resulting amplitude is at any time greater than that of the single component waves and has its maximum possible value; since the phase difference is an integer multiple of 2π , the cosines have the same value at each instant: when one of the two waves takes the value a , so does the other and the sum is always $2a$.

If, on the other hand, the component waves reach the point in *phase opposition*, that is at the given point the phases of the waves differ by an odd multiple of π , then we have a *destructive interference*: since the phase difference is an odd multiple of π , the cosines take opposite values at each instant; when one of the two waves takes the value a , the other takes the value $-a$ and the sum is always 0.

Of course, when the phase difference is in between the two extreme cases above (the component waves are said to be *out of phase*), the resulting amplitude will correspondingly be between 0 and its maximum possible value.

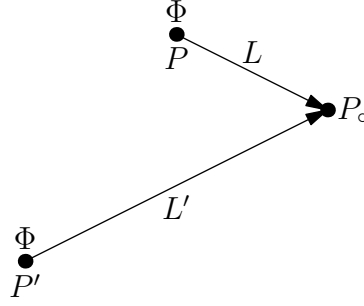


Figure 45: Two monodimensional waves come from two different points P and P' where they had the same phase Φ and travel through the same point $P_{\circ}$ after having covered a linear distance L and $L' > L$, respectively.

179. As it might be easily guessed and as we will actually see further on, the phase difference (also called phase shift) between the diffracted waves depends upon the difference in their optical path, that is, in simple words, upon the difference in the length of the path that each of them had to cover to reach the considered point. It should be apparent that:

- the waves will interfere constructively when the difference in the optical paths is equal to an *integer multiple* of the (common) wavelength
- the waves will interfere destructively when the difference in the optical paths is equal to an *odd multiple of the half of the wavelength*

In fact, consider two monodimensional waves having a common maximum amplitude A , angular frequency ω and wave length λ . Suppose that they come from two different points P and P' where they had the same phase Φ and travel through the same point $P_{\circ}$ after having covered a linear distance L and $L' > L$, respectively (refer to figure 45).

If we set the origin of time and space for each wave at the point where the (common) phase was Φ , then the time variation of the physical quantity represented by the two waves at $P_{\circ}$ will be:

$$a_{P_{\circ}}(t) = A \cos \left(\overbrace{\Phi + \frac{2\pi}{\lambda}L}^{\text{constant}} - \omega t \right)$$

$$a'_{P_{\circ}}(t) = A \cos \left(\overbrace{\Phi + \frac{2\pi}{\lambda}L'}^{\text{constant}} - \omega t \right)$$

respectively.

Now, if:

$$L' = L + n\lambda$$

we have:

$$\begin{aligned}
a'_{P_o}(t) &= A \cos\left(\Phi + \frac{2\pi}{\lambda}L' - \omega t\right) = A \cos\left(\Phi + \frac{2\pi}{\lambda}(L + n\lambda) - \omega t\right) \\
&= A \cos\left(\Phi + \frac{2\pi}{\lambda}L - \omega t + 2\pi n\right) = A \cos\left(\Phi + \frac{2\pi}{\lambda}L - \omega t\right) = a_{P_o}(t)
\end{aligned}$$

and thus the two waves take the same value at each instant at P_o and will give constructive interference.

If, at the opposite:

$$L' = L + (2n + 1)\frac{\lambda}{2}$$

then:

$$\begin{aligned}
a'_{P_o}(t) &= A \cos\left(\Phi + \frac{2\pi}{\lambda}L' - \omega t\right) = A \cos\left(\Phi + \frac{2\pi}{\lambda}\left(L + (2n + 1)\frac{\lambda}{2}\right) - \omega t\right) \\
&= A \cos\left(\Phi + \frac{2\pi}{\lambda}L - \omega t + (2n + 1)\pi\right) = -A \cos\left(\Phi + \frac{2\pi}{\lambda}L - \omega t\right) = -a_{P_o}(t)
\end{aligned}$$

and, in this case, the two waves take opposite values at each instant at P_o and will give destructive interference.

180. The difference of optical path depends upon the geometry of the scatterers and the point where the measurement of the interference is being done: more specifically, upon the distance between the scatterers and the angle made by the direction of the two diffracted waves with the direction orthogonal to the segment connecting the scatterers (we will analyse this aspect in more detail in a while; I have illustrated the idea in figure 46). In general, thus, if we place at a given distance from the scatterers a “screen” or detector able to convert the amplitude of an impinging wave into a visible spot, we will get an image with intense spots at the points of the detector where the conditions for a constructive interference are satisfied. The distribution of the spots on the screen is called *interference spectrum* or *diffraction spectrum* (since interference is a consequence of diffraction, very often the two terms are used interchangeably).

In order for two waves re-emitted by two scatterers to give measurable interference in the way I have just described it is necessary that the two scatterers be at a distance of the same order of magnitude of the wavelength of the incident wave.

181. The electromagnetic radiation as well as the “material waves” associated with quantum mechanical objects like electrons or neutrons can be diffracted by atoms.

A crystal is made up by atoms regularly and periodically repeating in space: it thus constitutes a *diffraction lattice*, exactly like a sequence of aligned and equispaced slits, which you perhaps already encountered in some other (physics?) course.

The interatomic distances in crystals are of the order of $\text{\AA}$ ($1 \text{\AA} = 1 \times 10^{-8} \text{ cm}$). The X rays (electromagnetic radiation) do have wave lengths of that order of magnitude and thus if we focus a X ray beam onto a crystal, the atoms of the latter will diffract the incoming X ray waves and the diffracted radiation will produce a measurable interference.

As we will see, also the waves associated with electrons have wave lengths comparable with the interatomic distances in crystals and this has important effects on the electronic structure of crystalline solids.

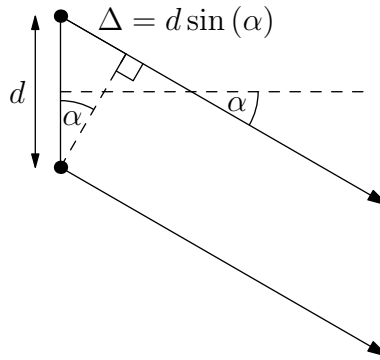


Figure 46: Two scatterers at a distance d generate two diffracted waves that travel along a direction which makes an angle α with respect to the horizontal axis (the scatterers do generate diffracted waves in all directions, but we focus on the two showed in the figure). The difference in optical path is $\Delta = d \sin \alpha$. Note that α is a function of the position of the point (assumed at infinite distance) where the effect of the interference will be measured.

182. In this section I will present some elementary aspects of the diffraction of plane waves by the atoms in a crystal. In particular, we will derive the condition for constructive interference of the diffracted waves.

This argument is the central focus of crystallography. The disposition of the atoms in a crystal (i.e. the crystal structure of a compound) can be determined by focusing a X ray beam on the crystal and measuring the intensity of the diffracted X rays as a function of the position on a screen placed behind the sample (figure 47) (in this regard, you might recall from physics that the intensity of an electromagnetic wave is a function of its amplitude).

From the analysis of the position and intensity of the maxima due to constructive interference of the diffracted X rays it is possible to obtain the atomic positions in the crystal.

Crystallography is a vast and complex argument and in this section we will come in contact with it only very superficially: the intent here is to establish some results that, as you will see, are essential for the understanding of the electronic structure of solids.

183. In what follows we will consider a plane wave (or a beam of monochromatic plane waves, that is: having a common wave length) impinging on a crystal whose structure, for the sake of keeping the discussion as simple as possible, is made by a single type of atoms placed at the points of a Bravais lattice.ⁱⁱ

As already mentioned, the electromagnetic radiation in the range of the X rays is able to interact with a crystal, producing well defined interference spectra and to fix the ideas we will assume that the incoming wave is a X ray beam (even if, as we will see, the kind of wave which we will be interested in is that associated with an electron).

2.7.1 The Laue model of diffraction

184. As I mentioned above, when a X ray beam is shot onto a crystal, the atoms contained in it behave as a three-dimensional diffraction lattice for the incoming radiation. The diffracted X rays will give interference and if we place a detecting screen behind the crystal (for example a

ⁱⁱThat is: we won't discuss the case of a crystal structure where a *polyatomic basis* is associated with each point of the Bravais lattice(point 135).

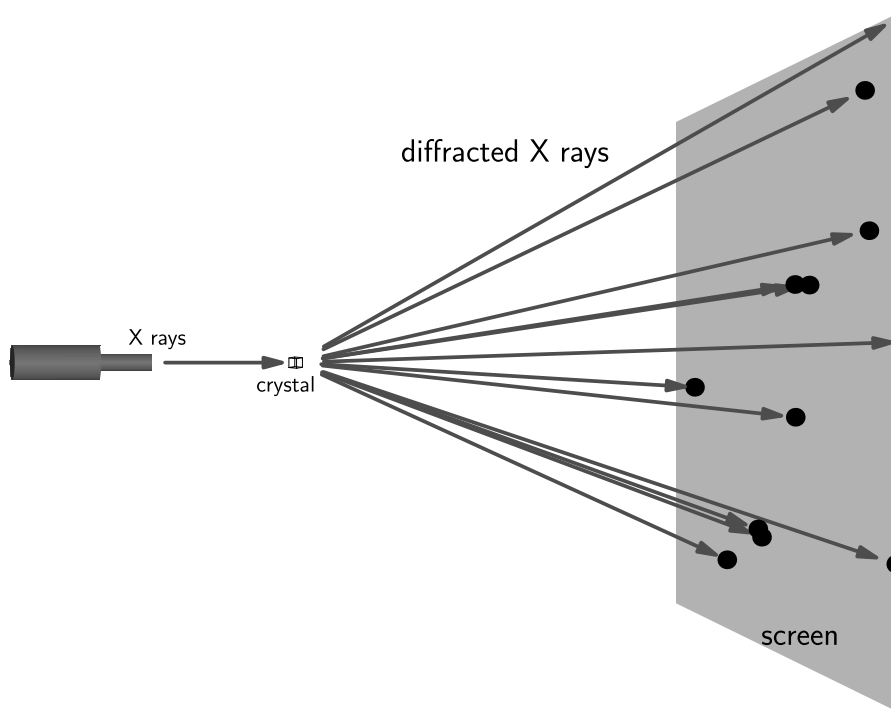


Figure 47: In a typical diffraction experiment a X ray beam is focused on a crystal and the interference maxima of the diffracted X rays are revealed as intense spots on a screen behind the sample.

photographic plate), intensity maxima, in the form of black spots on the screen, will be observed for those directions for which the interference is constructive (figure 47).

What we will do now is to derive the condition in order that in a given direction of the outgoing diffracted radiation an interference maximum is obtained. We will use the approach due to German physicist Max von Laue, who first presented it in the first years of 1900.

Let's begin by considering only two atoms positioned at O_1 and O_2 (the scatterers), whose relative position is defined by a vector $\vec{d}$ (refer to figures 48 and 49).

A plane wave (X rays, just to fix the idea) impinges on the two atoms. The direction of the incident wave is defined by a vector $\vec{n}$; the wave length is λ and thus the wave vector is:

$$\vec{k} = \frac{2\pi}{\lambda} \vec{n} \quad (336)$$

185. Due to the scattering, each of the two scatterers becomes a point-like source re-emitting the incident wave in all directions. To be rigorous, the re-emitted wave is not a plane wave, but rather a *spherical wave*, whose wave fronts are spheres and not planes. However, if we assume, as is always the case, to observe the effects of the interference at a sufficiently long distance from the scatterers, then the curvature of the wave fronts will be negligible and we can treat the diffracted waves as effective plane waves.

186. Since we assume the scattering to be elastic (p. 176), the wave length of the radiation diffracted by each atom is equal to that of the incident wave. Moreover, as mentioned, we

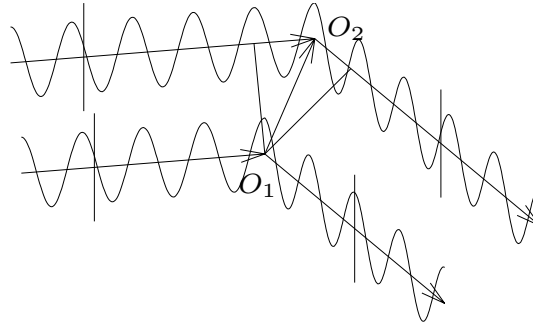


Figure 48: Two waves undergo scattering in the two points O_1 and O_2 . The vertical (with respect to the propagation direction) segments help to evaluate the phase difference of the two waves before and after the scattering. Before the scattering the waves do have the same phase; after the scattering and in the shown direction the waves have developed a phase shift. The latter is the result of the different optical path, as evidenced also by the segments originating from O_1 and orthogonal to the optical path of the wave diffracted by O_2 .

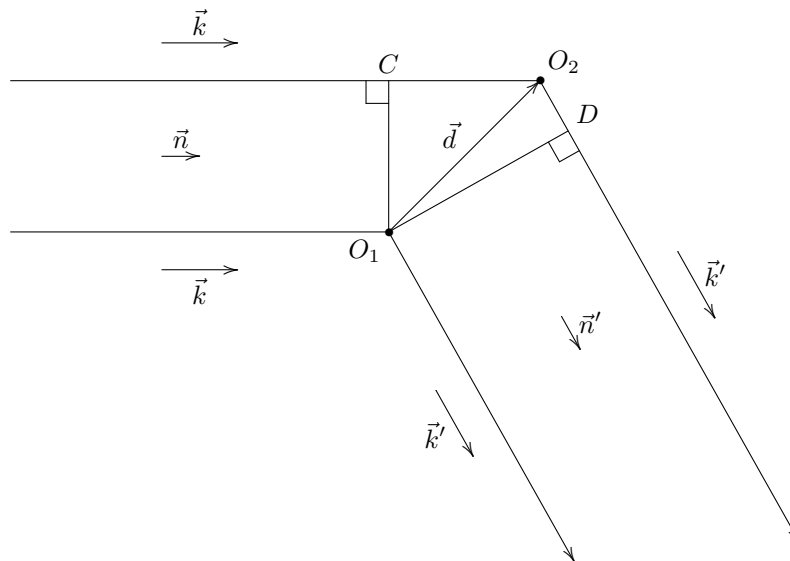


Figure 49: Representation of the scattering by a pair of scatterers, aiming at highlighting the different optical path and the relative orientation of the wave vectors of the incident and diffracted radiation.

assume that the diffracted waves have undergone the same phase shift at the point where the scattering took place; to make our lives even simpler, we will assume that this constant phase shift is equal to 0.

187. At a point behind the crystal along a given direction the diffracted radiation will produce an intensity maximum if the waves coming from the two scatterers interfere constructively; that is to say if the waves reach that point *in phase* (point 178).

Let's assume that the point where we observe the interference between the two diffracted waves is sufficiently far from the crystal such that their propagation directions can be considered as being parallel.

Let's call $\vec{k}'$ the wave vector of the waves re-emitted by the two atoms in a given direction, defined by a versor $\vec{n}'$; under our assumptions, $\vec{k}$ and $\vec{k}'$ share a common module ($2\pi/\lambda$, because the wave length has not changed), but have *different* direction.

Then, the two diffracted waves will reach the point in phase if the difference in optical path is equal to an integer multiple of the (common) wave length (point 179).

188. From figure 49 you can see that the path difference between the wave from O_1 and that from O_2 is:

$$\overline{CO_2} + \overline{O_2D} \quad (337)$$

This path difference must be equal to an integer multiple of λ :

$$\overline{CO_2} + \overline{O_2D} = m\lambda \quad m \in \mathbb{N} + \{0\} \quad (338)$$

We can express the LHS of 338 as a function of $\vec{d}$ and the two versors $\vec{n}$ and $\vec{n}'$.

The length of the segment $\overline{CO_2}$ is equal to that of the projection of $\vec{d}$ along the $\vec{n}$ direction; since $\vec{n}$ has unit modulus, the latter is simply given by the scalar product $\vec{d} \cdot \vec{n}$:

$$\overline{CO_2} = \vec{d} \cdot \vec{n} \quad (339)$$

In a similar way, the length of the segment $\overline{O_2D}$ is equal to that of the projection of $\vec{d}$ along the $\vec{n}'$ direction; also in this case, the latter is given by the scalar product $\vec{d} \cdot \vec{n}'$, but now this scalar product is negative (because the angle between $\vec{d}$ and $\vec{n}'$ is $> \pi/2$) and thus we must take it with a minus sign in order to get the length (always positive) of the segment $\overline{O_2D}$:

$$\overline{O_2D} = -\vec{d} \cdot \vec{n}' \quad (340)$$

Substituting above we obtain:ⁱⁱⁱ

$$\vec{d} \cdot \vec{n} - \vec{d} \cdot \vec{n}' = m\lambda \quad (341)$$

$$\vec{d} \cdot (\vec{n} - \vec{n}') = m\lambda \quad (342)$$

(multiply both sides by $2\pi/\lambda$)

$$\vec{d} \cdot \left(\frac{2\pi}{\lambda} \vec{n} - \frac{2\pi}{\lambda} \vec{n}' \right) = 2\pi m \quad (343)$$

$$\vec{d} \cdot (\vec{k} - \vec{k}') = 2\pi m \quad (344)$$

ⁱⁱⁱYou can verify by yourself that the result is the same not only for the geometry shown in figure 49, but also for any other relative orientation of the incoming and outgoing waves.

Note that $\vec{k}$ and $\vec{k}'$ have the same length, but different direction and thus their (vector) difference is *not* null.

189. Now we extend what we have obtained for only two atoms to a whole infinite Bravais lattice with an atom sitting on each lattice point; doing this is not difficult: if we want that the waves diffracted by all the atoms of the lattice reach a given point in phase (thus producing an intensity maximum at that point), eq. 344 must be satisfied at the same time *by all possible pairs of atoms of the lattice*. In this case, the vector defining the relative position of any atom pair is, trivially, a vector of the Bravais lattice: $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$, where n_1, n_2, n_3 are integers and $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are the primitive vectors.

The condition to be satisfied is thus:

$$\vec{R} \cdot (\vec{k} - \vec{k}') = 2\pi m, \quad m \in \mathbb{Z}, \quad \forall \vec{R} \quad (345)$$

But, based on section 1.3.4, this means that $(\vec{k} - \vec{k}')$ *must be a vector of the reciprocal lattice*. So we arrive at the following result:

the diffracted waves will produce an intensity maximum in the direction for which the difference between the incoming and outgoing wave vectors is equal to a vector of the reciprocal lattice

Eq. 345 is one of the forms in which the so called *Laue condition* can be written.

2.7.1.1 The geometric interpretation of the Laue condition

190. It is possible to reformulate the Laue condition in a way that allows a simple geometric interpretation of it.

As we have seen, under the assumption of elastic scattering, the $\vec{k}$ and $\vec{k}'$ wave vectors have different direction, but equal length:

$$|\vec{k}| = |\vec{k}'| \quad (346)$$

When the Laue condition 345 is satisfied it must be:

$$\vec{k} - \vec{k}' = \vec{K} \quad (347)$$

where $\vec{K}$ is a reciprocal vector.

Under these conditions, we can isolate $\vec{k}'$ in 347 and plug it into 346, thus obtaining:

$$k = |\vec{k} - \vec{K}| \quad (348)$$

(square both sides

and recall that: $|\vec{v}|^2 = \vec{v}^2$)

$$k^2 = (\vec{k} - \vec{K})^2 \quad (349)$$

$$k^2 = k^2 + K^2 - 2\vec{k} \cdot \vec{K} \quad (350)$$

$$= k^2 + K^2 - 2K\vec{k} \cdot \vec{n}_K \quad (351)$$

where the versor $\vec{n}_K$ in the direction of $\vec{K}$ has been introduced and so $\vec{K} = K\vec{n}_K$.

We can thus get our final result:

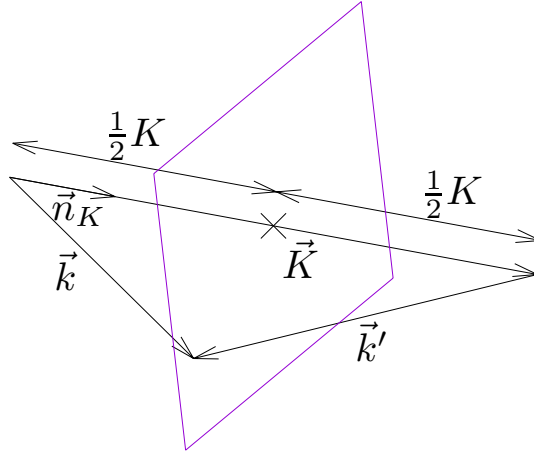


Figure 50: The geometric interpretation of eq.352.

$$\vec{k} \cdot \vec{n}_K = \frac{1}{2}K \quad (352)$$

First of all notice that we have rewritten the Laue condition 345 as a function of the incoming wave vector alone and of a corresponding vector of the reciprocal lattice (i.e. the outgoing wave vector has “disappeared”).

The geometric meaning of 352 is made apparent in figure 50.

The term $\vec{k} \cdot \vec{n}_K$ is nothing but the modulus of the projection of $\vec{k}$ along the direction of $\vec{K}$. Then 352 tells us that an intensity maximum of the diffracted wave will be obtained each time that the relative orientation of the incoming wave and the crystal sample is such that the length of the projection of the incoming wave vector along the direction of any reciprocal vector is equal to half the length of that reciprocal vector.

As can be seen in figure 50, this condition will be satisfied by all the wave vectors $\vec{k}$ leaning against a plane orthogonal to the reciprocal vector $\vec{K}$ and passing through its midpoint.

(Also note that $\vec{k}' = \vec{k} - \vec{K}$ is the symmetric image of $\vec{k}$ with respect to the plane orthogonal to $\vec{K}$)

Now: if you go back to section 2.6.4 on p. 105, then you realize immediately that the planes for which the Laue condition is satisfied *are the boundaries (that is: the faces) of the Brillouin zones*.

We have thus discovered a very important property of the Brillouin zones: any plane wave traveling through the crystal and having a wave vector which touches a boundary of a Brillouin zone will be diffracted giving constructive interference.

3 The Fermi gas model

191. In this section we will discuss the simplest model for the study of the behavior of electrons in metals; this model was introduced and developed by Arnold Sommerfeld starting from 1927.ⁱ

192. The model is also known as “*electron gas model*” and the reason is the following. A solid metal is considered as made up by metal ions (nuclei plus core electrons) at fixed positions, while the valence electrons are totally free to move in all the volume occupied by the solid. The valence electrons are thus assimilated to a “gas”, for their motion is random and they tend to occupy all the available space inside the solid.

As we will see, a key point for the treatment of the electron gas model at temperatures greater than 0 K is the Fermi–Dirac distribution law: for this reason, this model is often referred to as the *Fermi gas*.

193. A fundamental aspect of the model is that the “gas” electrons (that is the valence electrons) are:

independent	that is: they do not interact with each other
free	that is: they do not interact with the fixed ions

These assumptions might seem unrealistic (and indeed they are); nevertheless, the predictions that is possible to derive from the electron gas model are very often in excellent agreement with the experimental data. And this can be explained by considering that many properties of the metals depend mainly upon the mobility of their valence electrons and very little upon the way by which such mobility is influenced by their interactions either with each other or with the nuclei.

3.1 The time dependent monoelectronic Schrödinger equation

194. For all intents and purposes, the free and independent electron gas model is equivalent to considering the valence electrons of a metal confined within its volume V and as if each of them was completely alone.

Under these conditions, the accessible electronic states are found by solving the Schrödinger equation *for a single electron*. The ground state of the electron gas (that is the state occupation at 0 K) is then obtained by the well known “aufbau” principle, according to which the accessible states get “occupied” in order of increasing energy and in accordance with Pauli’s principle.

The most general form of the monoelectronic Schrödinger equation for the present case is:

$$-\frac{\hbar^2}{2m}\nabla^2\xi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\xi(\vec{r},t) \quad (353)$$

Eq. 353 is the time dependent monoelectronic Schrödinger equation. It is a partial differential equation. The solution $\xi(\vec{r},t)$ is a function of four variables: the three space coordinates ($\vec{r} = (x, y, z)$) and time t . m is the mass of the electron, $\hbar = h/2\pi$ and h is the Plank constant, $i = \sqrt{-1}$ is the imaginary unit.

In general, the operator which acts on the function $\xi(\vec{r},t)$ at the LHS is the hamiltonian operator (usually denoted by H): for the system we are considering (free and independent electron gas) the hamiltonian operator contains only the kinetic energy term:

ⁱActually, before the advent of quantum mechanics, Paul Drude developed an even simpler model, known as “Drude model”. In this model, the electrons are treated as classical particles obeying Boltzmann statistics. Despite the simplistic assumptions (and also thanks to genuine errors) the Drude model could successfully reproduce some very important experimental observations and thus enjoyed some good fortune before being replaced by the Sommerfeld model. The Drude model is presented and discussed in the first chapter of the book of Ashcroft and Mermin.⁷

$$H = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \quad (354)$$

195. Please, note also that in all this course we will always assume that the electronic state function can be factorized into a part depending only on the spatial coordinates, a part depending only on time and a part depending only on the electronic spin; if, as it will always be the case for us, the Hamiltonian operator is not spin dependent, then the spin dependent part of the state function will not appear in the Schrödinger equation (i.e. it will cancel out on both sides of the equation); this means that the solutions of the Schrödinger equation 353 will be always doubly degenerate with respect to the spin variable. In other words, a state which is solution of 353 can actually describe (“host”) two electrons with opposite spin ($\pm\hbar/2$).

3.2 Space/time factorization

196. Since in our case the hamiltonian operator at the LHS of eq. 353 is independent of time, its solutions can be obtained by assuming that the function $\xi(\vec{r}, t)$ can be written as the product of a function $\Psi(\vec{r})$ depending only on the spatial coordinates and a function $\Theta(t)$ depending only on time:

$$\xi(\vec{r}, t) = \Psi(\vec{r}) \Theta(t) \quad (355)$$

Substituting into 353 we get:

$$\Theta(t) \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}) \right) = \Psi(\vec{r}) \left(i\hbar \frac{\partial}{\partial t} \Theta(t) \right) \quad (356)$$

because $\Theta(t)$ behaves as a constant with respect to the hamiltonian at the LHS, which depends only on $\vec{r}$, while $\Psi(\vec{r})$ behaves as a constant with respect to the derivative at the RHS, which is done with respect to the time coordinate.

Upon dividing both sides by $\xi(\vec{r}, t) = \Psi(\vec{r}) \Theta(t)$ we arrive at:

$$\frac{1}{\Psi(\vec{r})} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}) \right) = \frac{1}{\Theta(t)} \left(i\hbar \frac{\partial}{\partial t} \Theta(t) \right) \quad (357)$$

The LHS is a function of the electron position $\vec{r}$ *only*, while the RHS is a function of time t *only*. The equation requires the equality of the LHS and RHS *for any possible value of $\vec{r}$ and t* : realize very well that this is possible if and only if both sides of the equation are separately equal to a same constant, which we will denote as ϵ .

197. The starting equation is thus equivalent to the two separate equations for $\Psi(\vec{r})$ and $\Theta(t)$:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}) = \epsilon \Psi(\vec{r}) \quad (358)$$

$$i\hbar \frac{d}{dt} \Theta(t) = \epsilon \Theta(t) \quad (359)$$

(in equation 359 above the partial derivative has turned into a total derivative because now it acts on a function of t only)

Being the eigenvalue of the hamiltonian operator in the first equation, the constant ϵ is a possible energy value for the electron.

3.3 The time equation

198. The time equation 359 is easily solved via separation of variables:

$$\frac{d\Theta}{\Theta} = \frac{\epsilon}{i\hbar} dt \quad (360)$$

$$\int \frac{d\Theta}{\Theta} = \frac{\epsilon}{i\hbar} \int dt \quad (361)$$

$$\ln \Theta = \frac{\epsilon}{i\hbar} t + C' \quad (362)$$

$$\Theta(t) = \exp\left(\frac{\epsilon}{i\hbar} t + C'\right) \quad (363)$$

$$\Theta(t) = C \exp\left(\frac{\epsilon}{i\hbar} t\right) = C \exp\left(-i\frac{\epsilon}{\hbar} t\right) \quad (364)$$

where $C = \exp(C')$ is a constant yet to be found.

If we make use of the Plank–Einstein relation which relates the energy ϵ to the (linear) frequency ν of a quantum particle:

$$\epsilon = h\nu \quad (365)$$

we obtain:

$$\Theta(t) = C \exp(-i\omega t) \quad (366)$$

where $\omega = 2\pi\nu$ is the angular frequency 9.

Since the function $\xi(\vec{r}, t)$ is the product of the two functions $\Psi(\vec{r})$ and $\Theta(t)$, we can safely assume $C = 1$ and transfer all the necessary adjustments on the constant that will appear in the spatial solution $\Psi(\vec{r})$.

In conclusion, we can take as the solution of the time equation the following:

$$\Theta(t) = \exp(-i\omega t) \quad (367)$$

199. The just obtained result is of general scope: for all the systems for which the factorization 355 is possible, the time dependence of the solution of the Schrödinger equation is obtained simply by multiplying the space solution (the $\Psi(\vec{r})$ in 355) by the exponential 367:

$$\xi(\vec{r}, t) = \Psi(\vec{r}) \exp(-i\omega t) \quad (368)$$

3.4 The space equation

200. We now turn to the solution of the time independent Schrödinger equation 358:

$$\text{eq. 358:} \quad -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}) = \epsilon \Psi(\vec{r})$$

This is an eigenvalue partial differential equation (because $\Psi(\vec{r}) = \Psi(x, y, z)$ is a function of three variables). Solving 358 means finding all the possible ϵ values and the corresponding $\Psi(\vec{r})$ functions (for each ϵ value there will be one or more corresponding $\Psi(\vec{r})$ functions) satisfying the equation.

201. Since we are considering a free electron having only kinetic energy, the energy appearing in 358 is always positive (we take as null the energy of a non-moving, stationary electron). It is then convenient to group all the constant terms in the equation in the following way:

$$k^2 = \frac{2m\epsilon}{\hbar^2} \quad (369)$$

Eq. 358 can thus be rewritten as:

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(x, y, z) + k^2 \Psi(x, y, z) = 0 \quad (370)$$

202. In a way very similar to what we did at point 196 with the factorization of $\xi(\vec{r}, t)$, also in this case we can propose that the function $\Psi(\vec{r})$ to be found has the form of a product of three functions, each depending on a single spatial variable:

$$\Psi(\vec{r}) = \Psi(x, y, z) = X(x)Y(y)Z(z) \quad (371)$$

Substituting into 370 and noting again that each partial derivative “treats” as constants the two functions not depending on the coordinate which it operates on, with steps similar to those seen in point 196 we easily arrive at:

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = -k^2 \quad (372)$$

Since each of the three functions X, Y, Z depends on a single coordinate and since the RHS is a constant, eq. 372 can be satisfied *for any value of x, y, z* if and only if each term on the LHS is separately equal to a constant. This means that eq. 372 is equivalent to the three separate equations:

$$\frac{1}{X} \frac{d^2 X}{dx^2} + k_x^2 = 0 \quad (373)$$

$$\frac{1}{Y} \frac{d^2 Y}{dy^2} + k_y^2 = 0 \quad (374)$$

$$\frac{1}{Z} \frac{d^2 Z}{dz^2} + k_z^2 = 0 \quad (375)$$

with the additional constraint that:

$$k_x^2 + k_y^2 + k_z^2 = k^2 \quad (376)$$

(as already noted, the partial derivatives have turned into total derivatives since each equation contains now a single variable)

203. Obviously, since the three equations just written are formally identical, it is enough to solve just one of them. Let’s take the one for x , which we rearrange in the following way:

$$\frac{d^2 X}{dx^2} + k_x^2 X = 0 \quad (377)$$

This is an ordinary linear and homogeneous differential equation of the second order and you can find the solution method on any textbook about this subject (for instance the textbook by Harris and Stocker¹³).

Equation 377 states that the seeked solution must be such that its second derivative is equal to itself multiplied by the factor $-k_x^2$. The exponential function enjoys the property that its derivative is equal to itself. We can then start from a proposal of the type $X(x) = C_x \exp(\lambda x)$ and substitute into the differential equation to obtain C_x and λ :

$$C_x \exp(\lambda x) (\lambda^2 + k_x^2) = 0 \quad (378)$$

Since the exponential never becomes null, it must necessarily be:

$$\lambda^2 + k_x^2 = 0 \quad (379)$$

or:

$$\lambda = \pm i k_x \quad (380)$$

Thus, eq. 377 admits two different solutions for each value of k_x^2 (that is, for each value of the energy ϵ , based on 369):

$$X(x) = C_x \exp(i k_x x) \quad \text{e} \quad X(x) = C_x \exp(-i k_x x) \quad (381)$$

The generic solution can be written as:

$$X(x) = C_x \exp(i k_x x) \quad (382)$$

with $k_x \in [-\infty; \infty]$ and C_x being a constant, for the moment, yet to be determined.

204. Of course, the other two equations have solutions formally identical:

$$Y(y) = C_y \exp(i k_y y) \quad k_y \in [-\infty; \infty] \quad (383)$$

$$Z(z) = C_z \exp(i k_z z) \quad k_z \in [-\infty; \infty] \quad (384)$$

and, thus, substituting into 371, we obtain:

$$\Psi(\vec{r}) = X(x) Y(y) Z(z) = C_x C_y C_z \exp(i(k_x x + k_y y + k_z z)) \quad (385)$$

k_x, k_y, k_z can be thought of as the components of a vector $\vec{k}$ in $\mathbb{R}^3$ space: $\vec{k} = (k_x, k_y, k_z)$ and this allows us to rewrite 385 in a more compact way:

$$\Psi(\vec{r}) = C \exp(i \vec{k} \cdot \vec{r}) \quad (386)$$

with $C = C_x C_y C_z$ and $\vec{r} = (x, y, z)$.

We see now that the solution of the time independent monoelectronic Schrödinger equation takes the form of the spatial part of a plane wave (eq. 256). The wave vector $\vec{k}$ is related to the energy of the electron by 376 and 369:

$$k_x^2 + k_y^2 + k_z^2 = |\vec{k}|^2 = k^2 = \frac{2m\epsilon}{\hbar^2} \quad (387)$$

3.5 The complete solution

205. The solution of the time dependent Schrödinger equation is obtained by plugging 386 and 367 into 355:

$$\xi(\vec{r}, t) = \Psi(\vec{r}) \Theta(t) = C \exp\left(i(\vec{k} \cdot \vec{r} - \omega t)\right) \quad (388)$$

from which we realize that the state function describing a free electron has the mathematical form of a traveling plane wave represented with a complex exponential (eq. 254).

It is worth noting at this point that the meaning of the state function is *not* that of a wave in a physical sense; that is: while the function describing a sea wave represents the height of sea water with respect to its average level (thus the values taken by the function are those of a well defined physical quantity), the physical interpretation of the state function describing an electron is not defined. What has a physical meaning, in this case, is the square modulus of the function, whose integral evaluated on a space region gives the probability that the electron is located inside that region at a given time.

In the following we will mainly concentrate on the study of the spatial part of the state function; this describes the dependence of the electron state from its position in space at a given (fixed) time (you can think of the $\Psi(\vec{r})$ as a “photograph” of the electron which captures its instantaneous state).

3.6 Consequences of the electron confinement

206. We have derived eq. 386 by assuming that the electron has no constraints whatsoever. This has two main implications: in the first place note that the energy of the electron is continuous, that is non quantized (the energy is related to the wave vector $\vec{k}$ by 369 and in the derivation nothing prevents the components of $\vec{k}$ to vary in a continuous way); in the second place, the constant C is still undefined (as I already mentioned, this constant includes also a term which refers to the time dependent part of the state function).

We will now see how these two aspects of the electron state do change when the latter is confined into the volume V of the solid sample.

3.6.1 Normalization

207. Requesting that the electron must remain inside the volume of the solid allows us to determine the constant C appearing in 386. The probability density associated with the $\Psi(\vec{r})$ is:

$$\Psi^*(\vec{r}) \Psi(\vec{r}) = |\Psi(\vec{r})|^2 \quad (389)$$

This probability density, integrated over a given space region, gives the probability of finding the electron in that region at a given time.

Since the electron cannot escape from the volume V of the solid, the probability of finding it in *any* point inside such volume must be unit. This allows to normalize the state function:

$$\int_V \Psi^*(\vec{r}) \Psi(\vec{r}) d\vec{r} = 1 \quad (390)$$

Substituting (and assuming for simplicity that C is real):

$$\int_V C \exp(-i\vec{k} \cdot \vec{r}) C \exp(i\vec{k} \cdot \vec{r}) d\vec{r} = C^2 \int_V d\vec{r} = C^2 V = 1 \quad (391)$$

from which we get:

$$C = \frac{1}{\sqrt{V}} \quad (392)$$

The expression of $\Psi(\vec{r})$ normalized with respect to the volume of the solid is thus:

$$\Psi(\vec{r}) = \frac{1}{\sqrt{V}} \exp(i\vec{k} \cdot \vec{r}) \quad (393)$$

3.6.2 Periodic boundary conditions

208. A second consequence of the confinement of the electron inside the volume V is that the state function must satisfy corresponding boundary conditions: these fix the behavior of the function at the boundaries of the region into which the electron is forced to stay.

At this point we must be more precise about the exact definition of the volume V of the solid sample. Since we are interested in the description of the behavior of the electrons *inside* the solid, the choice of its external shape has no importance. For this reason, it is most convenient to assume the simplest geometric shape, that is a cube of side $L = \sqrt[3]{V}$.

Moreover, in order to make any effect due to the solid surface insignificant, we impose so called *periodic boundary conditions* (also known as *Born and von Karman conditions*).

In practice, we assume that the cube of volume V which constitutes the solid sample is *the primitive cell of a “crystal”* and as such is replicated indefinitely in space. Note that such primitive cell is enormous with respect to that of a “real” crystal, since its dimensions are those of a macroscopic sample (cm), while the dimensions of the primitive cell of a true crystal are of the order of $\text{\AA}$, ($1 \text{\AA} = 1 \times 10^{-8} \text{ cm}$).

The periodic boundary conditions effectively remove any reference to the surface of the macroscopic sample, because under such conditions the cube faces are not exposed to the external ambient (for instance the empty space outside the sample); rather, each face is in contact with a periodic replica of the sample: this way, you can think that the sample *never ends*.

Each time that an electron crosses a face of the cube, it enters the adjacent cell (so it does not leave the sample); at the same time the replica of the electron in the cell opposing the one entered by the “escaping” electron enters the original cell with the same velocity (both modulus and direction): you might have already seen such an effect in some video game.

The logic behind the periodic boundary conditions for the 2D case is shown in figure 51. You can see an animated version of the same figure at the web site of the course.¹⁴

3.7 Quantization of the wave vector and energy

209. As you might have already realized, the periodic boundary conditions imply that the mono-electronic state function $\Psi(\vec{r})$ *must be periodic* over the Bravais lattice $\mathcal{R}$ of which the solid sample is the primitive cell.

We already know how such periodicity is expressed in a general form (eq.124):

$$\Psi(\vec{r} + \vec{R}) = \Psi(\vec{r}) \quad \forall \vec{R} \in \mathcal{R} \quad (394)$$

210. As we will now easily see, the periodicity of $\Psi(\vec{r})$ implies in turn the quantization of the wave vector $\vec{k}$.

Using 393 for the $\Psi(\vec{r})$ we have:

$$\begin{aligned} \Psi(\vec{r} + \vec{R}) &= \frac{1}{\sqrt{V}} \exp\left(i\vec{k} \cdot (\vec{r} + \vec{R})\right) \\ &= \frac{1}{\sqrt{V}} \exp\left(i\vec{k} \cdot \vec{r}\right) \exp\left(i\vec{k} \cdot \vec{R}\right) \\ &= \Psi(\vec{r}) \exp\left(i\vec{k} \cdot \vec{R}\right) \end{aligned}$$

Condition 394 can be satisfied if and only if:

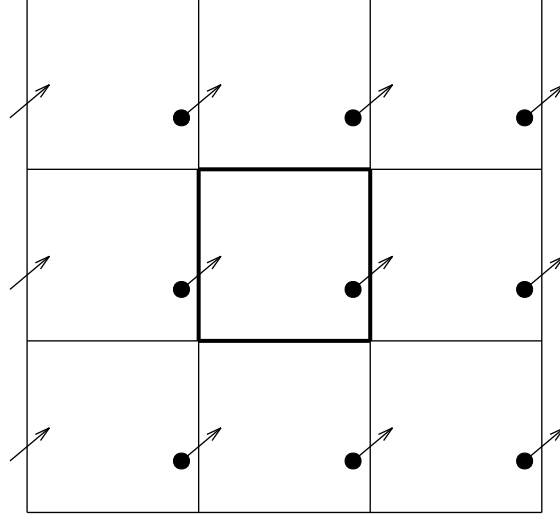


Figure 51: Periodic boundary conditions of Born and von Karman. The sample, highlighted with a thicker line, is considered as the primitive cell of a “crystal” and is repeated indefinitely in space. Whatever happens inside the sample, will happen, exactly at the same time, in all its infinite periodic images. If a moving electron (represented as a black dot) exits the sample, its periodic image in an adjacent cell will enter the sample from the opposite side.

$$\exp(i\vec{k} \cdot \vec{R}) = 1$$

or:

$$\vec{k} \cdot \vec{R} = 2\pi n \quad n \in \mathbb{Z} \quad \forall \vec{R} \in \mathcal{R} \quad (395)$$

Based on the definition 197, this is equivalent to say that $\vec{k}$ must be a vector of the reciprocal lattice $\mathcal{R}^*$ associated with the direct lattice $\mathcal{R}$ of which the solid sample is the primitive cell. Since we have supposed that $\mathcal{R}$ is a simple cubic lattice, then $\mathcal{R}^*$ will be also a simple cubic lattice: its generator vectors $\vec{b}_i$ will share a common modulus $2\pi/L$ and have the same direction as the direct primitive vectors $\vec{a}_i$ (review point 89 and keep in mind that the direct primitive vectors of a simple cubic lattice are all mutually orthogonal and share the same length).

211. In summary, the confinement of the electron inside the volume of the solid sample and the imposed periodic boundary conditions do limit the allowed wave vectors in 393 to the only vectors of $\mathcal{R}^*$, that is:

$$\vec{k} = n_x \vec{b}_1 + n_y \vec{b}_2 + n_z \vec{b}_3 \quad n_x, n_y, n_z \in \mathbb{Z} \quad (396)$$

If we orient the cubic sample with three edges along the three cartesian axes and the corresponding vertex at the origin, then the three reciprocal primitive vectors can be chosen as:

$$\begin{aligned} \vec{b}_1 &= \frac{2\pi}{L} (1, 0, 0) \\ \vec{b}_2 &= \frac{2\pi}{L} (0, 1, 0) \end{aligned}$$

$$\vec{b}_3 = \frac{2\pi}{L} (0, 0, 1)$$

and thus:

$$\begin{aligned} \vec{k} &= n_x \vec{b}_1 + n_y \vec{b}_2 + n_z \vec{b}_3 \\ &= n_x \frac{2\pi}{L} (1, 0, 0) + n_y \frac{2\pi}{L} (0, 1, 0) + n_z \frac{2\pi}{L} (0, 0, 1) \\ &= \left(\overbrace{n_x \frac{2\pi}{L}}^{k_x}, \overbrace{n_y \frac{2\pi}{L}}^{k_y}, \overbrace{n_z \frac{2\pi}{L}}^{k_z} \right) \end{aligned} \quad (397)$$

which shows in a formal way that the components of the allowed wave vectors are quantized by the three integers n_x, n_y, n_z .

212. Of course, the quantization of the vector $\vec{k}$ implies the quantization of the electron energy ϵ , which is related to the square modulus of $\vec{k}$ (eq. 369):

$$\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) \quad (398)$$

The relation between ϵ and k is called *dispersion relation* and the origin of the name will become apparent when we will introduce the concept of *bands* (point 334).

213. If you think a bit about it, the allowed wave vectors being all and only the points of $\mathcal{R}^*$ is not surprising.

If you compare the space part of the state function 393 with the Fourier expansion of a generic function $f(\vec{r})$ periodic over the Bravais lattice introduced by the conditions of Born and von Karman, eq. 126:

$$\begin{aligned} \Psi(\vec{r}) &= \frac{1}{\sqrt{V}} \exp(i\vec{k} \cdot \vec{r}) \quad \text{eq. 393} \\ f(\vec{r}) &= \sum_{\vec{k}} B_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) \quad \text{eq. 126} \end{aligned}$$

you should immediately realize that the state function is nothing but the generic exponential term of the Fourier expansion.

In section 1.3.3 we have derived the Fourier expansion for functions of two or three variables and in particular we have seen that the reciprocal lattice is defined precisely in such a way that all the exponential terms of the expansion are periodic over the Bravais lattice which defines the periodicity of the expanded function.

Thus, since the periodic boundary conditions imply that the state function $\Psi(\vec{r})$ must be periodic over the Bravais lattice introduced by them and since the analytical form of $\Psi(\vec{r})$ is identical to that of the Fourier expansion terms, it should not be surprising that the wave vector appearing in the expression of $\Psi(\vec{r})$ must be a vector of the reciprocal lattice.

Let's now make some remarks about the obtained result.

3.8 Counting the allowed states

214. Eq. 393 shows that the allowed states for the free and independent electron are indexed by the vector $\vec{k}$ (and precisely by the three integer numbers n_x, n_y, n_z that define its components through eq. 397): an allowed electron state corresponds to each $\vec{k}$ vector. We also established that the allowed wave vectors are all and only the points of the reciprocal lattice $\mathcal{R}^*$ associated with the direct Bravais lattice $\mathcal{R}$ which implements the periodic boundary conditions. It follows that the number of electronic accessible states in the Fermi gas is equal to the number of points of $\mathcal{R}^*$. This number is obviously infinite, but the points (that is the accessible states) are discrete.

Moreover, note that we derived the state function 393 under the implicit assumption that it does not depend upon the electronic spin. But then, by Pauli's principle, we can say that each state of type 393 can actually describe *two* electrons with opposite spin. Equivalently: a number N of allowed $\vec{k}$ vectors corresponds to twice a number ($2N$) of true *monoelectronic* accessible states.

3.9 Isoenergetic surfaces and degeneracy

215. Eq. 398 defines the relation between the electron energy and the wave vector indexing its quantum state.

Such relation in $\vec{k}$ space is of parabolic type:

$$\epsilon = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m} \quad (399)$$

Since the energy depends only on the modulus of the wave vector, it trivially follows that all the $\vec{k}$ points laying on a sphere centered at the origin will index states with the same energy, that is degenerate states.

The cartesian equation of such sphere is:

$$k_x^2 + k_y^2 + k_z^2 = \frac{2m\epsilon}{\hbar^2} \quad (400)$$

The electronic state with the lowest energy is that corresponding to the point $\vec{k} = (0, 0, 0)$ at the origin (for which $\epsilon = 0$). The immediately higher energy state is the one corresponding to the first neighbors of the origin (refer to figure 52). For the simple cubic reciprocal lattice which we are dealing with the number of these first neighbors is 6 and their common length is the cell constant of $\mathcal{R}^*$, that is $2\pi/L$; this is also the radius of the isoenergetic sphere which they lay on. The components of these vectors are:

$$\frac{2\pi}{L} (\pm 1, 0, 0) \quad \frac{2\pi}{L} (0, \pm 1, 0) \quad \frac{2\pi}{L} (0, 0, \pm 1) \quad (401)$$

These 6 points identify as many degenerate electronic states at energy:

$$\epsilon = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L} \right)^2 \quad (402)$$

The isoenergetic sphere immediately next corresponds to the 12 second neighbors of the origin. The common length of these vectors is (refer to figure 52b):

$$\sqrt{\left(\frac{2\pi}{L} \right)^2 + \left(\frac{2\pi}{L} \right)^2} = \frac{2\pi}{L} \sqrt{2} \quad (403)$$

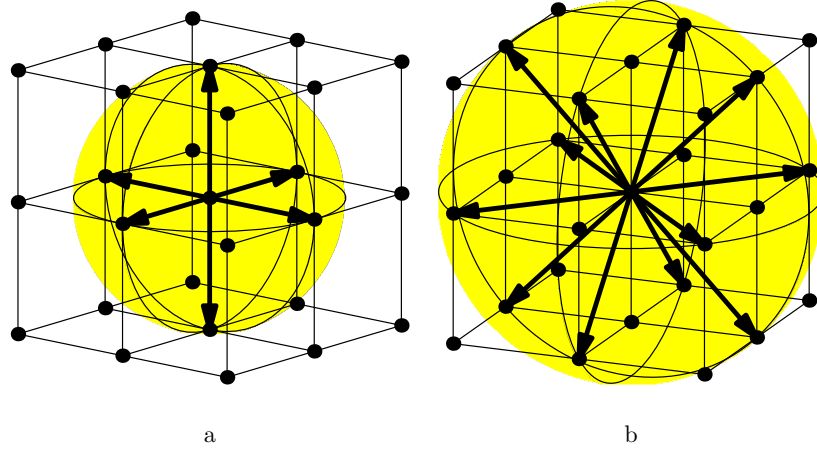


Figure 52: For a simple cubic lattice: a: isoenergetic sphere corresponding to the first neighbors of the origin; b: isoenergetic sphere corresponding to the second neighbors of the origin

and their components are:

$$\begin{array}{ll} \frac{2\pi}{L} (\pm 1, 0, 1) & \frac{2\pi}{L} (0, \pm 1, 1) \\ \frac{2\pi}{L} (\pm 1, 1, 0) & \frac{2\pi}{L} (\pm 1, -1, 0) \\ \frac{2\pi}{L} (\pm 1, 0, -1) & \frac{2\pi}{L} (0, \pm 1, -1) \end{array}$$

(the 12 second neighbors can be partitioned into three subsets of 4 elements each: there is a subset at an “elevation” of $2\pi/L$ along the vertical axis, a second subset at elevation of 0 and a third subset at an elevation of $-2\pi/L$)

Thus, the second isoenergetic sphere contains 12 degenerate states at energy:

$$\epsilon = \frac{\hbar^2 \left(\frac{2\pi}{L} \sqrt{2} \right)^2}{2m} \quad (404)$$

From what we said in point 145 it follows that at increasing energy, that is at increasing distance from the origin in $\vec{k}$ space, the number of degenerate $\vec{k}$ points, that is the $\vec{k}$ points laying on a given isoenergetic sphere (thus, ultimately, the degeneracy of an energy level, net of any possible contribution due to spin), tends to increase rather quickly (figure 26).

3.10 Spacing of the energy levels

216. To get an idea about the spacing of the energy levels we can calculate the energy difference between the first two isoenergetic spheres, of radii $2\pi/L$ and $\frac{2\pi}{L}\sqrt{2}$:

$$\frac{\hbar^2 \left(\frac{2\pi}{L} \sqrt{2} \right)^2}{2m} - \frac{\hbar^2 \left(\frac{2\pi}{L} \right)^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L} \right)^2 = 1.5 \times 10^{-14} \text{ eV} \quad (405)$$

where I have used $\hbar = 1.05 \times 10^{-34} \text{ J s}$, $m = 9.11 \times 10^{-31} \text{ kg}$, $L = 1 \times 10^{-2} \text{ m}$ and $1 \text{ J} = 6.24 \times 10^{18} \text{ eV}$.

This is a very small value. Just to appreciate it, consider that the energy difference between the $2s$ and $1s$ electronic levels in the hydrogen atom is 10.2 eV .

So: the energy levels of the Fermi gas are discrete, but the spacing is so tiny that in appropriate contexts they can be regarded as continuous.

3.11 Counting the $\vec{k}$ points inside a given region of Fourier space

217. Very often for the calculation of properties of solids and in general for the description of their electronic structure it is required to know how many allowed $\vec{k}$ points are contained within a given region of the reciprocal space. Moreover, usually, the region of interest contains a huge number of $\vec{k}$ points.

Under this condition, the sought number can be obtained practically exact as:

$$\frac{\text{volume of the region}}{\text{volume per } \vec{k} \text{ point}} \quad (406)$$

Since the allowed $\vec{k}$ points are all and only those of the reciprocal lattice, the volume per $\vec{k}$ point is just the volume of the primitive cell of $\mathcal{R}^*$. For the Fermi gas model which we are analysing here $\mathcal{R}^*$ is just a simple cubic lattice, so the volume per $\vec{k}$ point is:

$$\left(\frac{2\pi}{L} \right)^3 = \frac{8\pi^3}{V} \quad (407)$$

(the same result is obtained also using 294)

3.12 Fermi energy and Fermi surface

218. The ground state of a metal is the state of the metal at 0 K . At 0 K the electronic levels are occupied starting from the one at lowest energy (that is, in the Fermi gas model, the $\epsilon = 0$ level, corresponding to the $\vec{k}$ point at the origin) in order of increasing energy and in accordance with Pauli's principle. As we have already remarked, there are two monoelectronic states differing by the spin orientation for each allowed $\vec{k}$ point.

219. In general (that is, not only for the electron gas model) the maximum energy value of an occupied electronic state at 0 K is called the *Fermi energy*, ϵ_F .

Given any dispersion relation $\epsilon(\vec{k})$, the equation:

$$\epsilon(\vec{k}) = \epsilon(k_x, k_y, k_z) = \epsilon_F \quad (408)$$

defines an isosurface in $\vec{k}$ space (realize that the above is the implicit equation of a surface in the three scalar variables k_x, k_y, k_z).

The isosurface defined by 408 is called the *Fermi surface*.

By definition, all the states corresponding to $\vec{k}$ points laying on the Fermi surface have the Fermi energy ϵ_F .

Still by definition, the Fermi surface encloses all and only the $\vec{k}$ points corresponding to occupied states at 0 K (the ground state).

220. Note that the above implicit equation applies to the most general case of a 3D system. For 1D or 2D systems, the corresponding equations will be, of course:

$$\text{2D:} \quad \epsilon(\vec{k}) = \epsilon(k_x, k_y) = \epsilon_F \quad (409)$$

$$\text{1D:} \quad \epsilon(k) = \epsilon_F \quad (410)$$

and the corresponding Fermi “surfaces” will reduce to a trajectory on the k_x, k_y plane (2D) or to a single point on the k axis (1D).

221. The Fermi energy and the Fermi surface for the electron gas are easily found. Since the number of electrons N in a macroscopic metallic sample is huge (order of magnitude: Avogadro’s number) and since for the Fermi gas the energy of the electronic levels depends only on the length (modulus) of the wave vector, the Fermi surface (that is: the region of $\vec{k}$ space containing all the points corresponding to occupied levels in the ground state) is, for all intents and purposes, a sphereⁱⁱ(point 215) and is called the *Fermi sphere*. The radius of the Fermi sphere is called the *Fermi wave vector* k_F . Obviously, the Fermi energy and the Fermi wave vector are related by:

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m} \quad (411)$$

(see eq. 398)

The number of $\vec{k}$ points within the Fermi sphere is obtained as per point 217 above:

$$\frac{\text{volume of the Fermi sphere}}{\text{volume per } \vec{k} \text{ point}} = \frac{\frac{4}{3}\pi k_F^3}{\frac{8\pi^3}{V}} = \frac{k_F^3}{6\pi^2} V \quad (412)$$

On the other hand, the number of $\vec{k}$ points inside the Fermi sphere is equal to half the number of electrons N (recall that each state indexed by a $\vec{k}$ vector can host 2 electrons with opposite spin). Hence:

$$\frac{k_F^3}{6\pi^2} V = \frac{1}{2} N \quad (413)$$

The number of electrons N contained in a metallic sample is easily derived once we know its density ρ (in units of mass per volume), its molar mass M and the number of valence electrons Z (recall that in the Fermi gas model only the valence electrons are free to move inside the volume of the solid sample, while the remaining (core) electrons are “freezed” around the nuclei and are completely ignored):

$$N = (\text{moles of atoms}) \times N_o \times Z = \frac{\text{mass}}{M} \times N_o Z = \frac{V\rho}{M} N_o Z \quad (414)$$

ⁱⁱThe assumption of a huge number of electrons is to be taken into account for the following reason.

In principle, it might happen that *not all* the states at energy ϵ_F are occupied. In such case there would be $\vec{k}$ points corresponding to both occupied and non occupied states on the surface of the Fermi sphere, which, therefore, would not be a perfect sphere: there would be “downward steps” at the $\vec{k}$ points corresponding to empty states. However, if the number of electrons (i.e. occupied states) is huge, the sphere radius is enormous with respect to the volume per $\vec{k}$ point ($8\pi^3/V$) and this makes the steps completely negligible.

(N_o is Avogadro's number)
Substituting above:

$$\begin{aligned}
\frac{k_F^3}{6\pi^2} V &= \frac{1}{2} \frac{V\rho}{M} N_o Z \\
k_F^3 &= 3\pi^2 \frac{\rho}{M} N_o Z \\
&\text{(raise both sides to } 2/3) \\
k_F^2 &= \left(3\pi^2 \frac{\rho}{M} N_o Z \right)^{\frac{2}{3}} \\
&\text{(multiply both sides by } \frac{\hbar^2}{2m} \text{ and use 411)} \\
\frac{\hbar^2 k_F^2}{2m} = \epsilon_F &= \frac{\hbar^2}{2m} \left(3\pi^2 \frac{\rho}{M} N_o Z \right)^{\frac{2}{3}} \tag{415}
\end{aligned}$$

For instance, for a sodium sample ($Z = 1$, $M = 22.99 \text{ g/mol} = 22.99 \times 10^{-3} \text{ kg/mol}$, $\rho = 0.968 \text{ g/cm}^3 = 0.968 \times 10^3 \text{ kg/m}^3$) we have:

$$\begin{aligned}
\epsilon_F &= \underbrace{\frac{\overbrace{(1.05 \times 10^{-34} \text{ J s})^2}^{\hbar^2}}{2 \times 9.11 \times 10^{-31} \text{ kg}}}_{2m} \left(3\pi^2 \underbrace{\frac{\overbrace{0.968 \times 10^3 \text{ kg m}^{-3}}^{\rho}}{22.99 \times 10^{-3} \text{ kg mol}^{-1}}}_M \underbrace{6.02 \times 10^{23} \text{ mol}^{-1}}_{N_o} \times \underbrace{1}_Z \right)^{\frac{2}{3}} \\
&\times \underbrace{6.24 \times 10^{18} \text{ J eV}^{-1}}_{J \rightarrow eV} = 3.15 \text{ eV} \tag{416}
\end{aligned}$$

So: for a *Na* sample at 0 K and in the frame of the electron gas model, the most energetic electron has an energy of 3.15 eV and all the occupied states are those corresponding to the $\vec{k}$ vectors enclosed by a sphere in Fourier space whose radius is determined by that same energy value.

3.13 A physical meaning of the wave vector $\vec{k}$

222. The quantum operator representing the linear momentum of a particle is:

$$\frac{\hbar}{i} \nabla = \frac{\hbar}{i} \left(\hat{x} \frac{\partial}{\partial x} + \hat{y} \frac{\partial}{\partial y} + \hat{z} \frac{\partial}{\partial z} \right) \tag{417}$$

$\hat{x}$, $\hat{y}$, $\hat{z}$ are the three cartesian versors and the operator, being proportional to the gradient, is a three component vector; this is what we definitely expect, since linear momentum is a vectorial quantity.

Now: let's make the above operator act upon the state function $\Psi(\vec{r})$:

$$\frac{\hbar}{i} \nabla \Psi(\vec{r}) = \frac{\hbar}{i} \nabla \left(\frac{1}{\sqrt{V}} \exp(i\vec{k} \cdot \vec{r}) \right)$$

$$\begin{aligned}
&= \frac{\hbar}{i} \frac{1}{\sqrt{V}} \left(\hat{x} \frac{\partial}{\partial x} \exp(i(k_x x + k_y y + k_z z)) \right. \\
&\quad + \hat{y} \frac{\partial}{\partial y} \exp(i(k_x x + k_y y + k_z z)) \\
&\quad \left. + \hat{z} \frac{\partial}{\partial z} \exp(i(k_x x + k_y y + k_z z)) \right) \\
&= \frac{\hbar}{i} \frac{1}{\sqrt{V}} \left(\hat{x} (ik_x \exp(i\vec{k} \cdot \vec{r})) + \hat{y} (ik_y \exp(i\vec{k} \cdot \vec{r})) + \hat{z} (ik_z \exp(i\vec{k} \cdot \vec{r})) \right) \\
&= \frac{\hbar}{i} \frac{1}{\sqrt{V}} \exp(i\vec{k} \cdot \vec{r}) \left(\hat{x} k_x + \hat{y} k_y + \hat{z} k_z \right) \\
&= \hbar \vec{k} \Psi(\vec{r})
\end{aligned} \tag{418}$$

The result tells us that $\hbar \vec{k}$ (a vector) is the eigenvalue of $\Psi(\vec{r})$ with respect to the linear momentum operator; in other words, an electron described by $\Psi(\vec{r})$ has momentum $\vec{p} = \hbar \vec{k}$.

As already remarked, the electrons of a Fermi gas have only kinetic energy (they do not interact either with each other or with the ions); so, in the light of the above, we can recover the classical result. In fact, since $\hbar \vec{k} = \vec{p}$ is the linear momentum of the electron, eq. 398 can be rewritten as:

$$\epsilon = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} = \frac{(mv)^2}{2m} = \frac{1}{2}mv^2 \tag{419}$$

An electron having the Fermi energy ϵ_F will move at a velocity v_F , called *Fermi velocity*, given by:

$$v_F = \sqrt{\frac{2\epsilon_F}{m}} \tag{420}$$

Taking again a sodium sample as an example ($\epsilon_F = 3.15$ eV):

$$v_F = \sqrt{\frac{2\epsilon_F}{m}} = 1053 \text{ km/s} \tag{421}$$

This is a substantially high speed: it is about 0.35% of the speed of light in vacuum. In the frame of the Fermi gas model, this is the speed at which an electric signal travels in a metallic wire.

3.14 The Fermi–Dirac distribution

223. In the preceding section we have discussed the occupation of the energy levels for the electron gas in the ground state, that is at 0 K. In those conditions, N electrons will occupy the first $N/2$ $\vec{k}$ states in order of increasing energy (i.e. of increasing $\vec{k}$ modulus).

If temperature is > 0 K, then some electronic levels which were not occupied at 0 K become occupied and hence some corresponding levels which were occupied at 0 K will become empty.

A very important quantity regarding the dependence of the occupation of energy levels on the temperature is the probability that a given energy level is occupied at a given temperature > 0 K.

A function that assigns to each value of a random variable the corresponding probability is called in general *distribution function*.

What we are going to do in this section is to derive the distribution function which associates with each value of the variable representing the occupation of a given monoelectronic energy level the corresponding probability.

In the present context, by monoelectronic level I mean an energy level which can “host” a *single* electron; it will be thus uniquely defined by an allowed $\vec{k}$ point *and* by a particular spin orientation ($+\hbar/2$ or $-\hbar/2$).

As it will become clear during the derivation, the distribution function that will be obtained is completely general, that is to say: it holds for any case, not only the case of the electron gas.

224. It is easy to realize that the distribution function which we are speaking about must depend on both the energy of a monoelectronic level and temperature. For instance, at $T = 0$ K, the probability that the first N monoelectronic levels (that is, the first $N/2$ allowed $\vec{k}$ points) are occupied is exactly 1, while that of all the levels with energy greater than the Fermi energy (point 218) will be exactly 0.

For temperatures greater than 0 K, the occupation probability of the first N monoelectronic levels will decrease (with respect to the unit value) and that of the levels at higher energy will no more be exactly null.

The distribution function which we will derive is called Fermi–Dirac distribution. One fundamental aspect of this distribution is that, as we will see during the derivation, it takes into account Pauli’s principle. It is precisely this feature that has determined a drastic step forward in the description of the behavior of electrons in solids, with respect to the initial theories, in which electrons were considered as classical particles, thus unconstrained by Pauli’s principle.

225. You can appreciate the difference made by Pauli’s principle in the calculation of the occupation of the energy levels accessible by the electrons by considering the electron gas at 0 K: if the electrons were not subject to Pauli’s constraint, then all of them would occupy the same lowest possible level, that is that at $\epsilon = 0$ and the energy of the ground state would be null. Instead, each electron being constrained to be described by a sequence of quantum numbers different from that of any other (Pauli’s principle) implies that even at 0 K N electrons must occupy (also) levels at energy different from 0 (that is: the states corresponding to the first $N/2$ allowed $\vec{k}$ points, in order of increasing modulus; remember that a given $\vec{k}$ point means a triplet of quantum numbers, eq. 397). This, for example, means that, as we saw in point 218, the Fermi energy of solid sodium is 3.15 eV (and not 0 eV); or that metals can be electrical conductors even at 0 K, since even in those conditions the velocity of electrons is not null, eq. 420.

Pauli’s principle holds not only for electrons, but for all the quantum particles with *semiinteger* spin ($\pm\hbar(n + 1/2)$). Such particles are called *fermions* and are distinct from the quantum particles with *integer* spin, not constrained by Pauli’s principle and called *bosons*.

226. For the derivation of the Fermi–Dirac distribution I will follow the textbook of Ashcroft and Mermin.¹⁵

Let’s focus on a system at constant volume V and in thermal equilibrium at a given temperature T containing N electrons, each being able to occupy one of the same infinite sequence of accessible monoelectronic energy levels. Our goal is to find the function $f_N(\epsilon_i)$ giving the probability of occupation of the i –th monoelectronic state at energy ϵ_i in the system of N electrons in thermal equilibrium at temperature T .

The random variable which the Fermi–Dirac distribution refers to is the occupation of the monoelectronic level at energy ϵ_i : here Pauli’s principle enters as a crucial ingredient, since, by it, such variable can take only two possible values: 0 or 1. So, the Fermi–Dirac distribution assigns to these two possible occupation values two corresponding probabilities (of course, being only two the possible occupation values of a given monoelectronic state, we can anticipate that the two corresponding probabilities must add up to 1; in other words, only one probability is to be found, since the other is trivially obtained as the 1’s complement).

In a generic state of this system the electrons are distributed over N distinct monoelectronic states, since they have to obey Pauli's principle. We will call N -*electronic* or *multielectron* state a particular state of the system in which each electron occupies a given, monoelectronic state.

227. Let's start with the following observation.

The probability $f_N(\epsilon_i)$ that the monoelectronic state i is occupied can be written as the sum of the (independent) probabilities $P_N(E_\alpha^N)$ that the system is in the α -th N -electronic state in which the monoelectronic state i is occupied by an electron:

$$f_N(\epsilon_i) = \sum_{\alpha} P_N(E_\alpha^N) \quad (422)$$

(α runs over all the N -electronic states in which the monoelectronic state i is occupied)

228. Statistical mechanics gives us an analytic expression for the probability $P_N(E_\alpha^N)$; it is a general result that the probability of a system of N particles in thermal equilibrium at a given temperature T being in a given multielectron state at energy E_α^N is:¹⁷

$$P_N(E_\alpha^N) = \frac{\exp\left(-\frac{E_\alpha^N}{k_B T}\right)}{\sum_p \exp\left(-\frac{E_p^N}{k_B T}\right)} = \frac{\exp\left(-\frac{E_\alpha^N}{k_B T}\right)}{Q_N} \quad (423)$$

(k_B is the Boltzmann constant)

The sum in the denominator is called *partition function* and it runs over *all* the N -electronic accessible states of the system of N electrons.

The partition function is related to the Helmholtz free energy F , which, as you might recall from classical thermodynamics, is defined as:

$$F = U - TS \quad (424)$$

U and S being the internal energy and the entropy of the system, respectively.

The link between the partition function and the Helmholtz free energy of a system of N particles is:¹⁸

$$F_N = -k_B T \ln Q_N \quad (425)$$

or:

$$Q_N = \exp\left(-\frac{F_N}{k_B T}\right) \quad (426)$$

This allows to rewrite 423 in a more compact way:

$$P_N(E_\alpha^N) = \exp\left(-\frac{E_\alpha^N - F_N}{k_B T}\right) \quad (427)$$

Note: we take 423 and 425 for granted, without any derivation.

229. Let's go back to 422. As already mentioned, based on Pauli's principle, for a given monoelectronic state only two options are possible: either it is occupied by an electron or it is empty. From this it follows that the probability that state i is occupied can be equivalently written as the 1's complement of the probability $g_N(\epsilon_i)$ that state i is *not* occupied:

$$f_N(\epsilon_i) = 1 - g_N(\epsilon_i) \quad (428)$$

I want to remark here that this equality *follows directly* from the fact that the occupation of a given monoelectronic state can take only two values (0 or 1), and this, in turn, follows from Pauli's principle. Thus, you see that such principle is one of the key points underlying the Fermi–Dirac distribution.

To further clarify: in a system of N bosons (not constrained by Pauli's principle), the occupation of a given energy level can take $N + 1$ values because it can be occupied by $0, 1, 2 \dots N$ particles.

230. Similar to 422, the probability that state i is *not* occupied must be the sum of the probabilities $P_N(E_\gamma^N)$ that the system is in the γ -th N -electronic state in which the monoelectronic state i is *not* occupied by an electron:

$$g_N(\epsilon_i) = \sum_{\gamma} P_N(E_\gamma^N) \quad (429)$$

From here on I will use the indices α and γ to refer to energies of multielectronic states in which the monoelectronic state i *is* or *is not* occupied, respectively.

Substituting into 428:

$$f_N(\epsilon_i) = 1 - \sum_{\gamma} P_N(E_\gamma^N) \quad (430)$$

(γ runs over all the N -electronic states in which the monoelectronic state i *is not* occupied)

231. Now realize the following simple observation.

From every N -electronic state in which the monoelectronic state i *is not* occupied it is always possible to construct one and only one $(N + 1)$ -electronic state in which the monoelectronic state i *is* occupied, simply by leaving each of the N electrons in its level and adding a single electron to state i .

In a specular way, starting from any $(N + 1)$ -electronic state in which the monoelectronic state i *is* occupied, it is always possible to construct one and only one N -electronic state in which the monoelectronic state i *is not* occupied, simply by removing the single electron which occupies state i and leaving the remaining N electrons in the energy levels that they already occupy.

I have illustrated this idea in figure 53.

From this observation it follows that a bijective map exists between the set of N -electronic states in which the monoelectronic state i *is not* occupied and the set of $(N + 1)$ -electronic states in which the monoelectronic state i *is* occupied.

In particular, the energy of a N -electronic state in which the monoelectronic state i *is not* occupied is obtained from the energy of the corresponding $(N + 1)$ -electronic state in which the monoelectronic state i *is* occupied by simply subtracting the quantity ϵ_i :

$$E_\gamma^N = E_\alpha^{N+1} - \epsilon_i \quad (431)$$

(refer again to figure 53)

Note that using different indices in 431 would not be required because, based on what said above, to the γ -th N -electronic state in which the monoelectronic state i *is not* occupied it corresponds always and only the γ -th $(N + 1)$ -electronic state in which the monoelectronic state i *is* occupied. However, using different indices reminds us that the two energies refer to multielectronic states in which the monoelectronic state i *is not* (γ) or *is* (α) occupied (this way we are also consistent with the use of the index α in eq. 422).

232. Let's now turn our attention to the sum appearing in the RHS of eq. 430:

$$\sum_{\gamma} P_N(E_\gamma^N) \quad (432)$$

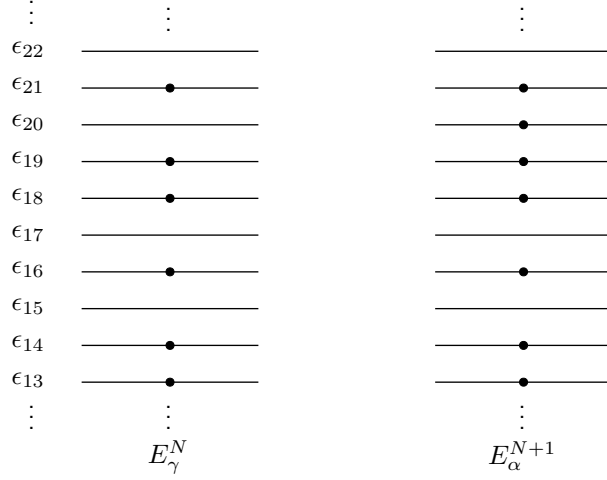


Figure 53: An N –electronic state ($N = 6$) in which the monoelectronic state at energy ϵ_{20} is not occupied is shown on the left. From this multielectronic state it is possible to construct one and only one $(N + 1)$ –electronic state in which the monoelectronic state ϵ_{20} *is* occupied: 6 electrons are left in the energy levels that they already occupied in the original N –electronic state and a seventh electron is placed into the ϵ_{20} monoelectronic state (diagram on the right).

Of course, also the viceversa holds: from the 7–electronic state on the right in which the monoelectronic state at energy ϵ_{20} *is* occupied it is possible to construct the 6–electronic state (and only it) on the left in which the monoelectronic state ϵ_{20} *is not* occupied: it is sufficient to remove the electron which occupies the monoelectronic state at energy ϵ_{20} while leaving the remaining 6 electrons in their respective levels.

The energies of the two multielectronic states are:

$$\begin{aligned} E_\gamma^6 &= \epsilon_{13} + \epsilon_{14} + \epsilon_{16} + \epsilon_{18} + \epsilon_{19} + \epsilon_{21} \\ E_\alpha^7 &= \epsilon_{13} + \epsilon_{14} + \epsilon_{16} + \epsilon_{18} + \epsilon_{19} + \epsilon_{20} + \epsilon_{21} \end{aligned}$$

And hence:

$$E_\gamma^6 = E_\alpha^7 - \epsilon_{20}$$

First of all, thanks to 431, it holds that:

$$P_N(E_\gamma^N) = P_N(E_\alpha^{N+1} - \epsilon_i) \quad (433)$$

In the second place, thanks to the bijective map which I have explained above all and only the terms of the sum, indexed by γ , can be equivalently obtained by making α run over all and only the possible $(N + 1)$ –electronic states in which the monoelectronic state i *is* occupied. In other words, also making use of 431, we have:

$$\sum_\gamma P_N(E_\gamma^N) = \sum_\alpha P_N(E_\alpha^{N+1} - \epsilon_i) \quad (434)$$

(again: I am using two different indices only for the sake of clarity; as γ and α vary, exactly the same N –electronic states and respective probabilities are identified)

233. Beware: do not be fooled by the $(N + 1)$ term on the RHS: the probabilities P_N on both sides of 434 are exactly the same and are referred to a system of N (*not* $N + 1$) electrons, that is the one we are dealing with. In other words, $P_N(E_\alpha^{N+1} - \epsilon_i)$ is the probability that N electrons occupy N monoelectronic states in which state i *is not* occupied: simply, the energy of

this N -electronic state is expressed through the energy of a (corresponding) $(N + 1)$ -electronic state.

234. In the light of 434, eq. 430 can be rewritten as:

$$f_N(\epsilon_i) = 1 - \sum_{\alpha} P_N(E_{\alpha}^{N+1} - \epsilon_i) \quad (435)$$

235. Now we make use of 427 to rewrite the terms of the sum:

$$P_N(E_{\alpha}^{N+1} - \epsilon_i) = \exp\left(-\frac{(E_{\alpha}^{N+1} - \epsilon_i) - F_N}{k_B T}\right)$$

Note that on the RHS there is F_N because the probability is that for a system of N electrons, as I said at point 233.

Add and subtract F_{N+1} :

$$\begin{aligned} &= \exp\left(-\frac{(E_{\alpha}^{N+1} - \epsilon_i) - F_{N+1} + F_{N+1} - F_N}{k_B T}\right) \\ &= \exp\left(-\frac{E_{\alpha}^{N+1} - F_{N+1} - \epsilon_i + (F_{N+1} - F_N)}{k_B T}\right) \\ &= \exp\left(-\frac{E_{\alpha}^{N+1} - F_{N+1}}{k_B T}\right) \exp\left(\frac{\epsilon_i - \overbrace{(F_{N+1} - F_N)}^{\mu}}{k_B T}\right) \\ &= \exp\left(\frac{\epsilon_i - \mu}{k_B T}\right) \exp\left(-\frac{E_{\alpha}^{N+1} - F_{N+1}}{k_B T}\right) \end{aligned} \quad (436)$$

236. $\mu = F_{N+1} - F_N$ is the change in Helmholtz free energy of the system when a single electron is added at constant T and V : classical thermodynamics tells us that μ is the chemical potential of the N electron system.

You realize this in the following way.

From the definition $F = U - TS$ we have:

$$dF = dU - TdS - SdT \quad (437)$$

The first law of thermodynamics for an open system containing only one type of particles is:

$$dU = TdS - PdV + \mu dN \quad (438)$$

Substituting above:

$$dF = TdS - PdV + \mu dN - TdS - SdT = -SdT - PdV + \mu dN \quad (439)$$

At constant T and V (our case):

$$dF = \mu dN \quad (440)$$

Now integrate both sides for a change in the number of particles from N to $N + 1$:

$$\int_{F_N}^{F_{N+1}} dF = \int_N^{N+1} \mu dN \quad (441)$$

Since the number of particles (the Fermi electrons) is enormous (order of magnitude is Avogadro's number) we can safely assume that the chemical potential will remain constant if a single electron is added to the system. So:

$$\int_{F_N}^{F_{N+1}} dF = \mu \int_N^{N+1} dN \quad (442)$$

$$F_{N+1} - F_N = \mu (N + 1 - N) = \mu \quad (443)$$

237. Looking at 427 we see that the second exponential of 436 is $P_{N+1}(E_\alpha^{N+1})$, that is the probability that a system of $N + 1$ electrons is in a state at energy E_α^{N+1} in which the monoelectronic state i is occupied. Thus, substituting 436 into 435 we arrive at:

$$f_N(\epsilon_i) = 1 - \exp\left(\frac{\epsilon_i - \mu}{k_B T}\right) \sum_{\alpha} P_{N+1}(E_\alpha^{N+1}) \quad (444)$$

(α runs over all the $(N + 1)$ -electronic states in which the monoelectronic state i is occupied; in addition, the exponential containing the chemical potential does not depend on α and can be factored out from the sum)

238. If you now take a look at 422, you should realize immediately that the sum on the RHS is nothing but the probability that in a system of $N + 1$ electrons the monoelectronic state at energy ϵ_i is occupied:

$$\sum_{\alpha} P_{N+1}(E_\alpha^{N+1}) = f_{N+1}(\epsilon_i) \quad (445)$$

We thus arrive at:

$$f_N(\epsilon_i) = 1 - \exp\left(\frac{\epsilon_i - \mu}{k_B T}\right) f_{N+1}(\epsilon_i) \quad (446)$$

If, as it is always the case for a real solid, N is of the order of magnitude of Avogadro's number, i.e. huge, it would be absurd to think that the addition of a single electron to the system might change the probability that state i is occupied by more than a totally insignificant amount. But then we can safely assume:

$$f_{N+1}(\epsilon_i) = f_N(\epsilon_i) \quad (447)$$

and thus:

$$f_N(\epsilon_i) = 1 - \exp\left(\frac{\epsilon_i - \mu}{k_B T}\right) f_N(\epsilon_i) \quad (448)$$

from which we get the final result:

$$f(\epsilon) = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) + 1} \quad (449)$$

where I have dismissed the indices N and i , being understood that ϵ is the energy (quantized according to 398) of an allowed state and the number of electrons is constant (it is fixed by the chemical potential through $\mu = F_{N+1} - F_N$).

In 449 $f(\epsilon)$ is the probability that in a system of fermions in thermal equilibrium at temperature T and confined in a volume V (like the Fermi gas which are dealing with) the single particle state at energy ϵ is occupied (i.e., in the general terms of a distribution function, $f(\epsilon)$ is the probability that the occupation of the monoelectronic state at energy ϵ takes the value 1).

Let's make some remarks about the obtained result.

3.14.1 Pauli's principle

239. If you retrace the derivation of the Fermi–Dirac distribution it should be evident that the assumption about the validity of Pauli's principle is crucial. The electrons can distribute themselves on the allowed levels in any way, but the obtained result does hold only under the assumption that each allowed monoelectronic state can describe *at most* a single electron (or no electrons at all).

This is a prerequisite drastically different from the assumptions underlying the Maxwell–Boltzmann distribution which applies to classical particles, in which the same state can be occupied by any number of particles.

3.14.2 The behavior of the Fermi–Dirac function

240. From a purely mathematical standpoint, the Fermi–Dirac distribution is a function of two variables: the energy ϵ and the temperature T (the chemical potential μ is not an independent variable because it is a function of the temperature T , besides depending also on the volume V and the number of electrons N , which, however, are constant in the Fermi gas). The main features of the function can be captured from a bidimensional graph in which the function is plotted versus the energy, for fixed values of temperature.

This is shown in figure 54, where I have plotted the function in the form:

$$f\left(\frac{\epsilon}{\mu}, \frac{k_B T}{\mu}\right) = \frac{1}{\exp\left(\frac{\epsilon/\mu - 1}{k_B T/\mu}\right) + 1} \quad (450)$$

with the quantity ϵ/μ on the abscissa for several fixed values of $k_B T/\mu$, so that the plot is independent on the particular value of μ .

- First of all, the plot is always included in the open interval $]0, 1[$:

$$0 < f < 1$$

This trivially follows from the fact that the exponential in the denominator takes values in the open interval $]0, +\infty[$:

$$0 < \exp\left(\frac{\epsilon/\mu - 1}{k_B T/\mu}\right) < +\infty$$

and thus:

- when the exponential tends to 0, the function tends to 1
- when the exponential tends to $+\infty$, the function tends to 0

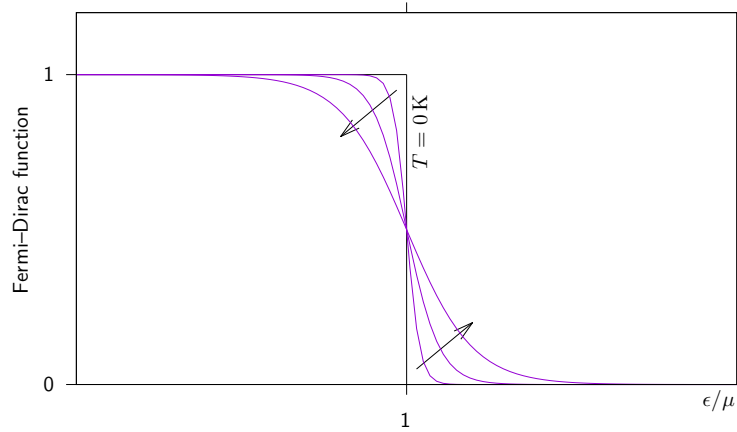


Figure 54: The behavior of the Fermi-Dirac distribution as a function of the energy and for fixed values of temperature; when $T = 0$ K the graph becomes a perfect step; the arrows show the direction of increasing temperature.

This is reassuring, since the physical meaning of the Fermi-Dirac function is that of being a probability.

- At a finite temperature, when $\epsilon/\mu \rightarrow -\infty$, the exponential in the denominator tends to 0 and thus the function tends to 1:

$$\lim_{\epsilon/\mu \rightarrow -\infty} \frac{1}{\underbrace{\exp\left(\frac{\epsilon/\mu - 1}{k_B T/\mu}\right) + 1}_{\rightarrow 0}} = 1 \quad (451)$$

- Conversely, when $\epsilon/\mu \rightarrow \infty$, the exponential tends to ∞ and the function tends to 0:

$$\lim_{\epsilon/\mu \rightarrow \infty} \frac{1}{\underbrace{\exp\left(\frac{\epsilon/\mu - 1}{k_B T/\mu}\right) + 1}_{\rightarrow \infty}} = 0 \quad (452)$$

- This is exactly what we would expect: at a given temperature the probability of states at very low energy being occupied is high, whereas the occupation of states at very high energy must be very little probable.
- Actually, as we will see in detail in section 3.14.3, for ordinary temperature values (and thus for ordinary values of chemical potential, since the latter depends on temperature), the denominator of the exponential, $k_B T/\mu$, is very small and thus as soon as ϵ/μ deviates from 1 even by a very small amount, the value taken by the function jumps to ≈ 1 , when $\epsilon/\mu < 1$, or ≈ 0 , when $\epsilon/\mu > 1$.

For example, when $T = 500$ K and $\mu = 10$ eV (order of magnitude of the chemical potential in ordinary conditions), we have:

$$\frac{k_B T}{\mu} = 0.0043$$

and hence:

$$\begin{aligned} \frac{\epsilon}{\mu} = 0.9 &\implies \exp\left(\frac{\frac{\epsilon}{\mu} - 1}{\frac{k_B T}{\mu}}\right) = 8.3 \times 10^{-11} \implies f = 0.9999999999205438 \\ \frac{\epsilon}{\mu} = 1.1 &\implies \exp\left(\frac{\frac{\epsilon}{\mu} - 1}{\frac{k_B T}{\mu}}\right) = 1.2 \times 10^{10} \implies f = 7.95 \times 10^{-11} \end{aligned}$$

- The Fermi energy ϵ_F is equal to the chemical potential of the electrons at 0 K.

This can be seen in the following way.

As already noted, the steepness of the 0/1 transition increases as the magnitude of the term $k_B T/\mu$ in the denominator of the exponential decreases; when $T \rightarrow 0$, also $k_B T/\mu \rightarrow 0$ ⁱⁱⁱ and thus the function takes the values 0 or 1 as soon as ϵ/μ is greater or less than 1, respectively, by an *infinitesimal* amount; that is: it becomes step shaped.

In mathematical symbols:

$$f_{T=0\text{ K}}(\epsilon/\mu) = \begin{cases} 1 & \epsilon/\mu < 1 \\ 0 & \epsilon/\mu > 1 \end{cases} \quad (453)$$

On the other hand, based on point 218, at 0 K the electronic states at energy less than or equal to the Fermi energy are completely filled, while those at energy greater than the Fermi energy are empty. The *physics* of a system of N fermions confined in a volume V requires that the occupation probability of the energy levels is:

$$f_{T=0\text{ K}}(\epsilon/\epsilon_F) = \begin{cases} 1 & \epsilon/\epsilon_F \leq 1 \\ 0 & \epsilon/\epsilon_F > 1 \end{cases} \quad (454)$$

Comparison of 453 and 454 gives us:

$$\mu = \epsilon_F \quad \text{at } 0\text{ K} \quad (455)$$

Note however that the chemical potential μ *depends* on temperature (while it is not so for the Fermi energy) and thus, as explicitly indicated, the just written equality holds only at

ⁱⁱⁱAs I explain in section 3.1 of the extracurricular part, the chemical potential μ cannot be null at $T = 0$ K and this ensures that:

$$\lim_{T \rightarrow 0} k_B T/\mu = 0$$

0 K. For temperatures greater than 0 K, the Fermi energy is unchanged (because the fixed temperature of 0 K is part of its *definition*), while the value of the chemical potential will be different from that at 0 K.

The dependence of the chemical potential on the temperature is evident from its definition as $\mu = F_{N+1} - F_N$ in eq. 436 and from the dependence of the Helmholtz free energy F on temperature (eqs. 424 and 425).

In general, in a quite large temperature range, the variation of the chemical potential with respect to its 0 K value (i.e. the Fermi energy) is very small: for this reason it is customary to assume validity of 455 also for temperatures > 0 , when high precision is not a constraint.

- At $T > 0$ K the Fermi–Dirac distribution progressively “smooths out”, because the $k_B T/\mu$ term in the denominator increases (see figure 54). In terms of occupation probability, this smoothing means that the occupation of some states which were occupied at 0 K becomes less probable and, correspondingly, the occupation of some states which were not occupied at 0 K becomes more probable. Equivalently, at higher temperature a fraction of the electrons is excited from the states it occupied in the ground state to higher energy states, again, under the constraint of the exclusion principle.
- In any case, as you can easily realize from eq. 449 and figure 54, the occupation probability of the states at an energy equal to the chemical potential μ is 50% at every temperature > 0 .

3.14.3 The occupation of the allowed states at $T > 0$ K

241. It is instructive to obtain a little more quantitative estimate of the broadening of the Fermi–Dirac distribution as a function of temperature.

It is possible to derive an expression for the amplitude of the energy interval centered at the chemical potential μ and containing the broadening of the distribution at a given temperature. Refer to figure 55.

The broadening of the step can be measured by the amplitude of the interval identified by the intersections of the tangent to the inflection point with the horizontal lines $y = 1$ and $y = 0$.

As already noted, the inflection point has an abscissa equal to μ at any positive temperature: you can verify this by equating to zero the second derivative with respect to the energy of the Fermi–Dirac function. Thus the slope of the tangent to the inflection point is obtained as the first derivative of the function evaluated at $\epsilon = \mu$.

We have:

$$\begin{aligned} \frac{df}{d\epsilon} &= \left(-\frac{1}{\left(\exp\left(\frac{\epsilon - \mu}{k_B T}\right) + 1 \right)^2} \right) \exp\left(\frac{\epsilon - \mu}{k_B T}\right) \left(\frac{1}{k_B T} \right) \\ \left. \frac{df}{d\epsilon} \right|_{\epsilon=\mu} &= -\frac{1}{4} \frac{1}{k_B T} \end{aligned} \quad (456)$$

The equation of the line having a slope given by 456 and passing through the point of coordinates $(\mu, 1/2)$ is:

$$y(\epsilon) = -\frac{1}{4k_B T} (\epsilon - \mu) + \frac{1}{2} \quad (457)$$

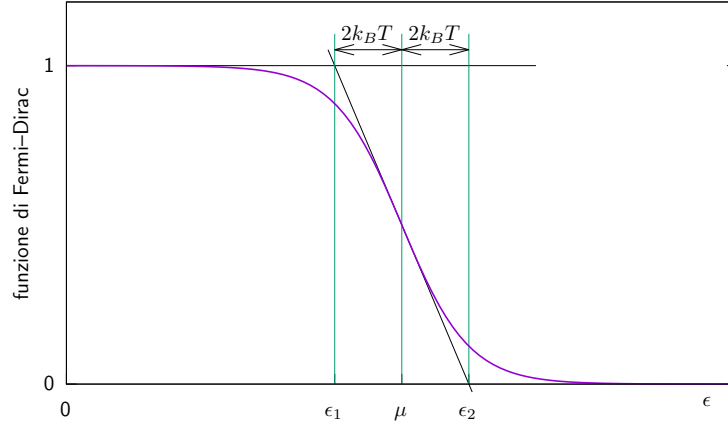


Figure 55: A possible measure of the broadening undergone by the Fermi-Dirac function at a temperature > 0 K: draw the tangent to the inflection point of the graph and locate the intersection ϵ_1 and ϵ_2 of such tangent with the horizontal lines $y = 1$ and $y = 0$, respectively. The amplitude $\epsilon_2 - \epsilon_1$ of the energy interval defined on the abscissa by the two intersections is a measure of the broadening undergone by the function.

The abscissas ϵ_1 and ϵ_2 of the intersections of this line with the horizontal line $y = 1$ and with the ϵ axis ($y = 0$) are:

$$-\frac{1}{4k_B T} (\epsilon_1 - \mu) + \frac{1}{2} = 1 \Rightarrow \epsilon_1 = \mu - 2k_B T \quad (458)$$

$$-\frac{1}{4k_B T} (\epsilon_2 - \mu) + \frac{1}{2} = 0 \Rightarrow \epsilon_2 = \mu + 2k_B T \quad (459)$$

(as you might have guessed, the Fermi-Dirac function is symmetric with respect to μ)

In conclusion:

$$\Delta\epsilon = \epsilon_2 - \epsilon_1 = 4k_B T \quad (460)$$

that is: the deformation undergone by the step (which is perfect at 0 K) at positive temperatures is contained into an energy interval centered at μ and having an amplitude of $4k_B T$.

At ambient temperature ($T = 300$ K) the value of $k_B T$ is:

$$k_B T = 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} \times 300 \text{ K} = 0.026 \text{ eV} \quad (461)$$

This is a very small value: for example it is only 0.8 % of the Fermi energy of sodium, eq. 416.

242. The just obtained result tells us that following an increase of temperature, for ordinary temperatures, only a very small fraction of the electrons in a metal is able to absorb energy and make transitions into excited levels, which, however, remain very close to the Fermi energy.

This is a direct consequence of Pauli's principle: if the excitation energies are small, only the electrons occupying levels which are "in contact" with empty levels are able to absorb energy, while the electrons in low energy states cannot be excited because they should make transitions into already occupied states, which are not available due to the exclusion principle.

243. An equivalent way to appreciate how small is the influence of the temperature on the Fermi–Dirac distribution is the following.

We have seen that, for non exaggerated temperatures, the energy due to thermal motion, $k_B T$, is very small as compared to the Fermi energy. We might ask ourselves at which temperature the energy of thermal motion would become equal to the Fermi energy. Evidently, such temperature T_F must satisfy:

$$k_B T_F = \epsilon_F \Rightarrow T_F = \frac{\epsilon_F}{k_B} \quad (462)$$

T_F is said *Fermi temperature*. As is easy to anticipate based on what we have found above, the value of the Fermi temperature is generally very high.

For example, for sodium it is:

$$T_F = \frac{\epsilon_F}{k_B} = \frac{3.15}{8.62 \times 10^{-5}} = 36543 \text{ K} \quad (463)$$

(8.62×10^{-5} is the value of the Boltzmann constant in eV/K)

3.14.4 A useful alternative interpretation of the Fermi–Dirac distribution

244. The Fermi–Dirac distribution gives us the probability that, at a given temperature, a monoelectronic state at energy ϵ is occupied.

Precisely for this reason, it can be also interpreted as *average occupation* or *average number of electrons* occupying the level at energy ϵ (at temperature T).

Beware not to make confusion: we said that due to Pauli’s principle the occupation of an energy level can be only 0 or 1, and this is definitely true. However, this refers to the *instantaneous* occupation, that is the occupation of a level at a given time.

A system of N electrons in thermal equilibrium at constant V and T (i.e. the one for which the Fermi–Dirac distribution holds) does not persist indefinitely in a single N –electronic state, but relentlessly “visits” the set of all the N –electronic states which are compatible with its equilibrium state. Due to this, a single monoelectronic state can be occupied at a given time, but it can become empty at a different time and so on. The average occupation of a monoelectronic state which I refer to in this section is thus the occupation of a given monoelectronic state *averaged over time*.

The justification of the meaning of *average occupation* of a monoelectronic level of the Fermi–Dirac distribution is very simple.

As we said, due to Pauli’s principle a monoelectronic state at energy ϵ and at a given time can contain 1 or 0 electrons.

Now: imagine that you have all the possible N –electronic states accessible by the system at a given temperature T (in a fixed volume V) in a bag, like the numbers of a bingo game (since electrons can distribute themselves over an infinite number of monoelectronic states, the number of possible N –electronic states accessible by the system is also infinite); if you perform a very big number $\mathcal{N}$ ($\rightarrow \infty$) of extractions of a N –electronic state from the bag and call $\mathcal{N}_\epsilon$ the number of extractions in which the monoelectronic state at energy ϵ was occupied, then the *average value* of the occupation of the state at energy ϵ is:

$$\left[\text{average occupation of the monoelectronic state at energy } \epsilon \right] = \lim_{\mathcal{N} \rightarrow \infty} \frac{\overbrace{1 + 1 + 1 + \dots + 1}^{\mathcal{N}_\epsilon \text{ terms}} + \overbrace{0 + 0 + 0 + \dots + 0}^{\mathcal{N} - \mathcal{N}_\epsilon \text{ terms}}}{\mathcal{N}}$$

$$\begin{aligned}
&= \lim_{\mathcal{N} \rightarrow \infty} \frac{\mathcal{N}_\epsilon \times 1 + (\mathcal{N} - \mathcal{N}_\epsilon) \times 0}{\mathcal{N}} \\
&= \lim_{\mathcal{N} \rightarrow \infty} \frac{\mathcal{N}_\epsilon}{\mathcal{N}} = f(\epsilon)
\end{aligned} \tag{464}$$

where the last equality is made possible by the interpretation of probability as the limit of the relative frequency of an event as the number of experiments in which such event can take place tends to infinite. In this case, the event is the monoelectronic level at energy ϵ being occupied by an electron (i.e. the value 1 for the occupation of such energy level); $\lim_{\mathcal{N} \rightarrow \infty} \frac{\mathcal{N}_\epsilon}{\mathcal{N}}$ is the probability of such event, or, by definition, the Fermi–Dirac distribution evaluated for energy ϵ at the fixed temperature T , that is $f(\epsilon)$.

245. From the interpretation of the Fermi–Dirac distribution as the average number of electrons occupying a given monoelectronic level it follows that it must satisfy a *normalization condition*. In fact, the total number of electrons N in a sample must be simply given by the sum of the average number of electrons in each single monoelectronic state performed over all the monoelectronic states, or:

$$N = \sum_i f(\epsilon_i) = \sum_i \frac{1}{\exp\left(\frac{\epsilon_i - \mu}{k_B T}\right) + 1} \tag{465}$$

where I have reintroduced the subscript for the energy of the states to remind us that the monoelectronic levels are discrete (even if their spacing in the Fermi gas is very small: point 216). The above written normalization condition allows (at least in principle) to express the chemical potential in terms of N , V , T , or, equivalently, in terms of the temperature T and the electron density $n = N/V$:

$$\mu = \mu(N, V, T) = \mu\left(\frac{N}{V}, T\right) \tag{466}$$

246. A second implication of the meaning of the Fermi–Dirac distribution as the average number of electrons occupying a given monoelectronic level is its use in the calculation of those properties of solids which are related to the occupied states. As we shall see in more detail at point 248, a property of this type (for example the electronic energy of a solid sample) must be calculated by adding over all the electronic levels the value of the property in each level multiplied by its occupation; this latter, as we have seen above, is precisely given by the Fermi–Dirac distribution.

3.14.5 Comparison between the Fermi–Dirac and Maxwell–Boltzmann distributions

247. In order to reiterate and better understand the importance of Pauli’s principle in the Fermi–Dirac distribution it is interesting to compare its behavior with that of the Maxwell–Boltzmann distribution; this latter applies to a system of classical particles and its essential feature, in our context, is that it does not pose any constraint on the number of particles that can occupy a given (I mean: *the same*) energy level.

The expression for the average occupation of a state at energy ϵ in a system obeying Maxwell–Boltzmann statistics is:^{iv}

^{iv}We will not derive the Maxwell–Boltzmann distribution. If you are interested in its derivation, you can find it in any standard physical chemistry or thermodynamics textbook; for example the one of Schroeder.¹⁶

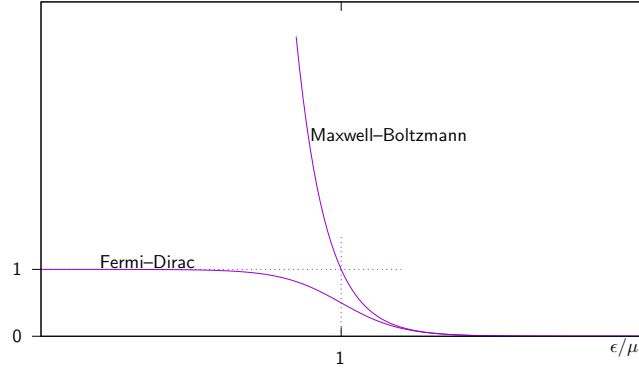


Figure 56: Comparison of the behavior of the average occupation of the single particle states according to Fermi–Dirac and Maxwell–Boltzmann distributions, for the same value of the $k_B T/\mu$ parameter.

$$b(\epsilon, T) = \exp\left(-\frac{\epsilon - \mu}{k_B T}\right) \quad (467)$$

The comparison between the two distributions is shown in figure 56.

Similar to figure 54, I have plotted also the Maxwell–Boltzmann function in the form:

$$b\left(\frac{\epsilon}{\mu}, \frac{k_B T}{\mu}\right) = \exp\left(-\frac{\epsilon/\mu - 1}{k_B T/\mu}\right) \quad (468)$$

Note how the two graphs diverge as energy decreases (at a fixed temperature): this is due to the Maxwell–Boltzmann distribution not imposing any constraint on the maximum number of particles that can occupy a single level, and thus such number can exceed 1; the exponential increase of the average occupation predicted by the Maxwell–Boltzmann statistics at decreasing energy is explained with the fact that, at any temperature, the occupation of low energy levels is always greater than that of high energy levels and this is enhanced as the energy of the levels is lower and lower.

Note also that at high energies the two distributions overlap. This is easy to justify formally if you consider the expression 449 of the Fermi–Dirac distribution; when:

$$\frac{\epsilon - \mu}{k_B T} \gg 1 \quad (469)$$

it reduces precisely to the form 467 of the Maxwell–Boltzmann distribution.

3.14.6 What is the Fermi–Dirac function useful for?

248. Many properties of solids of practical interest are related to the occupation of the mono-electronic states.

In general, letting $Q(\vec{k})$ be the value taken by a property in a single monoelectronic state identified by the wave vector $\vec{k}$, the value Q of the property for the whole solid sample is obtained by adding over all the levels the values taken on each single level, each value multiplied by the occupation of the corresponding level (because, trivially, only the occupied levels can give a contribute). Moreover, since the number of occupied levels must be equal to the number of

electrons in the sample and this latter is directly proportional to the sample volume, the value of the property is usually calculated or measured normalising it to the volume V of the sample:

$$Q = \frac{2}{V} \sum_{\vec{k}} Q(\vec{k}) \times [\text{occupation of the monoelectronic state } \vec{k}] \quad (470)$$

As already noted multiple times, the factor of 2 originates from the fact that there are two spin-degenerate monoelectronic states corresponding to each allowed $\vec{k}$ point (in the absence of any magnetic field, which would remove the degeneracy).

Based on what we have said in point 246, the expression becomes:

$$Q = \frac{2}{V} \sum_{\vec{k}} Q(\vec{k}) f(\epsilon(\vec{k})) \quad (471)$$

from which the importance and general usefulness of the Fermi–Dirac function should be apparent.

Note that the sum 471 contains an infinite number of terms (all the allowed $\vec{k}$ points).

In the next section we will introduce another very important quantity in the study of the electronic structure of solids, namely the *density of states*, which allows to turn the sum 471 into a more easily manageable object (point 280).

3.15 The density of states

249. Usually, the number of accessible states for the electrons of a solid sample is infinite (even if the states themselves are numerable). Also the accessible states for the electrons of an atom or molecule (in general I will call these “finite systems”, to emphasize that they are not periodic) are infinite, but there is a crucial difference between atomic/molecular systems and a solid sample: the number of electrons in a (real) solid sample is enormous (order of magnitude: Avogadro’s number) when compared with that of a molecule (even a macromolecule). This means that the electrons and corresponding occupied states in a solid simply cannot be treated individually (as is commonly done, conversely, in the study of atoms or molecules).

250. For this reason, a very important quantity in the analysis of the electronic structure of solids is the so called *Density of states* (DOS). Its physical meaning is very simple:

The density of states is the number of allowed electronic states per energy unit

In very crude terms (to be refined below): the allowed electronic states can be represented as points on an energy axis; take a unit interval on such axis and count how many allowed electronic states are within the interval: that number is the density of states.

To start refining the concept we make a first remark.

The number of allowed electronic states within a given energy interval depends linearly on the volume of the sample. In fact, in general, we already saw that the volumes of the direct and reciprocal cells are inversely proportional (eq. 294). So, referring for simplicity to the Fermi gas model (but this has actually a very general scope, as you will realize), if the volume of the solid sample doubles, the volume of the primitive cell of the reciprocal lattice introduced by the periodic boundary conditions is halved and hence the density of $\vec{k}$ points doubles (remember that each $\vec{k}$ identifies an allowed electronic state).

For this reason the density of states is referred to a unit volume of the solid sample, so that we update it’s definition as:

The density of states is the number of allowed electronic states per energy unit and volume unit of a solid sample

251. Another conceptual refinement is necessary.

In general, the number of allowed electronic states is not a linear function of the energy and thus the density of states *depends* upon the energy; that is: letting g be the density of states and ϵ be the energy, it will be:

$$g = g(\epsilon) \quad (472)$$

Coming back to the crude description given above, what I have just said means that if you “slide” your unit interval along the energy axis, the number of allowed electronic states within the interval varies with the position of the interval along the axis.

This means that the density of states has to be defined *punctually*, that is point by point on the energy axis (note that this is exactly the same as defining the mass per unit length of a rope of non constant density).

3.15.1 Density of states from the cumulative number of allowed states

252. Let $N(\epsilon)$ be the *cumulative* number of allowed states, that is the number of states whose energy is $\leq \epsilon$. N is trivially a function of ϵ , in particular it is a strictly increasing function of ϵ . If we know an explicit form of the function $N(\epsilon)$, then it is easily realized that the density of states can be obtained as:

$$g(\epsilon) = \frac{1}{V} \lim_{\Delta\epsilon \rightarrow 0} \frac{\overbrace{N(\epsilon + \Delta\epsilon) - N(\epsilon)}^{\text{n. of states in } [\epsilon, \epsilon + \Delta\epsilon]}}{\Delta\epsilon} = \frac{1}{V} \frac{dN(\epsilon)}{d\epsilon} \quad (473)$$

that is: the first derivative of $N(\epsilon)$ (normalized with respect to the volume of the solid sample, as said above).

Note that the limit in 473 is mandatory due to what I explained in point 251.

253. Before continuing it must be said that this method for obtaining the density of states is conceptually incorrect, for the reason I will explain further on. The formally correct approach to the evaluation of the density of states is based on the so called *Dirac delta function*, which we will introduce in section 3.15.2. On the other hand, the derivation based on the cumulative number of allowed states is more intuitive and therefore didactically useful.

254. From 473 another useful interpretation of the density of states can be derived:

$g(\epsilon) d\epsilon$ is the number of allowed states (dN) within the energy interval $[\epsilon, \epsilon + d\epsilon]$ (per unit volume of the solid sample):

$$g(\epsilon) d\epsilon = \frac{1}{V} dN(\epsilon) = \frac{1}{V} (N(\epsilon + d\epsilon) - N(\epsilon)) \quad (474)$$

From 473 it also follows that the number of allowed states within the *finite* interval $[\epsilon, \epsilon + \Delta\epsilon]$ is given by:

$$\begin{aligned} dN(\epsilon) &= V g(\epsilon) d\epsilon \\ \int_{\epsilon}^{\epsilon + \Delta\epsilon} dN(\epsilon) &= V \int_{\epsilon}^{\epsilon + \Delta\epsilon} g(\epsilon) d\epsilon \end{aligned}$$

$$N(\epsilon + \Delta\epsilon) - N(\epsilon) = V \int_{\epsilon}^{\epsilon + \Delta\epsilon} g(\epsilon) d\epsilon \quad (475)$$

255. Note how the concept of density of states is identical to that of, for example, spatial velocity: letting $s(t)$ be the function which relates the travelled *cumulative* space to time (i.e. the total space travelled starting from the initial time), the spatial velocity $v(t)$ (for the simplest monodimensional case) is defined as:

$$v(t) = \frac{ds(t)}{dt} \quad (476)$$

The spatial velocity can be thought of as a “density of space” with respect to time: great velocity means “big space in a small time”, i.e. a great “space density”; small velocity means “small space in a big time”, i.e. a small “space density”.

Identically to the density of states, $v(t) dt$ is the space travelled (ds) in the time interval $[t, t + dt]$ and the space travelled in the finite time interval $[t, t + \Delta t]$ is obtained with the integral:

$$s(t + \Delta t) - s(t) = \int_t^{t + \Delta t} v(t) dt \quad (477)$$

256. As mentioned above, being $N(\epsilon)$ the cumulative number of allowed states, it’s behavior is strictly increasing: as the energy increases, $N(\epsilon)$ can only increase or stay constant. This is reasonable, since $g(\epsilon)$, as a density, has to be always ≥ 0 . This is an obvious difference with regard to the analogy with the spatial velocity: in the case of the latter, the moving object can “move backward”, thus causing a negative “space density” (i.e. velocity).

3.15.1.1 The allowed energies are discrete (quantized)

257. I have already said above that evaluating the density of states as the derivative of the cumulative number of allowed states is not conceptually correct. Here I will explain this aspect in more detail.

An important difference between the density of states and the spatial velocity (thought of as density of space in time) is that while time is a *continuous* variable, the allowed energies in a quantum system are, in general, *discrete*. One or more distinct states correspond to each allowed energy (the number of states corresponding to a given energy level is > 1 when that energy level is degenerate). From this it follows that the graph of $N(\epsilon)$ is actually done by steps. To see this, let ϵ_i and ϵ_{i+1} be two consecutive allowed energy values (refer to figure 57). All the energies between ϵ_i and ϵ_{i+1} are forbidden and thus no allowed states correspond to them. $N(\epsilon_i)$ is the total number of allowed states with energy $\leq \epsilon_i$. Suppose that for $\epsilon = \epsilon_{i+1}$ the system has Δ allowed states more than at $\epsilon = \epsilon_i$: how will the graph of $N(\epsilon)$ be in the interval $[\epsilon_i, \epsilon_{i+1}]$? $N(\epsilon)$ takes the value $N(\epsilon_i)$ at $\epsilon = \epsilon_i$, then it *stays constant* for $\epsilon_i < \epsilon < \epsilon_{i+1}$ and eventually it *jumps vertically* by Δ for $\epsilon = \epsilon_{i+1}$ (figure 57).

That is: the graph shows a step for $\epsilon = \epsilon_{i+1}$. Of course, exactly the same argument applies for any pair of consecutive allowed energies and thus we conclude that the graph of $N(\epsilon)$ is stepwise, with discontinuous jumps at each allowed energy value.

This is the reason why evaluating the density of states as a derivative is (conceptually) problematic because the derivative 473 would become infinite at each step.

However, for all cases of practical interest, the spacing of the allowed energy values is very small (review point 216) and thus one can assume that the allowed energies are effectively continuous; moreover, again for all cases of interest, $N(\epsilon)$ quickly takes very large values, so that the vertical

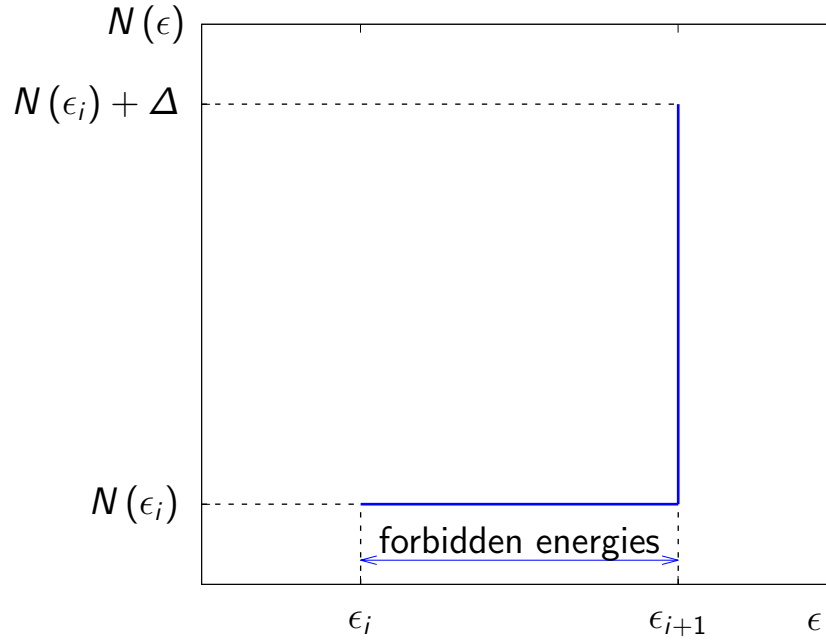


Figure 57: The cumulative number of allowed states varies *discontinuously* as a function of the energy. It stays constant for all the (forbidden) energies within to consecutive allowed values, ϵ_i and ϵ_{i+1} , and then jumps vertically by $\Delta \in \mathbb{N}$ when $\epsilon = \epsilon_{i+1}$

jumps at each step become for all intents and purposes infinitesimal with respect to the value of $N(\epsilon)$.

For these reasons, the expression 473, although conceptually flawed, can be used in practice if, as we will see in a while, one takes a continuous approximation to the actual (discontinuous) $N(\epsilon)$ function.

258. Figure 58 shows the behavior of $N(\epsilon)$ and of a continuous approximation to it (we will derive the latter in a moment) for the first 15 allowed energy levels of a Fermi gas confined in a solid sample of cubic shape.

The projection of the vertical lines of the stepped graph on the ϵ axis marks the allowed energy values; the height of a step is equal to the number of states corresponding to that particular allowed energy value (that is: its degeneracy): higher step means higher degeneracy, i.e. higher number of distinct states at the same energy.

3.15.1.2 The cumulative number of states for the Fermi gas

259. What we have said above is completely general. Let's now apply 473 to a system consisting of a Fermi gas confined in a cubic sample of volume V .

We must derive an expression for $N(\epsilon)$, that is the cumulative number of allowed states with energy $\leq \epsilon$, and then take its first derivative.

As we already know, for this system the allowed states are identified by the $\vec{k}$ points of the reciprocal lattice and the region of Fourier space containing all the states with energies $\leq \epsilon$ is a *sphere* (point 215).

Therefore, we can derive an expression for $N(\epsilon)$ in the way we described in general at point 217:

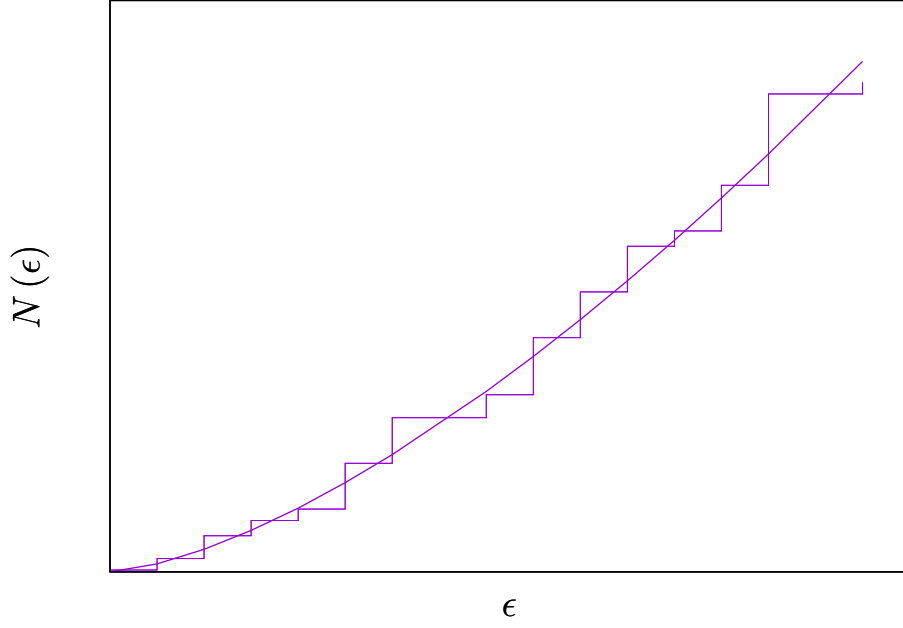


Figure 58: The stepped graph is that of the cumulative number of allowed states for the first 15 energy levels of a Fermi gas; the continuous graph is its analytical approximation (eq. 480).

$$N(\epsilon) = \frac{[\text{volume of the sphere corresponding to energy } \epsilon]}{[\text{volume corresponding to a single } \vec{k} \text{ point}]} = \frac{\frac{4}{3}\pi k_\epsilon^3}{\frac{8\pi^3}{V}} \quad (478)$$

where k_ϵ stands for the modulus (length) of the vector $\vec{k}$ such that the energy corresponding to it is ϵ and the denominator is the volume of the primitive cell of the reciprocal lattice (eq. 294). From the dispersion relation for the Fermi gas (eq. 398):

$$\epsilon = \frac{\hbar^2 k_\epsilon^2}{2m}$$

we can obtain k_ϵ^3 :

$$k_\epsilon^3 = (k_\epsilon^2)^{\frac{3}{2}} = \left(\frac{2m}{\hbar^2} \epsilon\right)^{\frac{3}{2}} = \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{3}{2}} \quad (479)$$

Substituting above we get:

$$N(\epsilon) = \frac{\frac{4}{3}\pi \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{3}{2}}}{\left(\frac{2\pi}{L}\right)^3} = \frac{V}{6\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{3}{2}} \quad (480)$$

Note how $N(\epsilon)$ is directly proportional to the volume of the sample and thus, as I anticipated on p. 158, it is convenient to normalize the density of states with respect to the latter.

260. As mentioned on p. 160, the obtained expression is a *continuous* approximation to a quantity, $N(\epsilon)$, which is intrinsically *discontinuous*. The approximation arises from the way in

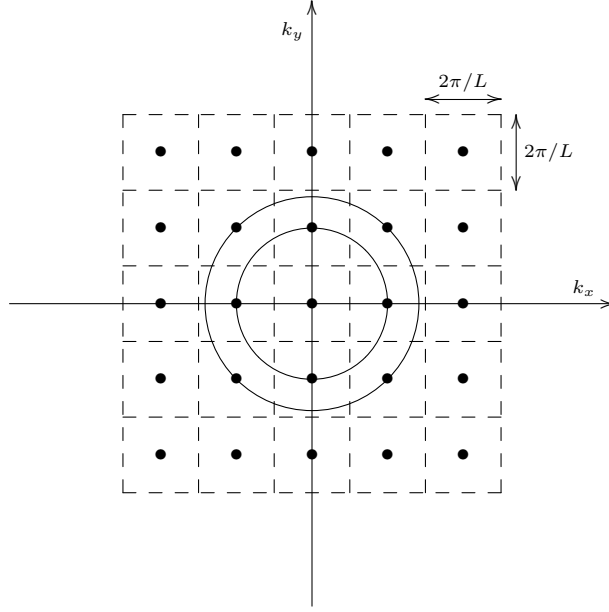


Figure 59: The first two isocircles for a bidimensional electron gas confined in a square sample of side L .

which we have derived $N(\epsilon)$, namely by dividing the volume of the isoenergetic sphere at energy ϵ by the *cubic* volume of the (primitive) cell corresponding to an allowed $\vec{k}$ point: it is trivial to realize that the result of this division will not be, in general, an integer number (as it should be for any allowed energy value) and the ultimate reason for this is that the volume of a sphere can be obtained *exactly* by adding the volume of n cubes only for few combinations of the sphere radius r , the cube edge a and the integer n :

$$\frac{4}{3}\pi r^3 = na^3 \iff r = \left(n \frac{3}{4\pi}\right)^{1/3} a \quad (481)$$

261. You can appreciate this in a more concrete way looking at figure 59, which refers to a bidimensional electron gas contained in a sample of square shape, with side L . If you retrace the steps taken to obtain the dispersion relation in the 3D case (eq. 398), you should easily find that for the 2D case the result is the same:

$$\epsilon = \frac{\hbar^2 k^2}{2m} \quad (482)$$

with, obviously:

$$\vec{k} = (k_x, k_y) = n_x \vec{b}_1 + n_y \vec{b}_2 = n_x \frac{2\pi}{L} \hat{x} + n_y \frac{2\pi}{L} \hat{y} \quad (483)$$

($\vec{b}_1, \vec{b}_2$ reciprocal primitive vectors, $\hat{x}, \hat{y}$ cartesian versors in reciprocal space)

Of course, in this case the isoenergetic surfaces reduce to circles centered at the origin and the bidimensional version of the (approximate) expression for $N(\epsilon)$ becomes:

$$\begin{aligned}
N(\epsilon) &= \frac{[\text{area of the isocircle at energy } \epsilon]}{[\text{area corr. to a single allowed } \vec{k} \text{ point}]} \\
&= \frac{\pi k_\epsilon^2}{\left(\frac{2\pi}{L}\right)^2}
\end{aligned} \tag{484}$$

First, for $\epsilon = 0$ (i.e. $k_\epsilon = 0$), the number of allowed states is 1, namely the state $(k_x, k_y) = (0, 0)$, while the result given by the continuous approximation is 0.

For the energy corresponding to the most inner isocircle the cumulative number of allowed $\vec{k}$ points is 5 (just count them in the figure), but the ratio between the area of the isocircle and that of the reciprocal primitive cell (which is the area corresponding to a single $\vec{k}$ point in 484) is less than 5. In particular, the radius of the first isocircle is equal to the side of the reciprocal primitive cell, $2\pi/L$, and thus:

$$N(\epsilon) = \frac{\pi k(\epsilon)^2}{\left(\frac{2\pi}{L}\right)^2} = \frac{\pi \left(\frac{2\pi}{L}\right)^2}{\left(\frac{2\pi}{L}\right)^2} = \pi < 5 \tag{485}$$

The same also holds for the energy corresponding to the second isocircle, which contains 9 allowed $\vec{k}$ points. Also in this case the result obtained with 484 is less than 9: the radius of the second isocircle is equal to the diagonal of the reciprocal primitive cell and thus:

$$N(\epsilon) = \frac{\pi k_\epsilon^2}{\left(\frac{2\pi}{L}\right)^2} = \frac{\pi \left(\sqrt{2} \left(\frac{2\pi}{L}\right)\right)^2}{\left(\frac{2\pi}{L}\right)^2} = 2\pi < 9 \tag{486}$$

262. Despite being approximate, eq. 480 works very nicely almost always. Moreover, it becomes more and more accurate as the energy increases, because the cubes become smaller and smaller with respect to the corresponding isosphere and thus the error decreases correspondingly).

263. Having obtained the cumulative number of allowed states as a continuous function, the density of states $g(\epsilon)$ is given by taking the first derivative and normalizing for the volume of the solid V (eq. 473):

$$g(\epsilon) = \frac{1}{V} \frac{d}{d\epsilon} N(\epsilon) = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} \tag{487}$$

The behavior of the functions $N(\epsilon)/V$ and $g(\epsilon)$ is shown in figure 60.

264. A first remark on the obtained result is that the density of states for a cubic sample containing a Fermi gas is an increasing function of the energy; this means that, given an infinitesimal energy interval $d\epsilon$, the number of allowed states $g(\epsilon)d\epsilon$ with energy between ϵ and $\epsilon + d\epsilon$ is greater at greater energy.

265. A second remark is that the obtained density of states is actually a density of allowed $\vec{k}$ points. Each $\vec{k}$ point identifies a corresponding state which *does not depend on the electronic spin*. Thus, according to Pauli's principle, two mono-electronic states differing by the spin value ($+\hbar/2$

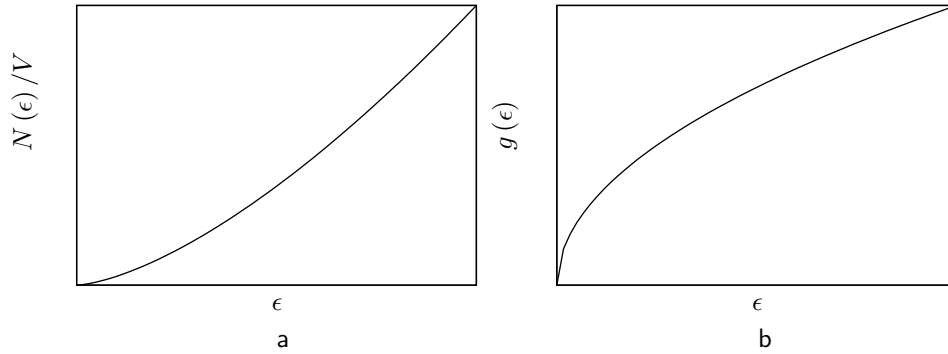


Figure 60: Graph of the cumulative number of allowed states (normalized by the volume of the sample) (a) and of the density of states (b) for a system consisting of a Fermi gas confined in a cubic volume. The graph in (b) is the derivative of that in (a).

or $-\hbar/2$) correspond to each allowed $\vec{k}$ point. In other words, the density of “true” monoelectronic states (per unit volume of the sample) is twice the density of allowed $\vec{k}$ points:

$$\frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} \quad (488)$$

266. A third remark is that you do not have to confuse the density of accessible states (expressed either in terms of $\vec{k}$ points or true monoelectronic states) with the density of *occupied* states. That is: one thing is the accessible (allowed) states and another thing is the states actually occupied by the electrons. These latter, and the corresponding density, depend first of all on the temperature of the sample. At 0 K only the lowest energy states are occupied and the number of electrons in the sample fixes the highest occupied level (namely the Fermi energy). At temperatures > 0 K a fraction of the electrons is excited to higher energy states, so leaving the states which were occupied at 0 K “empty”, according to the Fermi–Dirac distribution (eq. 449).

In other words: keep in mind that the density of accessible states is independent of the temperature, while the density of the occupied states is temperature dependent.

The density of the occupied states is obtained by multiplying the density of accessible states by the Fermi–Dirac function. For each energy, the Fermi–Dirac function gives the average occupation of the monoelectronic state having that energy and thus, when the density of accessible states (i.e. occupied or not) is multiplied by the Fermi–Dirac function, each state is counted (weighted) on the basis of its occupation: a completely occupied state will count 1, a partially occupied state will count a fraction < 1 and a non occupied state will not be counted at all.

At $T = 0$ K, the density of occupied states follows 487 up to the Fermi energy and then it falls vertically to 0; at $T > 0$ K the behavior will be smoothed, reflecting the corresponding smoothing in the Fermi–Dirac function. The density of occupied states is compared with the density of accessible states, for $T = 0$ K and $T > 0$ K, in figure 61.

267. Beware: expression 487 is valid for a 3D Fermi gas; you can verify (as an exercise) that the corresponding expressions for the 2D and 1D cases are different: in particular, for a monodimensional Fermi gas $g(\epsilon)$ depends on $\epsilon^{-1/2}$ while in the 2D case the density of accessible states is independent on ϵ (for this latter case refer to eq. 484).

268. An analytic expression for the cumulative number of allowed states is not always available (actually, it is almost never available). On the other hand, the dispersion relation for a real

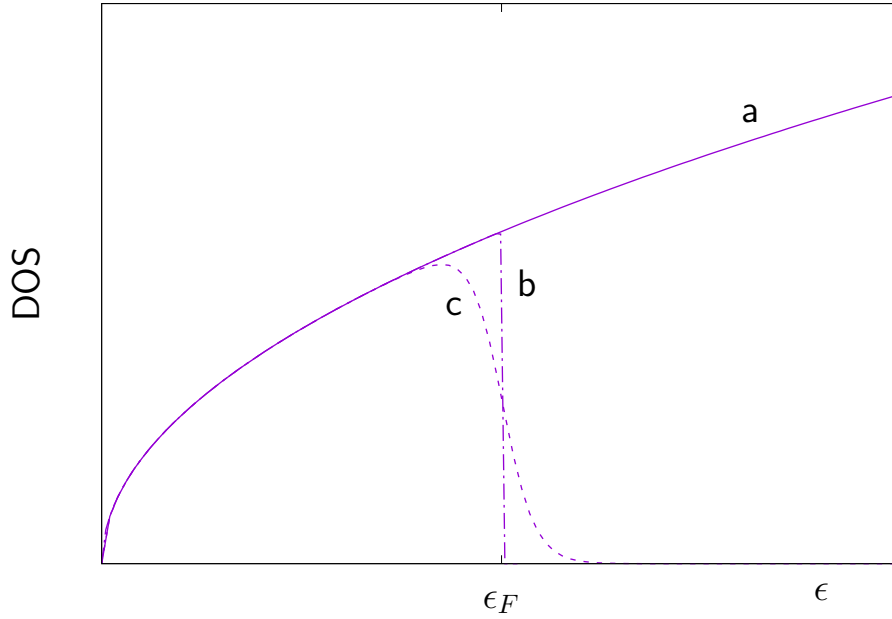


Figure 61: a: density of accessible states; b: density of occupied states at $T = 0$ K; c: density of occupied states at $T > 0$ K.

system can be determined either experimentally or computationally. Given the dispersion relation (obtained in *some* way) it is possible to derive the density of states from it, or, to be more precise, from its gradient. I used to present the procedure in these notes, but, due to lack of time, I had to move it to the extracurricular part (section 3.2).

3.15.2 The definition of the density of states with the Dirac delta function

269. As I already mentioned, the mathematically correct definition of the density of states is based on the so called Dirac delta function (δ). So we now open a parenthesis to introduce it together with some of its properties.

3.15.2.1 The Dirac delta function

270. Despite being usually called “function” (and we will also use that name), δ is not actually an “ordinary” function in a mathematical sense (in math language δ is a *distribution* or *generalized function*). This is apparent also by its definition, which is:

$$\left\{ \begin{array}{l} \int_{-\infty}^{\infty} \delta(x) dx = 1 \\ \delta(x) = 0 \quad \text{for } x \neq 0 \end{array} \right. \quad (489)$$

As you can see, δ is a strange object. It is null everywhere, but for $x = 0$, where, however, its value is undefined! Moreover, its integral evaluated over all the real axis is 1, despite it being non null on a single point (0). Note that for any “normal” function being null everywhere, but for a finite number of points, the same integral is null.

Despite these “anomalies”, the δ function is extremely useful from a theoretical standpoint. As you will see, in our context, its main usefulness is that it allows to treat discrete variables with mathematical tools which are normally used with continuous variables.

271. The best way to visualize the δ function is by realizing that it is the limit of some ordinary functions or of their derivatives.

Consider, for example, the following simple function:

$$f(x) = \begin{cases} 0 & x < -a \\ 1/(2a) & -a < x < a \\ 0 & x > a \end{cases} \quad (490)$$

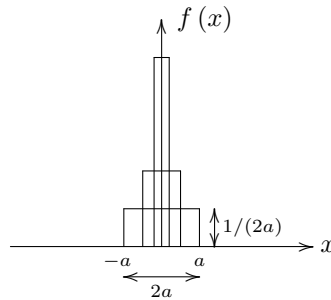
with $a > 0$.

This is a function whose graph is a rectangular pulse of height $1/(2a)$ and width $2a$. Its integral over all the x axis is trivially 1 $\forall a > 0$. Then: δ is the limit of this function when $a \rightarrow 0$:

$$\lim_{a \rightarrow 0} f(x) = \delta(x) \quad (491)$$

As a approaches 0, the pulse becomes narrower, but the value of its integral stays equal to 1: in the limit the function is null everywhere, but for $x = 0$, where it tends to plus infinite, and its integral evaluates to 1: this is precisely the definition of δ .

You can better appreciate this by looking at the following figure, where I show three rectangular pulses corresponding to three decreasing values of the parameter a .



Exactly the same argument applies to any function peaked at $x = 0$ and whose integral over all $\mathcal{R}$ is unit. For instance, the normalized Gauss function:

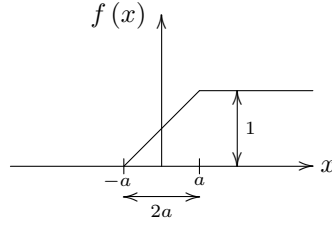
$$\lim_{\sigma \rightarrow 0} \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{x}{\sigma}\right)^2\right) = \delta(x) \quad (492)$$

272. The δ function can be equivalently obtained as the limit of the derivative of a step function. Consider the following function:

$$f(x) = \begin{cases} 0 & x < -a \\ \frac{1}{2a}(x+a) & -a < x < a \\ 1 & x > a \end{cases} \quad (493)$$

with $a > 0$.

Its graph is:



For its derivative we have:

$$f'(x) = \begin{cases} 0 & x < -a \\ 1/(2a) & -a < x < a \\ 0 & x > a \end{cases} \quad (494)$$

Note: the derivative of this function is just the rectangular pulse function we considered before. But then, it must be:

$$\lim_{a \rightarrow 0} f'(x) = \delta(x) \quad (495)$$

When $a \rightarrow 0$, the function $f(x)$ tends to become the so called Heaviside function, $H(x)$, in which the step centered at $x = 0$ is perfectly vertical. In these conditions, its derivative is null everywhere, but for $x = 0$, where it tends to infinite, ($\lim_{a \rightarrow 0} 1/(2a)$), since the graph in that point is vertical.

This allows an equivalent definition of the δ function, as the derivative of the Heaviside function:

$$\delta(x) = \frac{dH(x)}{dx} \quad (496)$$

In fact, even if with little mathematical rigour:

$$\delta(x) = \lim_{a \rightarrow 0} f'(x) = \lim_{a \rightarrow 0} \frac{df}{dx} = \frac{d}{dx} \overbrace{\lim_{a \rightarrow 0} f(x)}^{H(x)} = \frac{d}{dx} H(x)$$

More intuitively, if you think about the graph of the Heaviside function (unit step at $x = 0$):

$$\frac{dH(x)}{dx} = \begin{cases} 0 & x < 0 \text{ (} H(x) = 0, \text{ constant)} \\ \text{undefined} & (H(x) \text{ discontinuous, not differentiable)} \\ 0 & x > 0 \text{ (} H(x) = 1, \text{ constant)} \end{cases}$$

which is precisely the second part of the definition of δ (eq.489) (the integral of $dH(x)/dx$ is always 1, as already noted above).

Symmetrically, from 496 a definition of the Heaviside function in terms of the δ function follows^v:

$$\delta(x) = \frac{dH(x)}{dx} \implies dH(x) = \delta(x) dx \implies \int_{-\infty}^x dH(x) = \int_{-\infty}^x \delta(x) dx \implies H(x) = \int_{-\infty}^x \delta(x) dx$$

(in the last step one takes advantage of $\lim_{x \rightarrow -\infty} H(x) = 0$)

273. Leaving aside any formal definition, the “intuitive” description that you should keep about the δ function is that of a function which is null everywhere, but for $x = 0$, where it

^vThis definition of the Heaviside function is only heuristic: in fact it loses its meaning when $x = 0$, where the δ function is not defined.

“shoots a shot” or “makes a jump” or “takes a leap” (i.e. it generates a spike of null width). For this reason, one of its main uses is for “counting” objects, making it “shoot a shot” every time it encounters one; this is actually the use that we will make of the δ function, as will be clear in a moment.

274. Before closing this parenthesis about the Dirac δ function, we list some of its properties, which we will use in the following. For the sake of simplicity, we discuss these properties in 1D only, but they hold unaltered also in 2D or 3D.

1. The point where the δ “shoots its shot” can be moved anywhere along the x axis by applying a proper translation (point 111). So:

$$\delta(x - a) \quad (497)$$

is null everywhere, but for $x = a$.

Clearly, also for the translated function it must hold:

$$\int_{-\infty}^{\infty} \delta(x - a) dx = \int_{-\infty}^{\infty} \delta(x - a) d(x - a) = \int_{-\infty}^{\infty} \delta(y) d(y) = 1 \quad (498)$$

2. It is trivial to realize that, by definition, the following results hold:

$$a \notin [x_1, x_2] \implies \int_{x_1}^{x_2} \delta(x - a) dx = 0 \quad (499)$$

and

$$a \in [x_1, x_2] \implies \int_{x_1}^{x_2} \delta(x - a) dx = \int_{-\infty}^{\infty} \delta(x - a) dx = 1 \quad (500)$$

3. One of the most important and useful properties of the δ is the so called *sifting property*; given any function $f(x)$, it holds that:

$$\int_{-\infty}^{\infty} f(x) \delta(x - a) dx = f(a) \quad (501)$$

that is: if we multiply the argument of an integral by the δ function, the integral is equal to its argument, evaluated in the special point of the δ function.

This is called “sifting” property because all works as if the δ function sifts the values of $f(x)$, and only $f(a)$ is allowed to pass through.

In general, as we will see, the δ function is useful when it is under the integral operator; this is rather intuitive: while the only non null value of the function is undefined, the value of its integral over the whole real axis is defined ($= 1$).

The sifting property is easily proved.

Let’s start from the integral:

$$\int_{-\infty}^{\infty} f(x) \delta(x - a) dx \quad (502)$$

Since $\delta(x - a)$ is null everywhere, but for $x = a$, the value of the integral will not change if we replace $f(x)$ with $f(a)$:

$$= \int_{-\infty}^{\infty} f(a) \delta(x - a) dx$$

but now $f(a)$ does not depend on x and thus we can factor it out of the integral; the latter evaluates to 1 by definition and thus the property is proved:

$$= f(a) \int_{-\infty}^{\infty} \delta(x - a) dx = f(a) \times 1 = f(a) \quad (503)$$

4. Scaling property:

$$\delta(ax) = \frac{1}{a} \delta(x) \quad (504)$$

The proof goes like this:

$$\int_{-\infty}^{\infty} \delta(ax) dx = \int_{-\infty}^{\infty} \delta(ax) \frac{1}{a} d(ax) = \int_{-\infty}^{\infty} \frac{1}{a} \delta(y) dy \quad (505)$$

The proof follows from comparison of the first and third integral (obviously, the y symbol is completely arbitrary and it might have been x : I have used y only to avoid confusion with the x variable used in the preceeding steps).

Closed parenthesis about the Dirac δ function.

3.15.2.2 The (formally correct) definition of the density of states

275. The density of $\vec{k}$ states (remember that in our conditions, i.e. spin degeneracy, there are two “true” monoelctronic states corresponding to each $\vec{k}$ state) can be defined in a formally correct way with the δ function:

$$g(\epsilon(\vec{k}')) = \frac{1}{V} \sum_{\vec{k}} \delta(\epsilon(\vec{k}') - \epsilon(\vec{k})) \quad (506)$$

V is the volume of the sample, the sum runs over all allowed $\vec{k}$ states, $\vec{k}'$ is a generic point in $\vec{k}$ space (i.e. a generic point of $\mathbb{R}^3$, not necessarily belonging to the reciprocal lattice) and ϵ is the energy (which is a function of the position $\vec{k}'$ in Fourier space).

The meaning of the sum is the following. Each term is a δ function which shoots its shot when the energy $\epsilon(\vec{k}')$ becomes equal to that of an allowed level. It is important to note that in 506 $\epsilon(\vec{k}')$ is a continuous variable which is a function of $\vec{k}'$, namely a generic point in Fourier space. The graph of a single term in the sum 506 will be (I represent the spike of the δ with an arrow):



Since each term is null everywhere, but for a single energy value ($\epsilon(\vec{k})$), the whole sum will be null everywhere, but for the allowed energy levels (which correspond to the allowed $\vec{k}$ points of the reciprocal lattice).

$$\sum_{\vec{k}} \delta \left(\epsilon(\vec{k}') - \epsilon(\vec{k}) \right) : \quad \dots \quad \begin{array}{c} \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\ \epsilon(\vec{k}_i) \quad \epsilon(\vec{k}_{i+1}) \quad \epsilon(\vec{k}_{i+2}) \quad \epsilon(\vec{k}_{i+3}) \quad \epsilon(\vec{k}_{i+4}) \end{array} \quad \epsilon(\vec{k}') \quad \dots \quad (507)$$

So now you can see (as I anticipated on p. 168) how the sum effectively *counts* the allowed states: its graph as a function of energy produces a spike (a shot) each time that an allowed energy value is encountered.

3.15.2.3 Definition 506 is precisely the density of states

276. Now that we have understood what is the meaning of the sum in 506, we want to make sure that it actually is the density of states, as we know it (p. 158) (at a first sight, it seems difficult to be able to interpret eq. 506 as the number of allowed states per unit energy). For this purpose, let's go back to 475:

$$N(\epsilon + \Delta\epsilon) - N(\epsilon) = V \int_{\epsilon}^{\epsilon + \Delta\epsilon} g(\epsilon) d\epsilon$$

If definition 506 is correct, then by replacing $g(\epsilon)$ with it in 475 we must obtain the number of allowed states within the energy interval $[\epsilon, \epsilon + \Delta\epsilon]$.

But this is precisely what happens and we can verify it very easily.

Let's replace $g(\epsilon)$ with $\frac{1}{V} \sum_{\vec{k}} \delta \left(\epsilon(\vec{k}') - \epsilon(\vec{k}) \right)$ (the volume V of the solid cancels out; moreover, since we now think of the energy as a function of the position $\vec{k}'$, we explicitly rewrite $d\epsilon$ as $d\epsilon(\vec{k}')$; for the sake of a lighter notation, I do not write explicitly the $\vec{k}'$ dependence in the integration limits):

$$= \int_{\epsilon}^{\epsilon + \Delta\epsilon} \sum_{\vec{k}} \delta \left(\epsilon(\vec{k}') - \epsilon(\vec{k}) \right) d\epsilon(\vec{k}') \quad (508)$$

Thanks to the linearity of the integral operator, we can swap the integral and the sum ("the integral of a sum is equal to the sum of the integrals"):

$$= \sum_{\vec{k}} \int_{\epsilon}^{\epsilon + \Delta\epsilon} \delta \left(\epsilon(\vec{k}') - \epsilon(\vec{k}) \right) d\epsilon(\vec{k}')$$

Now: since the integrals are evaluated between ϵ and $\epsilon + \Delta\epsilon$, all the terms in the sum where $\epsilon(\vec{k})$ is outside of the integration interval must be identically null (property 2, p. 169). Thus we can restrict the sum to only those allowed $\vec{k}$ points satisfying $\epsilon(\vec{k}) \in [\epsilon, \epsilon + \Delta\epsilon]$:

$$= \sum_{\vec{k}: \epsilon(\vec{k}) \in [\epsilon, \epsilon + \Delta\epsilon]} \int_{\epsilon}^{\epsilon + \Delta\epsilon} \delta \left(\epsilon(\vec{k}') - \epsilon(\vec{k}) \right) d\epsilon(\vec{k}')$$

Now we note that, by definition, each integral in the sum is equal to 1. In fact, since the sum contains only those δ functions which shoot their shot inside the interval $[\epsilon, \epsilon + \Delta\epsilon]$, they are null everywhere outside such interval and thus it must hold:

$$\int_{\epsilon}^{\epsilon+\Delta\epsilon} \delta(\epsilon(\vec{k}') - \epsilon(\vec{k})) d\epsilon(\vec{k}') = \int_{-\infty}^{\infty} \delta(\epsilon(\vec{k}') - \epsilon(\vec{k})) d\epsilon(\vec{k}') = 1 \quad (509)$$

(property 2, p. 169)

And then we can conclude the chain of equalities with:

$$= \sum_{\vec{k}: \epsilon(\vec{k}) \in [\epsilon, \epsilon + \Delta\epsilon]} 1 \quad (510)$$

In the expression we have arrived at, 1 is added for each $\vec{k}$ point such that the energy corresponding to it is within the interval $[\epsilon, \epsilon + \Delta\epsilon]$: but this is just *counting* how many allowed $\vec{k}$ states are contained in the finite energy interval $[\epsilon, \epsilon + \Delta\epsilon]$, that is precisely eq. 475.

277. Remarks:

- We now understand the reason why definition 506 is formally correct, while that based on the cumulative number of allowed states, eq. 473, is not. In 506, the *discrete* nature of the electronic allowed energies (a peculiar quantum mechanical fact) is “naturally” taken into account with the use of the Dirac δ function, which, as we already remarked (p. 168), was invented precisely for this reason.
- As already mentioned multiple times, eq. 506 is the density of allowed $\vec{k}$ points and since two monoelectronic states with opposite spin correspond to each allowed $\vec{k}$ point, the density of allowed *monoelectronic states* is 506 with an additional factor of 2.

3.15.2.4 Application to the Fermi gas

278. As we did with definition 473, it is instructive to verify that also 506 leads to the same result for an electron gas confined into a cubic sample of side L .

Let's start from definition 506:

$$g(\epsilon(\vec{k}')) = \frac{1}{V} \sum_{\vec{k}} \delta(\epsilon(\vec{k}') - \epsilon(\vec{k}))$$

Multiply and divide by the volume of the reciprocal cell $\Delta\vec{k}' = \frac{8\pi^3}{V}$ ($\Delta\vec{k}'$ is the finite version of the notation I introduced on p. 41):

$$= \frac{1}{V} \frac{1}{\frac{8\pi^3}{V}} \sum_{\vec{k}} \delta(\epsilon(\vec{k}') - \epsilon(\vec{k})) \Delta\vec{k}' = \frac{1}{8\pi^3} \sum_{\vec{k}} \delta(\epsilon(\vec{k}') - \epsilon(\vec{k})) \Delta\vec{k}'$$

Since the density of states is normalized by the volume of the sample, it does not depend on it and so we do not lose generality if we consider a sample so large ($V \rightarrow \infty$) that the volume of the reciprocal primitive cell, $\Delta\vec{k}' = 8\pi^3/V$, can be considered infinitesimal (remember that the volume of the direct cell and that of the primitive cell are inversely proportional, eq. 294). Under this assumption, the sum becomes equal to a corresponding integral over the whole $\vec{k}$ space:

$$= \frac{1}{8\pi^3} \int_{\text{all } \vec{k} \text{ space}} \delta(\epsilon(\vec{k}') - \epsilon(\vec{k})) d\vec{k}'$$

where $d\vec{k}'$ is the infinitesimal volume element of Fourier space. Now recall that, for the Fermi gas, the relation:

$$\epsilon(\vec{p}) = \frac{\hbar^2 p^2}{2m}$$

holds for *any* point $\vec{p}$ of the reciprocal space (that is: not necessarily an allowed wave vector): review the derivation of the solution of the Schrödinger equation, in particular eq. 387.

This allows us to express the two energies in the argument of the δ function as:

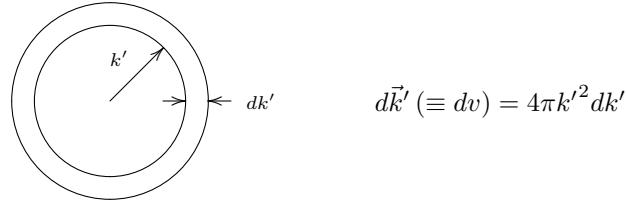
$$\epsilon(\vec{k}') = \frac{\hbar^2 k'^2}{2m} \quad (511)$$

$$\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m} \quad (512)$$

and thus we can continue with:

$$= \frac{1}{8\pi^3} \int_{\text{all } \vec{k} \text{ space}} \delta\left(\frac{\hbar^2 k'^2}{2m} - \frac{\hbar^2 k^2}{2m}\right) d\vec{k}'$$

Since in the Fermi gas the energy depends only on the length (modulus) of the the vector $\vec{k}$ (spherical symmetry), it is convenient to express the infinitesimal integration volume $d\vec{k}'$ as the volume of a spherical shell of radius k' and thickness dk' :



$$\begin{aligned} d\vec{k}' (\equiv dv) &= \frac{4}{3}\pi (k' + dk')^3 - \frac{4}{3}\pi k'^3 \\ &= \frac{4}{3}\pi \left(\cancel{k'^3} + \overbrace{3k' dk'^2}^{\approx 0} + 3k'^2 dk' + \overbrace{dk'^3}^{\approx 0} \cancel{k'^3} \right) = 4\pi k'^2 dk' \end{aligned}$$

(infinitesimals dk'^2 and dk'^3 are negligible with respect to dk')

This way, the integral becomes:

$$= \frac{1}{8\pi^3} \int_0^\infty 4\pi k'^2 \delta\left(\frac{\hbar^2 k'^2}{2m} - \frac{\hbar^2 k^2}{2m}\right) dk' = \frac{1}{2\pi^2} \int_0^\infty k'^2 \delta\left(\frac{\hbar^2 k'^2}{2m} - \frac{\hbar^2 k^2}{2m}\right) dk'$$

(note that the integration limits have changed, since now the integration variable is the modulus of the generic position vector $\vec{k}'$ in reciprocal space)

We can now take advantage of the scaling property (property 4, p. 170) to simplify the argument of the Dirac function:

$$= \frac{1}{2\pi^2} \int_0^\infty k'^2 \left(\frac{2m}{\hbar^2} \right) \delta(k'^2 - k^2) dk' = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right) \int_0^\infty k'^2 \delta(k'^2 - k^2) dk'$$

And now the integral can be solved by performing the following change of variable:

$$y = k'^2$$

We have:

$$\begin{aligned} k' &= y^{\frac{1}{2}} \\ dk' &= \frac{1}{2} y^{-\frac{1}{2}} dy \\ k' = 0 &\implies y = 0 \\ k' \rightarrow \infty &\implies y \rightarrow \infty \end{aligned}$$

Substituting above:

$$= \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right) \int_0^\infty y \delta(y - k^2) \frac{1}{2} y^{-\frac{1}{2}} dy = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right) \int_0^\infty y^{\frac{1}{2}} \delta(y - k^2) dy$$

Since $k^2 \geq 0$, the lower integration limit can be extended to $-\infty$ (property 3, p. 169):

$$= \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right) \int_{-\infty}^\infty y^{\frac{1}{2}} \delta(y - k^2) dy$$

And now, for the sifting property of the δ function (property 3, p. 169), the integral is immediate:

$$\int_{-\infty}^\infty y^{\frac{1}{2}} \delta(y - k^2) dy = (k^2)^{\frac{1}{2}} = k = \left(\frac{2m}{\hbar^2} \right)^{\frac{1}{2}} \epsilon^{\frac{1}{2}}$$

(in the last step we have taken advantage of the dispersion relation for the Fermi gas, eq. 398) Eq. 487 is eventually obtained:

$$g(\epsilon) = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right) \left(\frac{2m}{\hbar^2} \right)^{\frac{1}{2}} \epsilon^{\frac{1}{2}} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}}$$

3.15.3 OK: but what do we do with the density of states?

279. Good, we now know very well what the density of states is: but what do we do with it? The most general answer is:

The density of states (which can be obtained either experimentally or computationally) allows us to turn (otherwise intractable) discrete sums into (more tractable) integrals.

280. As we saw (eq. 471), any property Q related to the occupied monoelectronic states in a solid sample can be obtained by multiplying the value taken by the property in a given electronic state $Q(\epsilon(\vec{k}))$ by the occupation of that state (the occupation is given by the Fermi–Dirac function (point 244), $f(\epsilon(\vec{k}))$), summing over all the electronic states and normalizing with respect to the sample volume V :

$$Q = \frac{2}{V} \sum_{\vec{k}} Q(\epsilon(\vec{k})) f(\epsilon(\vec{k}))$$

281. In this context, the important thing to note is that the number of occupied electronic levels in a solid sample is of the order of Avogadro’s number and thus dealing directly with a sum such the one shown above is impossible (as already noted, this is one of the aspects most drastically different in the comparison between the analysis of the electronic structure of solids and isolated systems, like atoms or molecules).

And that is where the density of states comes in.

Thanks to the sifting property of the δ function (property 3, p. 169) the following holds:

$$Q(\epsilon(\vec{k})) f(\epsilon(\vec{k})) = \int_{\text{all } \vec{k} \text{ space}} Q(\epsilon(\vec{k}')) f(\epsilon(\vec{k}')) \delta(\epsilon(\vec{k}') - \epsilon(\vec{k})) d\epsilon(\vec{k}') \quad (513)$$

and thus we can rewrite the sum as:

$$\begin{aligned} \sum_{\vec{k}} Q(\epsilon(\vec{k})) f(\epsilon(\vec{k})) \\ = \sum_{\vec{k}} \int_{\text{all } \vec{k} \text{ space}} Q(\epsilon(\vec{k}')) f(\epsilon(\vec{k}')) \delta(\epsilon(\vec{k}') - \epsilon(\vec{k})) d\epsilon(\vec{k}') \end{aligned} \quad (514)$$

If we now swap the sum and the integral operators (integral is linear), we get:

$$= \int_{\text{all } \vec{k} \text{ space}} \sum_{\vec{k}} Q(\epsilon(\vec{k}')) f(\epsilon(\vec{k}')) \delta(\epsilon(\vec{k}') - \epsilon(\vec{k})) d\epsilon(\vec{k}')$$

Both $Q(\epsilon(\vec{k}'))$ and $f(\epsilon(\vec{k}'))$ do not depend on $\vec{k}$ and hence:

$$= \int_{\text{all } \vec{k} \text{ space}} Q(\epsilon(\vec{k}')) f(\epsilon(\vec{k}')) \sum_{\vec{k}} \delta(\epsilon(\vec{k}') - \epsilon(\vec{k})) d\epsilon(\vec{k}')$$

and you recognize that the sum is just the density of states (multiplied by V) (eq. 506):

$$= \int_{\text{all } \vec{k} \text{ space}} Q(\epsilon(\vec{k}')) f(\epsilon(\vec{k}')) V g(\epsilon(\vec{k}')) d\epsilon(\vec{k}') \quad (515)$$

In summary, as anticipated, we have turned an intractable sum into a more tractable integral (even though this kind of integrals are generally not simple, they are anyway simpler than the direct sum).

In conclusion, the following holds:

$$\frac{2}{V} \sum_{\vec{k}} Q(\epsilon(\vec{k})) f(\epsilon(\vec{k})) = 2 \int_{\text{all } \vec{k} \text{ space}} Q(\epsilon(\vec{k}')) f(\epsilon(\vec{k}')) g(\epsilon(\vec{k}')) d\epsilon(\vec{k}') \quad (516)$$

If you are interested, I present an alternative derivation of the integral 515 in the extracurricular part (section 3.4).

3.15.4 Two examples of application

282. As a first example of application of 516, consider the evaluation of the electronic energy of a solid (I mean: the electronic *only* contribution to the total energy of a macroscopic sample). In this case, we simply have:

$$Q\left(\epsilon(\vec{k})\right) = \epsilon(\vec{k}) \quad (517)$$

and thus, letting u be the electronic energy per unit volume of the solid, we get:

$$u = \frac{2}{V} \sum_{\vec{k}} \epsilon(\vec{k}) f\left(\epsilon(\vec{k})\right) = 2 \int_{\text{all } \vec{k} \text{ space}} \epsilon(\vec{k}') f\left(\epsilon(\vec{k}')\right) g\left(\epsilon(\vec{k}')\right) d\epsilon(\vec{k}') \quad (518)$$

and the integral can be tackled once we have the dispersion relation $\epsilon(\vec{k}')$ (either analytical, as in the Fermi gas, or, almost always, experimental), the Fermi–Dirac distribution and the density of states (also this latter is obtained almost always experimentally).

283. In a similar way, the density of electrons n (number of electrons per unit volume, another quite important property) is obtained from 516 by putting:

$$Q\left(\epsilon(\vec{k})\right) = 1 \quad (519)$$

since in this case the property to be considered for each electronic level is its *occupation*, that is the Fermi–Dirac function evaluated for the energy of the level.

Thus:

$$n = \frac{2}{V} \sum_{\vec{k}} f\left(\epsilon(\vec{k})\right) = 2 \int_{\text{all } \vec{k} \text{ space}} f\left(\epsilon(\vec{k}')\right) g\left(\epsilon(\vec{k}')\right) d\vec{k}' \quad (520)$$

By the way, note that this is nothing but a re–edition of the normalization condition 465, in which the sum is run over the allowed $\vec{k}$ points (instead of the “true” monoelectronic levels) and we divide by the volume V of the sample to obtain the density of electrons, instead of their total number.

4 The electronic structure of crystalline solids

(You can find the material of this part of the notes in the books by Ashcroft and Mermin¹⁹ and/or Kittel²⁰ and/or Ibach and Lüth.²²)

284. The Fermi gas model which we discussed in the previous section describes a solid sample simply as a “container” of free and independent (valence) electrons; no assumption is made regarding the presence of the ions inside the sample (actually, they are completely ignored by the model). Since the electrons do not interact with each other nor with the ions, the (stationary and mono-electronic) wave equation that we studied was:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r}) = \epsilon\Psi(\vec{r})$$

that is: the hamiltonian contained only the kinetic energy operator.

In this part we extend the description of a solid to include the interactions of the electrons with the ions (as already mentioned, by “ions” I mean the nuclei surrounded by the core electrons which, these latter, are assumed completely localized around the nuclei, so they do not move in the volume of the solid).

285. The first remark to be put forward is that we will not study just any solid: the system of our interest will be a *crystalline solid*, namely a solid sample in which a primitive cell is present which generates the whole sample by periodic repetition along the three directions defined by its primitive vectors.

As you will see, this assumption will allow us to develop a mathematical description of the electronic structure which would be impossible for an amorphous (i.e. non crystalline) solid.

286. The model that we are going to study in this part of the course differs from the Fermi gas model in two related aspects:

1. now we will make a well defined assumption about the *internal structure* of the solid sample, which is made by ions located on the nodes of a Bravais lattice (in the electron gas model, the solid sample was just a “box” containing the (valence) electrons, free to move everywhere within its volume)
2. we will consider the interactions between the valence electrons and the ions of the crystalline lattice. For this reason, the Schrödinger equation which we will be dealing with now contains also a potential energy term $U(\vec{r})$:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\Psi(\vec{r}) = \epsilon\Psi(\vec{r}) \quad (521)$$

287. A particularly important aspect of the model which I am introducing here is about the mathematical form of the potential operator $U(\vec{r})$. The potential energy of the system is due to the nuclei (plus core electrons) and since these are located on the nodes of a periodic lattice, the potential they generate *must possess the same periodicity* (point 136).

288. Figure 62 qualitatively shows how the function $U(\vec{r})$ might likely be for the case of a bidimensional crystal with a square primitive cell: the potential energy of an electron due to nuclear attraction is constant and approximately 0 in regions far from the nuclei, while it quickly falls to $-\infty$ as the electron approaches a nucleus.

289. Before going on it is appropriate to remark that the general problem of describing a system of electrons in a solid (even if simplified by having a periodic nature) is much more complex than what we will introduce in this section; in rigorous terms it is a many body problem in which not only the forces exerted by the nuclei on the electrons, but also the internuclear and interelectronic

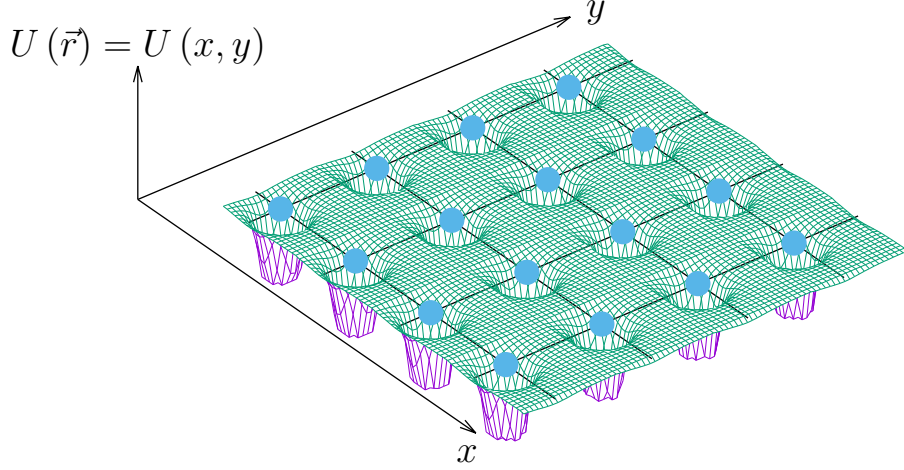


Figure 62: Qualitative representation of the potential felt by an electron in a bidimensional crystal; the Bravais lattice on which the crystal structure is based is shown with straight lines; the nuclei (shown as filled spheres) are located on the nodes of the lattice. The potential $U(\vec{r}) = U(x, y)$ is close to 0 in the internuclear regions, but it quickly falls towards $-\infty$ as the distance from a nucleus decreases. It should be apparent that $U(\vec{r})$ is a (bidimensional) periodic function with the same periodicity as the Bravais lattice.

interactions should be taken into account; thus, using a *monoelectronic* hamiltonian is already a big approximation. Another complication is that the ions are not fixed; instead, in a real solid, they vibrate around their lattice positions and this is an additional aspect that should be taken into account.

One can think that these (and other) additional difficulties can be somehow overcome by defining an “effective” potential which can account for them; however, the important thing in our context is that whatever the specific definition of the potential, it *must be periodic* on the same Bravais lattice which defines the crystal structure.

4.1 The definition of the system

290. We consider a solid with a crystalline structure based on a Bravais lattice $\mathcal{R}$ whose primitive cell is defined by the three primitive vectors:

$$\vec{a}_i, \quad i = 1, 2, 3 \quad (522)$$

A generic vector (point) of the Bravais lattice is given by the linear combination:

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 = \sum_{i=1}^3 n_i \vec{a}_i, \quad n_i \in \mathbb{Z} \quad (523)$$

We will assume that the base of the crystal structure is monoatomic; that is: there is a single ion on each lattice node. Of course, this implies that the crystal whose electronic structure we are interested in is that of an element (and not of a chemical compound).

The periodicity of the potential function is mathematically expressed by (eq. 124):

$$U(\vec{r} + \vec{R}) = U(\vec{r}) \quad \forall \vec{R} \in \mathcal{R} \quad (524)$$

which is to say that $U(\vec{r})$ takes the same value when we move in space by any translation vector of the Bravais lattice $\mathcal{R}$ (look at figure 62).

We are interested in the solutions of the stationary and monoelectronic Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\Psi(\vec{r}) = \epsilon\Psi(\vec{r}) \quad (525)$$

4.2 The Bloch theorem

291. Dealing with the differential equation 525 is not simple; however, a theorem exists that offers a big help in this regard: it is known as *Bloch theorem* (from the name of the Swiss physicist who proved it) and it has allowed all the solid state physics to make a fundamental step forward. The Bloch theorem does not give the solution of eq. 525, but limits the possible solutions to a well defined class of functions.

292. There are two equivalent statements of the Bloch theorem.

1. The solutions of eq. 525 can be written as the product of a plane waveⁱ and a function having the same periodicity of the Bravais lattice $\mathcal{R}$. That is:

$$\Psi_{\vec{k}n}(\vec{r}) = \overbrace{\exp(i\vec{k} \cdot \vec{r})}^{\text{plane wave}} u_{\vec{k}n}(\vec{r}) \quad (526)$$

with:

$$u_{\vec{k}n}(\vec{r} + \vec{R}) = u_{\vec{k}n}(\vec{r}) \quad \forall \vec{R} \in \mathcal{R} \quad (527)$$

The eigenfunction $\Psi(\vec{r})$ and the periodic function $u(\vec{r})$ are indexed by the wave vector $\vec{k}$, but also by a second index n : for its definition and description you must await until point 327.

2. Any possible solution $\Psi(\vec{r})$ of eq. 525 must be such that its value after a translation by any lattice vector $\vec{R}$ is equal to the product of the value before the translation and a “phase factor” $\exp(i\vec{k} \cdot \vec{R})$:

$$\Psi_{\vec{k}n}(\vec{r} + \vec{R}) = \exp(i\vec{k} \cdot \vec{R}) \Psi_{\vec{k}n}(\vec{r}) \quad \forall \vec{R} \in \mathcal{R} \quad (528)$$

293. You see how Bloch’s theorem places very specific constraints to the functional form of the solutions of the Schrödinger equation containing a periodic potential: they can be expressed as the product of a plane wave and a function ($u_{\vec{k}n}(\vec{r})$) having the same periodicity of the Bravais lattice $\mathcal{R}$.

Note that Bloch’s theorem says nothing about the function $u(\vec{r})$, but that it must be periodic on $\mathcal{R}$: in fact, finding the function $u(\vec{r})$ means solving the Schrödinger problem, since afterwards it is sufficient to multiply $u(\vec{r})$, by the plane wave $\exp(i\vec{k} \cdot \vec{r})$; note, however, that also the plane

ⁱAs already noted previously, we will speak about a plane wave even when we actually mean the spatial part alone of it.

wave contains a parameter which needs to be sorted out: the wave vector $\vec{k}$. In the following, we will have a lot to say about this.

The exact form of the function $u(\vec{r})$ depends on the form of the periodic potential $U(\vec{r})$ and, in general, finding it is not simple; however, Bloch's theorem states that, whatever the specific form of $u(\vec{r})$, it *must* be $\mathcal{R}$ periodic.

294. Beware not to make confusion: the solution of Schrödinger's equation, $\Psi(\vec{r})$, is *not* periodic on the Bravais lattice (this is also apparent from 528); and, in fact, there is no reason why it should be so: the eigenfunction of the hamiltonian 525 defines the state of an electron in the solid sample and thus it is a function whose domain is *the whole sample*.

The fact that the sample is crystalline and thus consists of the repetition of an identical primitive cell (and, therefore, that the potential appearing in the Hamiltonian is periodic) narrows the class of possible solutions to that of the Bloch functions, namely functions *not* having the same periodicity of the lattice, but given by the product of a plane wave and a $\mathcal{R}$ periodic function.

295. Having clarified the above, you will see that, actually, the function $\Psi(\vec{r})$ *is* periodic, but *not* on the Bravais lattice on which the crystalline structure of the sample is based; in a way similar to what we have already seen on p. 135, the periodicity of $\Psi(\vec{r})$ originates from the boundary conditions which we will enforce for the solution of the Schrödinger equation (point 302).

4.2.1 Equivalence of the two statements of Bloch's theorem

296. Before continuing, let's prove the equivalence of the two statements of Bloch's theorem.

526 and 527 $\implies$ 528 Using 526 evaluate $\Psi(\vec{r} + \vec{R})$:

$$\Psi(\vec{r} + \vec{R}) = \exp\left(i\vec{k} \cdot (\vec{r} + \vec{R})\right) u(\vec{r} + \vec{R}) \quad (529)$$

Expand the exponential:

$$\Psi(\vec{r} + \vec{R}) = \exp\left(i\vec{k} \cdot \vec{R}\right) \exp\left(i\vec{k} \cdot \vec{r}\right) u(\vec{r} + \vec{R}) \quad (530)$$

Due to 527:

$$\Psi(\vec{r} + \vec{R}) = \exp\left(i\vec{k} \cdot \vec{R}\right) \exp\left(i\vec{k} \cdot \vec{r}\right) u(\vec{r}) \quad (531)$$

or:

$$\Psi(\vec{r} + \vec{R}) = \exp\left(i\vec{k} \cdot \vec{R}\right) \Psi(\vec{r}) \quad (532)$$

which is 528.

528 $\implies$ 526 and 527 Eq. 528 can be rewritten as:

$$\Psi(\vec{r}) = \exp\left(-i\vec{k} \cdot \vec{R}\right) \Psi(\vec{r} + \vec{R}) \quad (533)$$

Add and subtract $\vec{r}$ in the argument of the exponential:

$$= \exp\left(-i\vec{k} \cdot (\vec{r} + \vec{R} - \vec{r})\right) \Psi(\vec{r} + \vec{R}) \quad (534)$$

$$= \exp \left(i\vec{k} \cdot \vec{r} \right) \overbrace{\exp \left(-i\vec{k} \cdot \left(\vec{r} + \vec{R} \right) \right) \Psi \left(\vec{r} + \vec{R} \right)}^{\text{call this } u(\vec{r} + \vec{R})} \quad (535)$$

$$= \exp \left(i\vec{k} \cdot \vec{r} \right) u \left(\vec{r} + \vec{R} \right) \quad (536)$$

It can be easily verified that the above defined $u \left(\vec{r} + \vec{R} \right)$ is periodic on the Bravais lattice. In fact, for any vector $\vec{R} \in \mathcal{R}$:

$$u \left(\vec{r} + \vec{R} \right) = \exp \left(-i\vec{k} \cdot \left(\vec{r} + \vec{R} \right) \right) \Psi \left(\vec{r} + \vec{R} \right) \quad (537)$$

use 528, which holds by hypothesis

$$= \exp \left(-i\vec{k} \cdot \left(\vec{r} + \vec{R} \right) \right) \exp \left(i\vec{k} \cdot \vec{R} \right) \Psi \left(\vec{r} \right) \quad (538)$$

$$= \exp \left(-i\vec{k} \cdot \vec{r} \right) \Psi \left(\vec{r} \right) = u \left(\vec{r} \right) \quad (539)$$

and so 536 can be rewritten as:

$$\Psi \left(\vec{r} \right) = \exp \left(i\vec{k} \cdot \vec{r} \right) u \left(\vec{r} \right) \quad (540)$$

which just proves 526 and 527, since we have written $\Psi \left(\vec{r} \right)$ as the product of a plane wave and a function $(u \left(\vec{r} \right))$ periodic on the Bravais lattice.

4.2.2 Proof of Bloch's theorem

(This is the proof on p. 134 of the book by Ashcroft and Mermin⁷)

297. We will prove Bloch's theorem in the form of eq. 528.

We start by defining a translation operator $T_{\vec{R}}$ for each vector $\vec{R}$ of the Bravais lattice (there are infinite $\vec{R}$ vectors, thus infinite $T_{\vec{R}}$ operators).

When applied to any function of position, $f \left(\vec{r} \right)$, the $T_{\vec{R}}$ operator translates it by $\vec{R}$ (point 111):

$$T_{\vec{R}} f \left(\vec{r} \right) = f \left(\vec{r} + \vec{R} \right) \quad (541)$$

What we want to do in the first place is to show that all the $T_{\vec{R}}$ operators commuteⁱⁱ with both the hamiltonian and with each other.

Let's see the commutation with the hamiltonian (defined in eq. 525).

Given *any* function $\Psi \left(\vec{r} \right)$, we must verify that:

$$T_{\vec{R}} \left(H \left(\vec{r} \right) \Psi \left(\vec{r} \right) \right) = H \left(\vec{r} \right) \left(T_{\vec{R}} \Psi \left(\vec{r} \right) \right) \quad (542)$$

where I have emphasized that also the Hamilton operator depends on $\vec{r}$ (eq. 525).

By definition, the $T_{\vec{R}}$ operator translates by $\vec{R}$ its argument and so:

$$T_{\vec{R}} \left(H \left(\vec{r} \right) \Psi \left(\vec{r} \right) \right) = H \left(\vec{r} + \vec{R} \right) \Psi \left(\vec{r} + \vec{R} \right) \quad (543)$$

ⁱⁱTwo operators O and P are said to commute when the order of their application does not matter, namely when $O P = P O$

It is easy to verify that:

$$H\left(\vec{r} + \vec{R}\right) = H\left(\vec{r}\right) \quad (544)$$

In fact:

$$H\left(\vec{r} + \vec{R}\right) = -\frac{\hbar^2}{2m}\nabla_{\vec{r}+\vec{R}}^2 + U\left(\vec{r} + \vec{R}\right) \quad (545)$$

By hypothesis $U\left(\vec{r}\right)$ is $\mathcal{R}$ periodic and so:

$$U\left(\vec{r} + \vec{R}\right) = U\left(\vec{r}\right) \quad (546)$$

Moreover, setting:

$$\begin{aligned} \vec{r} &= (x, y, z) \\ \vec{R} &= (R_x, R_y, R_z) \end{aligned}$$

for a generic function $f\left(\vec{r}\right) = f\left(x, y, z\right)$ we have:

$$\nabla_{\vec{r}+\vec{R}}^2 f = \frac{\partial^2 f}{\partial (x + R_x)^2} + \frac{\partial^2 f}{\partial (y + R_y)^2} + \frac{\partial^2 f}{\partial (z + R_z)^2} \quad (547)$$

Setting:

$$u(x) = x + R_x \quad (548)$$

$$v(y) = y + R_y \quad (549)$$

$$w(z) = z + R_z \quad (550)$$

we have:

$$\begin{aligned} x &= u - R_x \\ y &= v - R_y \\ z &= w - R_z \end{aligned} \quad (551)$$

and thus $f(x, y, z)$ can be equivalently thought of as a function of (u, v, w) .

In order to continue, we need to recall the so called “chain rule” for partial derivatives. For the function:

$$f = f(x, y, z \dots)$$

with:

$$x = x(u, v, w \dots)$$

$$\begin{aligned}
y &= y(u, v, w \dots) \\
z &= z(u, v, w \dots) \\
&\dots
\end{aligned}$$

thinking of f as a function of $u, v, w, \dots$, the chain rule states that:

$$\begin{aligned}
\frac{\partial f}{\partial u} &= \frac{\partial f}{\partial x} \frac{\partial x}{\partial u} + \frac{\partial f}{\partial y} \frac{\partial y}{\partial u} + \frac{\partial f}{\partial z} \frac{\partial z}{\partial u} + \dots \\
\frac{\partial f}{\partial v} &= \frac{\partial f}{\partial x} \frac{\partial x}{\partial v} + \frac{\partial f}{\partial y} \frac{\partial y}{\partial v} + \frac{\partial f}{\partial z} \frac{\partial z}{\partial v} + \dots \\
\frac{\partial f}{\partial w} &= \frac{\partial f}{\partial x} \frac{\partial x}{\partial w} + \frac{\partial f}{\partial y} \frac{\partial y}{\partial w} + \frac{\partial f}{\partial z} \frac{\partial z}{\partial w} + \dots \\
&\dots
\end{aligned} \tag{552}$$

Then, for the second derivative of the function with respect to $(x + R_x)$ (namely the second term on the RHS of 547) we have:

$$\frac{\partial^2 f}{\partial (x + R_x)^2} = \frac{\partial^2 f}{\partial u^2} = \frac{\partial}{\partial u} \frac{\partial f}{\partial u} \tag{553}$$

apply the chain rule for the first derivative $\frac{\partial f}{\partial u}$:

$$= \frac{\partial}{\partial u} \left(\frac{\partial f}{\partial x} \frac{\partial x}{\partial u} + \frac{\partial f}{\partial y} \frac{\partial y}{\partial u} + \frac{\partial f}{\partial z} \frac{\partial z}{\partial u} \right) \tag{554}$$

based on 551 we have: $\frac{\partial x}{\partial u} = 1, \frac{\partial y}{\partial u} = \frac{\partial z}{\partial u} = 0$

$$= \frac{\partial}{\partial u} \left(\frac{\partial f}{\partial x} \right) \tag{555}$$

apply again the chain rule for the first derivative with respect to u of $\frac{\partial f}{\partial x}$:

$$= \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial x} \right) \frac{\partial x}{\partial u} + \frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right) \frac{\partial y}{\partial u} + \frac{\partial}{\partial z} \left(\frac{\partial f}{\partial x} \right) \frac{\partial z}{\partial u} \tag{556}$$

again, based on 551 we have: $\frac{\partial x}{\partial u} = 1, \frac{\partial y}{\partial u} = \frac{\partial z}{\partial u} = 0$

$$= \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial x} \right) = \frac{\partial^2 f}{\partial x^2} \tag{557}$$

The same identical steps are repeated for the remaining two partial derivatives $\partial^2 f / \partial (y + R_y)^2$ and $\partial^2 f / \partial (z + R_z)^2$ in 547 and we arrive at:

$$\begin{aligned}
\nabla_{\vec{r} + \vec{R}}^2 f &= \frac{\partial^2 f}{\partial (x + R_x)^2} + \frac{\partial^2 f}{\partial (y + R_y)^2} + \frac{\partial^2 f}{\partial (z + R_z)^2} \\
&= \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} = \nabla_{\vec{r}}^2 f
\end{aligned} \tag{558}$$

which, together with 546, validates 544.

Remark: we have just proved the invariance of the kinetic energy operator $(\nabla_{\vec{r}}^2)$ with respect to any vector $\vec{R} \in \mathcal{R}$, but if you review the steps leading to 558, you should realize very easily that they hold for *any* vector, not only for the vectors of $\mathcal{R}$. So: the kinetic energy operator is invariant to *any translation*. Pin this remark, since we will make use of it also on other occasions (point 482).

Eventually:

$$\begin{aligned} T_{\vec{R}}(H(\vec{r})\Psi(\vec{r})) &= H(\vec{r} + \vec{R})\Psi(\vec{r} + \vec{R}) = H(\vec{r})\Psi(\vec{r} + \vec{R}) \\ &= H(\vec{r})(T_{\vec{R}}\Psi(\vec{r})) \end{aligned} \quad (559)$$

which proves the commutativity of the two operators $T_{\vec{R}}$ and $H(\vec{r})$.

Given any two vectors $\vec{R}$ and $\vec{R}'$ of $\mathcal{R}$, it is trivial to see that the corresponding translation operators commute with each other. For any function $\Psi(\vec{r})$:

$$\begin{aligned} T_{\vec{R}}(T_{\vec{R}'}\Psi(\vec{r})) &= T_{\vec{R}}\Psi(\vec{r} + \vec{R}') = \Psi(\vec{r} + \vec{R}' + \vec{R}) \\ &= \Psi(\vec{r} + \vec{R} + \vec{R}') = T_{\vec{R}'}\Psi(\vec{r} + \vec{R}) = T_{\vec{R}'}(T_{\vec{R}}\Psi(\vec{r})) \end{aligned} \quad (560)$$

At this point, we have proved that all the (infinite) $T_{\vec{R}}$ operators do commute with both the hamiltonian and with each other.

In the light of this result, we can now invoke an important theorem of quantum mechanics: for a set of operators which commute with each other it is always possible to find a set of functions being eigenfunctions of all the operators of the set *at the same time* (you can find the proof of this theorem in any base textbook of quantum mechanics; for instance, at section 4-9 of the book by McQuarrie²³).

Thus it is possible to find the eigenfunctions of the hamiltonian H such that they are eigenfunctions of all the translation operators $T_{\vec{R}}$; in other words, letting $\Psi(\vec{r})$ be the generic eigenfunction of the hamiltonian, it is possible to chose it such that:

$$H\Psi(\vec{r}) = \epsilon\Psi(\vec{r}) \quad (561)$$

$$T_{\vec{R}}\Psi(\vec{r}) = C(\vec{R})\Psi(\vec{r}) \quad \forall \vec{R} \in \mathcal{R} \quad (562)$$

Please note: $\Psi(\vec{r})$ is an eigenfunction of both H and all the $T_{\vec{R}}$'s, but the eigenvalues are different. In particular, the eigenvalues $C(\vec{R})$ of the $T_{\vec{R}}$ operators will depend on the particular $T_{\vec{R}}$ operator, i.e., as I have explicitly indicated above, they will be functions of $\vec{R}$.

There is a simple relation between the eigenvalues of the $T_{\vec{R}}$ operators. For any two translation vectors $\vec{R}$ and $\vec{R}'$ we have:

$$T_{\vec{R}}(T_{\vec{R}'}\Psi(\vec{r})) = T_{\vec{R}}C(\vec{R}')\Psi(\vec{r}) = C(\vec{R})C(\vec{R}')\Psi(\vec{r}) \quad (563)$$

but also:

$$\begin{aligned} T_{\vec{R}}(T_{\vec{R}'}\Psi(\vec{r})) &= T_{\vec{R}}\Psi(\vec{r} + \vec{R}') = \Psi(\vec{r} + \vec{R}' + \vec{R}) \\ &= T_{\vec{R} + \vec{R}'}\Psi(\vec{r}) = C(\vec{R} + \vec{R}')\Psi(\vec{r}) \end{aligned} \quad (564)$$

($\vec{R} + \vec{R}'$ is still a vector of $\mathcal{R}$ (point 142))
and thus, by comparison:

$$C(\vec{R} + \vec{R}') = C(\vec{R})C(\vec{R}') \quad (565)$$

From 565 two simple corollaries follow.

$$\begin{aligned} C(\vec{R}_1 + \vec{R}_2 + \vec{R}_3 + \dots) &= C(\vec{R}_1)C(\vec{R}_2 + \vec{R}_3 + \dots) \\ &= C(\vec{R}_1)C(\vec{R}_2)C(\vec{R}_3 + \dots) = C(\vec{R}_1)C(\vec{R}_2)C(\vec{R}_3) \dots \end{aligned}$$

or:

$$C\left(\sum_i \vec{R}_i\right) = \prod_i C(\vec{R}_i) \quad (566)$$

Moreover, $\forall m \in \mathbb{Z}$, we also have:

$$C(m\vec{R}) = C(\overbrace{\vec{R} + \vec{R} + \dots + \vec{R}}^{m \text{ times}}) = \overbrace{C(\vec{R})C(\vec{R}) \dots C(\vec{R})}^{m \text{ times}} = \left(C(\vec{R})\right)^m \quad (567)$$

Now: the three primitive vectors of $\mathcal{R}$, $\vec{a}_j$, are, trivially, themselves translation vectors of the lattice and thus also for them the following holds:

$$T_{\vec{a}_j}\Psi(\vec{r}) = C(\vec{a}_j)\Psi(\vec{r}) \quad (568)$$

Since, in general, $\Psi(\vec{r})$ is a function of a real (vector) variable ($\vec{r}$), but with complex values (for instance, recall the solution of the Schrödinger equation for the Fermi gas, eq. 393), the eigenvalues of the operators that we are dealing with are to be assumed, a priori, as complex numbers. Moreover, obviously, we are not considering the case of a null eigenvalue: in such case, the corresponding eigenfunction would be identically null and thus it could not describe an electron, because the probability of finding the electron in any point of space would be always null:

$$\begin{aligned} T_{\vec{R}}\Psi(\vec{r}) &= \Psi(\vec{r} + \vec{R}) = 0 \cdot \Psi(\vec{r}) \quad \forall \vec{r} \implies \Psi(\vec{r} + \vec{R}) = 0 \quad \forall \vec{r} \\ &\implies \Psi(\vec{r}) = 0 \quad \forall \vec{r} \implies |\Psi(\vec{r})|^2 = 0 \quad \forall \vec{r} \end{aligned}$$

We now make the following remark.

For any non null complex number $C(\vec{a}_j)$ it is always possible to find a complex number x_j such that:

$$C(\vec{a}_j) = \exp(i2\pi x_j) \quad (569)$$

In fact, by expressing $C(\vec{a}_j)$ in polar form:

$$C(\vec{a}_j) = \rho(\cos(\theta) + i\sin(\theta)) \quad (\rho > 0 \text{ because } C(\vec{a}_j) \neq 0) \quad (570)$$

taking advantage of Euler's identity, we have:

$$\begin{aligned} \rho(\cos(\theta) + i\sin(\theta)) &= \rho \exp(i\theta) = \overbrace{\exp(\ln(\rho)) \exp(i\theta)}^{\text{can do this because } \rho > 0} \\ &= \exp(i\theta + \ln(\rho)) = \exp(i2\pi x_j) \end{aligned}$$

and so x_j is uniquely defined by the equation:

$$i\theta + \ln(\rho) = i2\pi x_j \implies x_j = \frac{i\theta + \ln(\rho)}{i2\pi} = \frac{\theta - i\ln(\rho)}{2\pi} \quad (571)$$

You will see, however, that, thanks to the boundary conditions which we will enforce, we will be able to ensure that the x_j will actually be real numbers, (point 306).

Let's now focus on the generic translation vector $\vec{R} \in \mathcal{R}$; as we know very well, it can be expressed as a linear combination with integer coefficients of the three primitive vectors a_j (eq. 139):

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

Let's see then how the eigenvalue corresponding to $\vec{R}$ can be conveniently expressed based on 566 and 567:

$$\begin{aligned} C(\vec{R}) &= C(n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3) = C(n_1 \vec{a}_1) C(n_2 \vec{a}_2) C(n_3 \vec{a}_3) \quad (\text{eq. 566}) \\ &= C(\vec{a}_1)^{n_1} C(\vec{a}_2)^{n_2} C(\vec{a}_3)^{n_3} \quad (\text{eq. 567}) \end{aligned}$$

or, based on 569:

$$\begin{aligned} C(\vec{R}) &= \exp(i2\pi n_1 x_1) \exp(i2\pi n_2 x_2) \exp(i2\pi n_3 x_3) \\ &= \exp(i2\pi (n_1 x_1 + n_2 x_2 + n_3 x_3)) \end{aligned} \quad (572)$$

Next step is to realize that the term $2\pi(n_1 x_1 + n_2 x_2 + n_3 x_3)$ in the exponential can be simply rewritten as:

$$2\pi(n_1 x_1 + n_2 x_2 + n_3 x_3) = \vec{k} \cdot \vec{R} \quad (573)$$

with:

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \quad (574)$$

$$\vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3 \quad (575)$$

where the b_j 's are the three vectors defining the primitive cell of the reciprocal lattice $\mathcal{R}^*$ (and thus: $a_i \cdot b_j = 2\pi\delta_{ij}$, eq. 135).

Note that, for the moment, $\vec{k}$ is *not* a vector of $\mathcal{R}^*$, since the coefficients in 575 are generic complex numbers.

In conclusion:

$$C(\vec{R}) = \exp\left(i\vec{k} \cdot \vec{R}\right) \quad (576)$$

and we are done with the proof of Bloch's theorem, because:

$$\Psi(\vec{r} + \vec{R}) = T_{\vec{R}}\Psi(\vec{r}) = C(\vec{R})\Psi(\vec{r}) = \exp\left(i\vec{k} \cdot \vec{R}\right)\Psi(\vec{r}) \quad (577)$$

which is precisely the thesis of Bloch's theorem, expressed in the form 528.

4.3 The definition of the boundary conditions

298. We are dealing with the following problem:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\Psi(\vec{r}) = \epsilon\Psi(\vec{r})$$

$$\text{with: } U(\vec{r} + \vec{R}) = U(\vec{r}) \quad \forall \vec{R} \in \mathcal{R}$$

and we have proved Bloch's theorem, which limits the possible solutions to a well defined class of functions.

The above problem, however, still requires the definition of proper boundary conditions which fix the behavior of the solutions at the "boundaries" of the system.

299. In the case of the Fermi gas we made the assumption that the solid sample (the system) was a cube of side L , inside which the electrons were moving without any interaction with each other and/or with the ions. And we did setup periodic boundary conditions, p. 135.

Also in the present case we will adopt the same periodic boundary conditions, but before dealing with this aspect, it is necessary to dwell on the choice of the *shape* of the solid sample.

In the case of the Fermi gas there was not any constraint enforced by the internal structure of the sample; actually, the sample did not have *any* internal structure (by all intents and purposes it was just an empty container).

On the other hand, in the present case the sample is explicitly assumed to be a crystal: thus inside it the ions (which we now take into account) are located on the nodes of a Bravais lattice and there is a primitive cell repeating itself along the three directions defined by the primitive vectors of the lattice.

Under these conditions, it is convenient to consider a macroscopic sample whose shape is *commensurate* with the primitive cell of the crystal structure.

Actually, this is the reason why I introduced and described to some extent commensurate lattices in section 2.3.1, and this is the time to review that section.

Assuming that the solid sample is commensurate with the primitive cell of its crystal structure means that it can be considered a *supercell* (point 147) of the primitive cell.

That is: if $\vec{a}_j, (j=1,3)$ are the vectors defining the primitive cell of the crystal structure of the sample, then, letting N_j be three corresponding integer numbers, the sample itself is assumed to be a (macroscopic) parallelepiped defined by the three vectors:

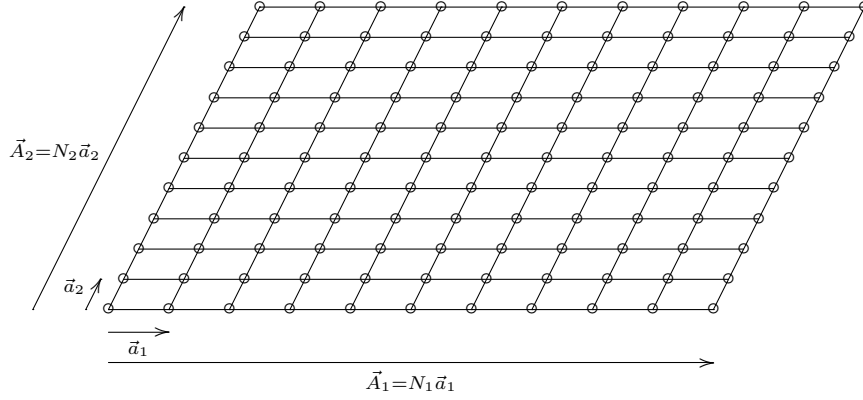


Figure 63: The macroscopic cristalline sample which we will be studying is *commensurate* with its primitive cell; in practice, the sample is a supercell made by an enormous number (of the order of Avogadro's number) of primitive cells

$$\vec{A}_1 = N_1 \vec{a}_1 \quad (578)$$

$$\vec{A}_2 = N_2 \vec{a}_2 \quad (579)$$

$$\vec{A}_3 = N_3 \vec{a}_3 \quad (580)$$

In less formal, but perhaps more intuitive terms you can imagine that the macroscopic sample has been obtained by “scaling” the primitive cell of the crystal structure by N_1 times along the $\vec{a}_1$ direction, N_2 times along the $\vec{a}_2$ direction and N_3 times along the $\vec{a}_3$ direction.

Please note that the supercell which we are talking about here contains a *huge* number of primitive cells (order of magnitude: Avogadro's number): for instance, the number of cubic primitive cells of side $10 \text{ \AA}$ contained in a commensurate macroscopic cubic sample of side 1 cm would be $(10^8)^3/10^3 = 10^{21}$ (just think of how many primitive cells are contained in a crystal sample of ordinary dimensions, for example a *NaCl* or sugar crystal that you can find at your home).

300. The graphical representation of what I am introducing here is shown in figure 63 for a bidimensional case (compare figure 63 with figure 31).

Of course, the supercell shown in the figure is not realistic with regard to its dimensions relative to those of the primitive cell: the latter has been replicated only 10 times along the two directions of $\vec{a}_1$ and $\vec{a}_2$.

However, looking at the figure (and reviewing section 2.3.1) it should be now clear what I mean by saying that the shape and volume of the solid sample are assumed to be commensurate with those of the primitive cell.

301. If the macroscopic sample is a $N_1 \times N_2 \times N_3$ supercell of its primitive cell, then this means that it contains:

$$N = N_1 N_2 N_3 \quad (581)$$

primitive cells (property a. on p. 92).

As already mentioned, in this case N is of the order of Avogadro's number.

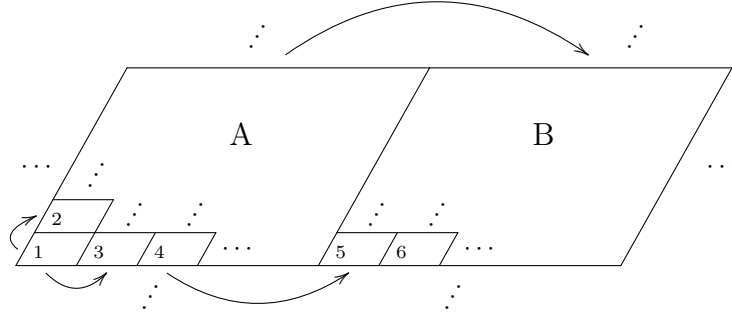


Figure 64: The two different periodicities corresponding to the two Bravais lattices $\mathcal{R}_M$ and $\mathcal{R}_\mu$. A and B are two identical replicas of the macroscopic sample, i.e. of the macroscopic primitive cell $\mathcal{C}_M$; 1, 2, ..., 6 are replicas of the microscopic primitive cell $\mathcal{C}_\mu$.

Likewise, the volume v of the primitive cell and the volume V of the macroscopic sample are related by:

$$V = N_1 N_2 N_3 v = N v \quad (582)$$

(property b. on p. 93)

4.3.1 The macroscopic and the microscopic lattices

302. We now turn to the boundary conditions.

As already said, also in this case we shall assume periodic boundary conditions of Born and von Karman, which allow us to completely neglect any “border” effect (section 3.6.2) and concentrate on the behavior of electrons in the *bulk* of the solid, which is our target.

This means that $\Psi(\vec{r})$ must satisfy (point 57):

$$\Psi(\vec{r} + \vec{Q}) = \Psi(\vec{r}) \quad \forall \vec{Q} = p_1 \vec{A}_1 + p_2 \vec{A}_2 + p_3 \vec{A}_3, \quad p_j \in \mathbb{Z} \quad (583)$$

where, as shown, $\vec{Q}$ is a generic vector of the (Bravais) lattice corresponding to the $N_1 \times N_2 \times N_3$ *supercell* which constitutes the macroscopic solid sample (from here on I will call this “the *macroscopic* Bravais lattice” and will use the symbol $\mathcal{R}_M$ for it and the symbol $\mathcal{C}_M$ for its primitive cell (that is, the $N_1 \times N_2 \times N_3$ supercell); symmetrically, I will call the Bravais lattice of the crystal structure “the *microscopic* Bravais lattice”, with corresponding notation $\mathcal{R}_\mu$ and $\mathcal{C}_\mu$).

In other words, we are requiring that the solution $\Psi(\vec{r})$ of the Schrödinger equation is *periodic on the macroscopic Bravais lattice* (and this is the meaning of what I anticipated on p. 180).

303. Be careful not to make confusion: $\Psi(\vec{r})$ is *not* periodic on the microscopic lattice $\mathcal{R}_\mu$ (the one defined by the vectors $\vec{a}_i$, $i = 1, 3$); that periodicity is displayed by the potential energy operator $U(\vec{r})$, eq. 525, and by the factor $u(\vec{r})$ which appears in Bloch’s theorem, eq. 526. Instead, and this is purely a consequence of the periodic boundary conditions that we have adopted, $\Psi(\vec{r})$ is periodic on $\mathcal{R}_M$, namely the Bravais lattice defined by the supercell which constitutes the macroscopic solid sample, i.e. the supercell defined by the vectors $\vec{A}_i$, $i = 1, 3$, eqs. 578–580.

I have tried to further clarify the situation in figure 64, for a bidimensional crystalline sample.

A and B are two replicas of the supercell constituting the macroscopic sample. Of course, the sample is one and only one (for example, supercell A), but application of the periodic boundary conditions makes things work as if the sample was periodically repeated *ad infinitum* (the repetition of the replicas is suggested by the dots in the figure). Inside each of the two replicas some primitive cells of the microscopic lattice $\mathcal{R}_\mu$ are shown ($1, \dots, 6$). The eigenfunction of the hamiltonian $\Psi(\vec{r})$ is defined on a whole supercell (say supercell A) and repeats itself periodically when we go to another supercell (say supercell B). The potential energy operator $U(\vec{r})$ is defined on a primitive cell of the microscopic lattice (for example, focus on the primitive cell 1) and repeats itself periodically, as indicated by the arrows, in all other microscopic primitive cells ($2, \dots, 6 \dots$); the “graph”ⁱⁱⁱ of $\Psi(\vec{r})$ is different (in the sense that it does *not* repeat) when we move in the solid sample from one microscopic primitive cell to another. Of course, the portion of the graph of $\Psi(\vec{r})$ contained, for example, in the primitive cell 1 is identical to that contained in the primitive cell 5, but this is simply because the two cells are periodic images of each other in the macroscopic Bravais lattice $\mathcal{R}_M$. However, the portion of the graph contained in the primitive cell 2 will be different from that contained in the primitive cell 6, or that contained in the primitive cell 4.

304.

The comparison between the macroscopic and the microscopic Bravais

	microscopic lattice: $\mathcal{R}_\mu$	macroscopic lattice: $\mathcal{R}_M$
cell vectors	$\vec{a}_1, \vec{a}_2, \vec{a}_3$	$\vec{A}_1 = N_1 \vec{a}_1, \vec{A}_2 = N_2 \vec{a}_2, \vec{A}_3 = N_3 \vec{a}_3$
cell volume	v	$V = N_1 N_2 N_3 v = N v$
periodic functions	$U(\vec{r}), u(\vec{r})$	$\Psi(\vec{r})$

Remember also that all the points of $\mathcal{R}_M$ are at the same time points of $\mathcal{R}_\mu$, while the opposite does not hold in general, that is: *not* all the points of $\mathcal{R}_\mu$ are at the same time points of $\mathcal{R}_M$ (property c. on p. 93).

4.3.2 Consequences of the periodic boundary conditions

305. We have seen that, by virtue of Bloch’s theorem, $\Psi(\vec{r})$ must satisfy the condition (eq. 528):

$$\Psi(\vec{r} + \vec{R}) = \exp(i\vec{k} \cdot \vec{R}) \Psi(\vec{r}) \quad \forall \vec{R} \in \mathcal{R}_\mu$$

Bloch’s theorem does not pose any limitation on the wave vector $\vec{k}$, leaving it free to vary *with continuity* in both modulus and direction. In fact, we saw (eq. 575) that this latter is a linear combination of the three vectors which define the primitive cell of the reciprocal lattice of $\mathcal{R}_\mu$ with coefficients that are *generic complex numbers*:

$$\vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3$$

(in the following, we will call the reciprocal lattice of $\mathcal{R}_\mu$ “microscopic reciprocal lattice” and will use the symbol $\mathcal{R}_\mu^*$ for it and $\mathcal{C}_\mu^*$ for its primitive cell).

However, as we will now easily see, the periodic boundary conditions 583 imply that the $\vec{k}$ vectors of Bloch’s theorem are *discrete*, that is: only certain wave vectors $\vec{k}$ are compatible with

ⁱⁱⁱIn the 3D case we cannot speak of the “graph” of $\Psi(\vec{r})$, at least not in the usual sense of the term: in this case $\Psi(\vec{r})$ is a function of three variables and so its graph would require a 4-dimensional space.

the conditions of Born and von Karman (the number of allowed wave vectors remains infinite, but now the $\vec{k}$'s become numerable).

Please, note that the quantization of the $\vec{k}$ vectors in Bloch's theorem is specifically a consequence of the periodic boundary conditions: as noted above, Bloch's theorem itself does not limit in any way the modulus or direction of the $\vec{k}$'s.

Let's see how the quantization of the $\vec{k}$ vectors follows from the periodic boundary conditions. Since the vectors $\vec{A}_j = N_j \vec{a}_j$, ($j=1,3$) are trivially vectors of both $\mathcal{R}_M$ and $\mathcal{R}_\mu$, eqs. 528 and 583 must hold at the same time:

$$\begin{aligned} \text{Bloch's theorem: eq. 528 : } \quad \Psi(\vec{r} + N_j \vec{a}_j) &= \exp(i\vec{k} \cdot N_j \vec{a}_j) \Psi(\vec{r}) \\ \text{periodic boundary conditions: eq. 583 : } \quad \Psi(\vec{r} + N_j \vec{a}_j) &= \Psi(\vec{r}) \\ j &= 1, 3 \end{aligned}$$

By comparison we deduce that it must be:

$$\exp(i\vec{k} \cdot N_j \vec{a}_j) = 1 \quad (584)$$

Replacing $\vec{k}$ with expression 575 we obtain:

$$\exp(i\vec{k} \cdot N_j \vec{a}_j) = \exp\left(iN_j \left(x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3\right) \cdot \vec{a}_j\right) = \exp(iN_j 2\pi x_j) = 1 \quad (585)$$

(recall that $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$, eq. 135)

The last equality can be satisfied if and only if the argument of the exponential is an integer multiple of 2π , that is:

$$N_j x_j = m_j \implies x_j = \frac{m_j}{N_j} \quad m_j \in \mathbb{Z} \quad (586)$$

306. As anticipated, the periodic boundary conditions limit the possible wave vector appearing in the statement of Bloch's theorem to only the ones given by:

$$\vec{k} = \frac{m_1}{N_1} \vec{b}_1 + \frac{m_2}{N_2} \vec{b}_2 + \frac{m_3}{N_3} \vec{b}_3 \quad m_1, m_2, m_3 \in \mathbb{Z} \quad (587)$$

and since the m_i 's are integers, the wave vectors are *discrete*.

Note also that, as I mentioned on p. 186, the coefficients appearing in the expression of $\vec{k}$ (eq. 575) must be pure real numbers, because they are ratios of integer numbers.

4.3.2.1 The allowed wave vectors are all and only the points of the macroscopic reciprocal lattice

307. In point 299 et seq. we said that the macroscopic solid sample we consider is a supercell (defined by the vectors $\vec{A}_j = N_j \vec{a}_j$, $j = 1, 3$) of the microscopic primitive cell $\mathcal{C}_\mu$. The periodic boundary conditions have introduced a macroscopic lattice $\mathcal{R}_M$, whose primitive cell $\mathcal{C}_M$ is the above mentioned supercell (section 4.3.1).

The vectors $\vec{B}_i$ which define the primitive cell of the reciprocal lattice of $\mathcal{R}_M$ (in the following, for brevity, "the macroscopic reciprocal lattice", symbol: $\mathcal{R}_M^*$, symbol for its primitive cell: $\mathcal{C}_M^*$) are given by (eq. 159):

$$\vec{B}_1 = 2\pi \frac{N_2 \vec{a}_2 \times N_3 \vec{a}_3}{N_1 \vec{a}_1 \cdot N_2 \vec{a}_2 \times N_3 \vec{a}_3} = \frac{1}{N_1} 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{1}{N_1} \vec{b}_1 \quad (588)$$

$$\vec{B}_2 = 2\pi \frac{N_3 \vec{a}_3 \times N_1 \vec{a}_1}{N_1 \vec{a}_1 \cdot N_2 \vec{a}_2 \times N_3 \vec{a}_3} = \frac{1}{N_2} 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{1}{N_2} \vec{b}_2 \quad (589)$$

$$\vec{B}_3 = 2\pi \frac{N_1 \vec{a}_1 \times N_2 \vec{a}_2}{N_1 \vec{a}_1 \cdot N_2 \vec{a}_2 \times N_3 \vec{a}_3} = \frac{1}{N_3} 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{1}{N_3} \vec{b}_3 \quad (590)$$

where the $\vec{b}_i$'s are the vectors defining $\mathcal{C}_\mu^*$.

If you review eq. 587, you immediately realize that it can be rewritten as:

$$\vec{k} = m_1 \vec{B}_1 + m_2 \vec{B}_2 + m_3 \vec{B}_3 \quad m_1, m_2, m_3 \in \mathbb{Z} \quad (591)$$

which precisely means that the allowed wave vectors are all and only the points of $\mathcal{R}_M^*$.

308. Let's take stock of the current situation.

For a cristalline solid sample commensurate with its primitive cell (which is, therefore, a $N_1 \times N_2 \times N_3$ supercell of the primitive cell of the Bravais lattice underlying the crystal structure), we are studying the monoelectronic and stationary Schrödinger equation:

$$\begin{aligned} \left(-\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) \right) \Psi(\vec{r}) &= \epsilon \Psi(\vec{r}) \\ U(\vec{r} + \vec{R}) &= U(\vec{r}) \quad \forall \vec{R} \in \mathcal{R}_\mu \\ \Psi(\vec{r} + \vec{Q}) &= \Psi(\vec{r}) \quad \forall \vec{Q} \in \mathcal{R}_M \end{aligned}$$

with periodic boundary conditions.

Thanks to Bloch's theorem and to the periodic boundary conditions we can claim that the solution must be of the following type:

$$\Psi_{\vec{k}n}(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) u_{\vec{k}n}(\vec{r}) \quad (592)$$

with $u_{\vec{k}n}(\vec{r})$ periodic on $\mathcal{R}_\mu$ and $\vec{k} \in \mathcal{R}_M^*$.

Note how the indexing of the solutions (which we anticipated in eq. 526) has been partially clarified: each solution is indexed by an allowed wave vector $\vec{k}$, namely by the three integers which define the latter through eq. 591. Those integers are thus three quantum numbers for our solution. We are still left with the task of clarifying the fourth index n : for that, you must have a little more of your patience (point 327).

4.3.3 Comparison of the two reciprocal lattices $\mathcal{R}_\mu^*$ and $\mathcal{R}_M^*$

309. We have introduced the microscopic and macroscopic lattices: $\mathcal{R}_\mu$ and $\mathcal{R}_M$.

The former is the lattice defined by the primitive vectors $\vec{a}_i$ and underlies the crystal structure of the solid sample; the latter was introduced by the adoption of the periodic boundary conditions of Born and von Karman, and is defined by the primitive vectors $\vec{A}_i = N_i \vec{a}_i$, that is by the sides of the parallelepiped which constitutes the macroscopic sample.

The two direct lattices are strictly related: they are commensurate with each other; $\mathcal{R}_M$ (the less “dense”) is “immersed” into $\mathcal{R}_\mu$, the “denser”: all points of $\mathcal{R}_M$ are also points of $\mathcal{R}_\mu$, while the viceversa does not hold.

Like any other Bravais lattice, each of the two direct lattices has a corresponding reciprocal lattice:

$$\begin{aligned}\mathcal{R}_\mu &\implies \mathcal{R}_\mu^* \\ \mathcal{R}_M &\implies \mathcal{R}_M^*\end{aligned}$$

310. The expressions relating the primitive vectors of the two reciprocal lattices derived in point 307 can be rewritten as:

$$\vec{b}_1 = N_1 \vec{B}_1 \quad (593)$$

$$\vec{b}_2 = N_2 \vec{B}_2 \quad (594)$$

$$\vec{b}_3 = N_3 \vec{B}_3 \quad (595)$$

From which it follows that the primitive cell of the microscopic reciprocal lattice ($\mathcal{R}_\mu^*$) is a $(N_1 \times N_2 \times N_3)$ supercell of that of the macroscopic reciprocal lattice ($\mathcal{R}_M^*$).

From this, in turn, it immediately follows that:

1. $\mathcal{R}_\mu^*$ and $\mathcal{R}_M^*$ are commensurate, with, at the opposite of what happens for the corresponding direct lattices, $\mathcal{R}_\mu^*$ “immersed” into $\mathcal{R}_M^*$ (so, this time, $\mathcal{R}_\mu^*$ is less “dense” and $\mathcal{R}_M^*$ is “denser”)
2. the primitive cell of $\mathcal{R}_\mu^*$, $\mathcal{C}_\mu^*$, contains $N = N_1 N_2 N_3$ allowed $\vec{k}$ vectors, since a single allowed $\vec{k}$ point is contained in a single primitive cell $\mathcal{C}_M^*$ of $\mathcal{R}_M^*$
3. letting v^* and V^* be the volumes of $\mathcal{C}_\mu^*$ and $\mathcal{C}_M^*$, respectively, we have:

$$v^* = NV^* \quad (596)$$

Remember that $N = N_1 N_2 N_3$ is the number of primitive cells of the direct microscopic lattice ($\mathcal{R}_\mu$) contained in the solid sample: a huge number.

Note the symmetry: in point 299 we saw that the primitive cell of $\mathcal{R}_M$ is a $(N_1 \times N_2 \times N_3)$ supercell of that of $\mathcal{R}_\mu$; when we consider the reciprocal cells the situation is perfectly specular.

In less formal, but more intuitive terms:

$$\text{larger direct cell} \iff \text{smaller reciprocal cell}$$

(the umpteenth reciprocity relation: we have seen this inverse proportionality in general in section 2.6.3)

The situation is illustrated in figure 65 for the bidimensional case. I have drawn 6 primitive cells of $\mathcal{R}_\mu^*$, $A \dots F$, whose generator vectors are $\vec{b}_1$ and $\vec{b}_2$; a primitive cell of $\mathcal{R}_M^*$ is also highlighted (up/left), whose generator vectors are $\vec{B}_1 = \vec{b}_1/4$ e $\vec{B}_2 = \vec{b}_2/3$ ^{iv}.

^{iv}As already noted for figure 63, also for this figure the relative dimensions of the two reciprocal cells are not realistic: keep always in mind that $N = N_1 N_2 N_3$ is of the order of Avogadro’s number.

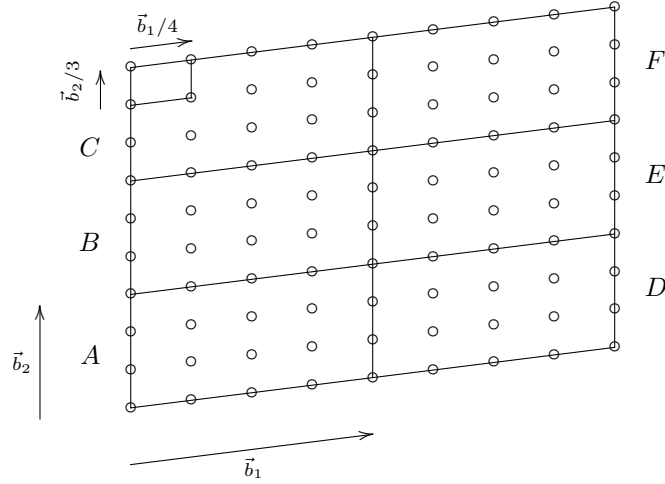


Figure 65: Relation between the microscopic reciprocal lattice $\mathcal{R}_\mu^*$, cells A – F, and the macroscopic reciprocal lattice $\mathcal{R}_M^*$, of which only the primitive cell in the up/left part of the figure has been highlighted.

Thus, in the bidimensional example of the figure, $\mathcal{C}_\mu^*$ is a (4×3) supercell of $\mathcal{C}_M^*$ and therefore contains $4 \times 3 = 12$ primitive cells of $\mathcal{R}_M^*$, that is 12 allowed $\vec{k}$ points.

As already noted for the direct lattices (point 304), all the points of $\mathcal{R}_\mu^*$ (larger primitive cell) are at the same time points of $\mathcal{R}_M^*$ (smaller primitive cell); the opposite is not true, that is *not all* the points of $\mathcal{R}_M^*$ are also points of $\mathcal{R}_\mu^*$.

311. It is still worth noting that the volume $\Delta\vec{k}$ of reciprocal space *per* allowed $\vec{k}$ point is clearly equal to the volume of $\mathcal{C}_M^*$, that is, as we established in general in section 2.6.3:

$$\Delta\vec{k} = \frac{(2\pi)^3}{V} \quad (597)$$

where V is the volume of the solid sample.

4.4 The central equation

312. We will now derive an equation, which Kittel⁵ calls *the central equation*, that gives the formal solution to the Schrödinger equation which we are dealing with.

As an additional bonus, the central equation offers a second proof of Bloch's theorem (point 331). I anticipate here the layout of the derivation.

Since the potential operator is periodic on the microscopic lattice $\mathcal{R}_\mu$, we can expand it in a Fourier series on the points of $\mathcal{R}_\mu^*$ (time to review the chapter about the Fourier series and point 51 in particular).

Similarly, since $\Psi(\vec{r})$ is periodic on the macroscopic lattice $\mathcal{R}_M$, we can expand it in a Fourier series on the points of $\mathcal{R}_M^*$ (which, recall, are also the allowed $\vec{k}$ points, point 307).

Of course, since $\Psi(\vec{r})$ is unknown, so will be the coefficients of its Fourier expansion: we turn the task of finding $\Psi(\vec{r})$ into the task of finding its Fourier coefficients.

We will plug the two Fourier expansions into the Schrödinger equation and we will derive an equation (the central equation, precisely) from the solution of which it is possible to obtain the Fourier coefficients of $\Psi(\vec{r})$, which is our target.

Besides the Fourier coefficients of the unknown wave function, the central equation will contain also its corresponding eigenvalue, which is another unknown to be sorted out.

Actually, as you will see, the equation we will arrive at is a homogeneous system of infinite dimension, therefore an object quite difficult to deal with. Despite of this, the central equation is a tool of paramount importance in solid state physics, from both a practical point of view (in the sense that it represents the starting point for almost all the computational methods) and a theoretical standpoint.

4.4.1 The re-edition of Schrödinger's equation in Fourier space

(In this part I will use the notation of Kittel and Ibach e Lüth, according to which the points of $\mathcal{R}_\mu^*$ are denoted with the symbol $\vec{G}$ while those of $\mathcal{R}_M^*$ are denoted with the symbol $\vec{k}$)

313. Before diving into the math, a foreword is appropriate.

In the course of this derivation we will make use of the properties of commensurate lattices which were introduced in general in section 2.3.1. In particular, we will take advantage of property f.. Now: in section 2.3.1 we did speak about two commensurate *direct* lattices; but everything holds unchanged in our present context, where we are dealing with the reciprocal lattices $\mathcal{R}_\mu^*$ and $\mathcal{R}_M^*$: you already know very well that the reciprocal lattice *is* a Bravais lattice (2.6.1) and we have established in point 310 that $\mathcal{R}_\mu^*$ and $\mathcal{R}_M^*$ are commensurate. It should be clear that the correspondence between the present situation and the general statements in section 2.3.1 is:

present section	section 2.3.1
$\mathcal{R}_M^*$	$\mathcal{R}_S$
$\mathcal{R}_\mu^*$	$\mathcal{R}_B$

314. As anticipated, being periodic over $\mathcal{R}_\mu$, we can expand the potential $U(\vec{r})$ in Fourier series in the following way:

$$U(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}) \quad \vec{G} \in \mathcal{R}_\mu^* \quad (598)$$

where the sum runs over all the vectors $\vec{G}$ of the microscopic reciprocal lattice:

$$\vec{G} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3 \quad m_1, m_2, m_3 \in \mathbb{Z} \quad (599)$$

($\vec{b}_1, \vec{b}_2, \vec{b}_3$ are the primitive vectors of $\mathcal{R}_\mu^*$)

The $U_{\vec{G}}$'s are the Fourier coefficients of the potential (eq. 153):

$$U_{\vec{G}} = \frac{1}{v} \int_{\mathcal{C}_\mu} U(\vec{r}) \exp(-i\vec{G} \cdot \vec{r}) d\vec{r} \quad (600)$$

and the integral is evaluated on the volume v of the primitive cell $\mathcal{C}_\mu$ of the direct microscopic lattice. Note that we assume that the $U_{\vec{G}}$'s are known, since the potential is assumed to be known^v.

315. Similarly, being periodic over $\mathcal{R}_M$ (by virtue of the periodic boundary conditions), we can expand the unknown wave function in Fourier series:

^vActually, also the definition of the potential $U(\vec{r})$ is far from simple. In fact, as I mentioned in point 289, usually it is an "effective" potential which has to take into account and compensate as best as possible for the many approximations without which tackling this problem would be simply impossible; however, in principle, we assume $U(\vec{r})$ to be known in our context.

$$\Psi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) \quad \vec{k} \in \mathcal{R}_M^* \quad (601)$$

where the sum runs over all the $\vec{k}$ points of $\mathcal{R}_M^*$.

The $C_{\vec{k}}$ coefficients are our unknowns: finding them means to solve the Schrödinger problem, since the wave function is then given by the above written sum.

316. Now we plug the two Fourier expansions into the Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right)\Psi(\vec{r}) = \epsilon\Psi(\vec{r}) \quad (602)$$

to obtain:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \sum_{\vec{G}} U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r})\right) \sum_{\vec{k}} C_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) = \epsilon \sum_{\vec{k}} C_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) \quad (603)$$

For what concerns the action of the first term of the hamiltonian on the sum over $\vec{k}$ we have:

$$-\frac{\hbar^2}{2m}\nabla^2 \left(\sum_{\vec{k}} C_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) \right) = \sum_{\vec{k}} -\frac{\hbar^2}{2m} C_{\vec{k}} \nabla^2 \exp(i\vec{k} \cdot \vec{r}) \quad (604)$$

The following holds:

$$\begin{aligned} \nabla^2 \exp(i\vec{k} \cdot \vec{r}) &= \\ \frac{\partial^2}{\partial x^2} \exp(i(k_x x + k_y y + k_z z)) &+ \frac{\partial^2}{\partial y^2} \exp(i(k_x x + k_y y + k_z z)) + \\ \frac{\partial^2}{\partial z^2} \exp(i(k_x x + k_y y + k_z z)) &= \\ ik_x \frac{\partial}{\partial x} \exp(i(k_x x + k_y y + k_z z)) &+ ik_y \frac{\partial}{\partial y} \exp(i(k_x x + k_y y + k_z z)) + \\ ik_z \frac{\partial}{\partial z} \exp(i(k_x x + k_y y + k_z z)) &= \\ (ik_x)^2 \exp(i(k_x x + k_y y + k_z z)) &+ (ik_y)^2 \exp(i(k_x x + k_y y + k_z z)) + \\ (ik_z)^2 \exp(i(k_x x + k_y y + k_z z)) &= \\ -(k_x^2 + k_y^2 + k_z^2) \exp(i\vec{k} \cdot \vec{r}) &= -k^2 \exp(i\vec{k} \cdot \vec{r}) \end{aligned} \quad (605)$$

In conclusion, substituting above:

$$-\frac{\hbar^2}{2m}\nabla^2 \left(\sum_{\vec{k}} C_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) \right) = \sum_{\vec{k}} \frac{\hbar^2}{2m} k^2 C_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) \quad (606)$$

317. Now we must work out the action of the second term of the hamiltonian on the wave function.

To this end, we take advantage of the following fact.

Claim: it holds:

$$\Psi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) = \sum_{\vec{k}} C_{\vec{k}-\vec{G}} \exp(i(\vec{k}-\vec{G}) \cdot \vec{r}) \quad (607)$$

where $\vec{G}$ is a given (fixed) vector of the microscopic reciprocal lattice $\mathcal{R}_{\mu}^*$.

The justification is simple.

Since the index of the sum runs over all the *infinite* $\vec{k}$ points and since there is always a vector $\vec{G}$ connecting two $\vec{k}$ points (belonging to the same subset generated by a $\vec{k}$ point inside a given primitive cell of $\mathcal{R}_{\mu}^*$, property f. in section 2.3.1), the two sums contain exactly the same terms. In other words, the j -th term:

$$C_{\vec{k}_j} \exp(i\vec{k}_j \cdot \vec{r}) \quad (608)$$

is obtained when $\vec{k} = \vec{k}_j$ in the first sum or, equivalently, when $\vec{k} = \vec{k}_j + \vec{G}$ in the second one.

318. Based on what just established, for the reason which will be clear in a moment, having to evaluate the result of applying the potential energy operator on the wave function it is convenient to rewrite its Fourier expansion as the RHS of equality 607.

Thus:

$$\begin{aligned} & \sum_{\vec{G}} U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}) \left(\sum_{\vec{k}} C_{\vec{k}-\vec{G}} \exp(i(\vec{k}-\vec{G}) \cdot \vec{r}) \right) \\ &= \sum_{\vec{G}} \left(U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}) \underbrace{\sum_{\vec{k}} C_{\vec{k}-\vec{G}} \exp(i(\vec{k}-\vec{G}) \cdot \vec{r})}_{\text{under-brace}} \right) \end{aligned}$$

This is a sum over $\vec{G}$ of sums over $\vec{k}$. Then, in each of the sums over $\vec{k}$ (highlighted with the under-brace) we take as the fixed $\vec{G}$ vector of 607 the same one which indexes $U_{\vec{G}}$; this allows us to move $U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r})$ inside the sum over $\vec{k}$:

$$\begin{aligned} &= \sum_{\vec{G}} \sum_{\vec{k}} U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}) C_{\vec{k}-\vec{G}} \exp(i(\vec{k}-\vec{G}) \cdot \vec{r}) \\ &= \sum_{\vec{k}} \sum_{\vec{G}} U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}) C_{\vec{k}-\vec{G}} \exp(i(\vec{k}-\vec{G}) \cdot \vec{r}) \\ &= \sum_{\vec{k}} \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} \exp(i\vec{k} \cdot \vec{r}) \quad (609) \end{aligned}$$

(do you see now why rewriting the sum as shown in 607 was convenient? that has allowed us to make the $\vec{G}$ vector in the argument of the exponential “disappear”)

319. Ultimately, Schrödinger’s equation becomes:

$$\sum_{\vec{k}} \frac{\hbar^2}{2m} k^2 C_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) + \sum_{\vec{k}} \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} \exp(i\vec{k} \cdot \vec{r}) = \epsilon \sum_{\vec{k}} C_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) \quad (610)$$

or, collapsing the three sums over $\vec{k}$ into a single sum and factoring out the term $\exp(i\vec{k} \cdot \vec{r})$:

$$\sum_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) \left\{ \left(\frac{\hbar^2}{2m} k^2 - \epsilon \right) C_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} \right\} = 0 \quad (611)$$

Note that the expression we have just obtained is nothing but a re-edition of Schrödinger's equation "in the space of Fourier coefficients"; that is, we have turned the problem of integrating a partial differential equation in which the unknown is a function, into the algebraic problem of solving an equation in which the unknowns are the coefficients $C_{\vec{k}}$ of the Fourier expansion of $\Psi(\vec{r})$, plus the corresponding eigenvalue ϵ .

The LHS of the equation is an infinite sum which runs over all the $\vec{k}$ vectors of the macroscopic reciprocal lattice $\mathcal{R}_M^*$.

Each term of the sum in 611 is the product of a plane wave of the Fourier expansion and the term between braces.

320. Now: since eq. 611 must hold for *any* $\vec{r}$ and the exponential can not be null, the only way the equation can be satisfied is that all the factors which multiply the plane waves:

$$\left\{ \left(\frac{\hbar^2}{2m} k^2 - \epsilon \right) C_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} \right\} \quad (612)$$

must be null (I provide an alternative (somehow more formal) proof of this claim in the extracurricular part 4.1).

That is:

$$\left(\frac{\hbar^2}{2m} k^2 - \epsilon \right) C_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} = 0 \quad \forall \vec{k} \in \mathcal{R}_M^* \quad (613)$$

This is the final form of the central equation.

321. As you can see, the central equation is not actually a single equation, but rather a linear homogeneous system counting an infinite number of equations: there are as many equations as there are $\vec{k}$ vectors (note the " $\forall \vec{k} \in \mathcal{R}_M^*$ " in 916).

The unknowns to be sorted out are the $C_{\vec{k}}$ coefficients and the ϵ eigenvalues.

As you probably already learned from other quantum chemistry courses, the general technique to solve such systems is the following.

The system admits a so called "trivial" solution in which all the $C_{\vec{k}}$'s are identically null. Of course, this is uninteresting and one wants to find non-trivial solutions, i.e. solutions for which *not all* the $C_{\vec{k}}$'s are identically null.

The condition to be satisfied such that the system admits non-trivial solutions is that the determinant built with the coefficients that multiply the $C_{\vec{k}}$'s is null. By imposing this condition a so called *secular equation* is obtained:

$$P(\epsilon) = 0$$

where $P(\epsilon)$ is a polynomial in the ϵ unknown.

The solution of the secular equation gives all the possible eigenvalues of the problem (in very simplistic terms, the polynomial equation admits as many solutions as the degree of the polynomial).

When all the possible ϵ values have been found, they are plugged back one by one in the original system, which can now be solved for the set of $C_{\vec{k}}$'s (that is, a $\Psi(\vec{r})$ function, via 601) corresponding to each ϵ value.

4.4.2 The structure of the central equation

(**Beware:** also for this part it is crucial to keep in mind that $\mathcal{R}_\mu^*$ and $\mathcal{R}_M^*$ are commensurate (point 310) and I warmly suggest you to review/refresh all the discussion in section 2.3.1, with the correspondance map I already showed you in point 313.)

322. It is important to understand very well the structure of the central equation.

First of all: each equation of the system is indexed by a specific $\vec{k}$ vector (realize that each equation contains a *single* $\vec{k}$ vector: the one in $C_{\vec{k}-\vec{G}}$ is the same as that in $C_{\vec{k}}$ because the sum is over the $\vec{G}$'s); the number of equations is equal to the number of $\vec{k}$ vectors, that is: an infinite number.

The equation corresponding to a given $\vec{k}$ vector contains a sum of $U_{\vec{G}}C_{\vec{k}-\vec{G}}$ terms, each indexed by a $\vec{G}$ vector (point of $\mathcal{R}_\mu^*$); the number of terms in the sum is equal to the number of $\vec{G}$ vectors, that is, again, an infinite number.

So you see that the central equation looks like a formidable problem: a system of infinite dimension of equations each containing an infinite number of terms.

323. Nevertheless, the difficulty in handling the central equation can be mitigated with the following possible rearrangement (attention: this is a crucial step!):

Claim:

The whole system 916 can be partitioned into a *finite* number of subsystems, each being solvable independently from the others.

To see how this can be achieved let's start by considering a given primitive cell of the microscopic reciprocal lattice $\mathcal{R}_\mu^*$: almost invariably, even if this would not be necessary in principle, the first Brillouin zone is taken as this reference primitive cell (point 2.6.4 on p. 105) (from here on, when I will mention the first Brillouin zone, I will always refer to the first Brillouin zone of $\mathcal{R}_\mu^*$; moreover, I will use the symbol $\mathcal{B}_Z$ to represent it). We know that such cell (as any other primitive cell of $\mathcal{R}_\mu^*$) contains N $\vec{k}$ points of the macroscopic reciprocal lattice $\mathcal{R}_M^*$ (point 301): let's number these N $\vec{k}$ points inside the $\mathcal{B}_Z$ from 1 to N : $\vec{k}_1, \vec{k}_2, \dots, \vec{k}_N$.

Suppose also to number (in some way: the precise numbering algorithm is unimportant) all the vectors of $\mathcal{R}_\mu^*$: $\vec{G}_1, \vec{G}_2, \vec{G}_3, \dots$ (note: while the $\vec{k}$ vectors inside the $\mathcal{B}_Z$ are in a finite number, N , the $\vec{G}$'s are infinite). Among the $\vec{G}$ vectors there is also the null vector (i.e. the point of $\mathcal{R}_\mu^*$ at the origin): for the reason that will be clear in a moment, let $\vec{G}_1$ be such null vector.

324. Let's now consider the *subsystem* of 916 composed by the equation indexed by $\vec{k}_1$, inside the $\mathcal{B}_Z$, plus all the equations corresponding to the $\vec{k}$ vectors given by:

$$\vec{k}_1 - \vec{G}_i \quad i = 2, \dots, \infty$$

(Note: i starts from 2 to avoid overcounting $\vec{k}_1$. In fact, since we have assumed $\vec{G}_1 = 0$ (above), the point $\vec{k}_1 - \vec{G}_1$ would just coincide with $\vec{k}_1$, which therefore would get counted twice)

It is important to realize here that $\vec{k}_1 - \vec{G}_i$ is still a point of $\mathcal{R}_M^*$ (because $\mathcal{R}_\mu^*$ and $\mathcal{R}_M^*$ are commensurate: see p. f.). Therefore there will be one (and only one) equation of the system 916 indexed by $\vec{k}_1 - \vec{G}_i$: this equation will be that whose first term (the one not involved in the sum over $\vec{G}$) contains $\vec{k}_1 - \vec{G}_i$. In math notation:

$$\forall i \in \mathbb{N} \exists! \vec{k} \in \mathcal{R}_M^* : \left\{ \begin{array}{l} \vec{k} = \vec{k}_1 - \vec{G}_i \\ \left(\frac{\hbar^2}{2m} \underbrace{|\vec{k}_1 - \vec{G}_i|^2}_{|\vec{k}|^2 = k^2} - \epsilon \right) C_{\underbrace{\vec{k}_1 - \vec{G}_i}_{\vec{k}}} + \sum_{\vec{G}} U_{\vec{G}} C_{\underbrace{\vec{k}_1 - \vec{G}_i - \vec{G}}_{\vec{k}}} = 0 \end{array} \right.$$

(please, thoroughly convince yourself that the above equation is the one indexed by the vector $\vec{k}_1 - \vec{G}_i$ among the infinite equations represented by 916; if you cannot, come to my room and I will convince you!)

The subsystem we obtain in this way is:

$$\begin{aligned} & \left(\frac{\hbar^2 k_1^2}{2m} - \epsilon \right) C_{\vec{k}_1} + U_{\vec{G}_1} C_{\vec{k}_1 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_1 - \vec{G}_2} + \dots = 0 \\ & \left(\frac{\hbar^2 \underbrace{|\vec{k}_1 - \vec{G}_2|^2}}{2m} - \epsilon \right) C_{\underbrace{\vec{k}_1 - \vec{G}_2}_{\vec{k}}} + U_{\vec{G}_1} C_{\underbrace{\vec{k}_1 - \vec{G}_2 - \vec{G}_1}_{\vec{k}}} + U_{\vec{G}_2} C_{\underbrace{\vec{k}_1 - \vec{G}_2 - \vec{G}_2}_{\vec{k}}} + \dots = 0 \\ & \left(\frac{\hbar^2 \underbrace{|\vec{k}_1 - \vec{G}_3|^2}}{2m} - \epsilon \right) C_{\underbrace{\vec{k}_1 - \vec{G}_3}_{\vec{k}}} + \overbrace{U_{\vec{G}_1} C_{\underbrace{\vec{k}_1 - \vec{G}_3 - \vec{G}_1}_{\vec{k}}} + U_{\vec{G}_2} C_{\underbrace{\vec{k}_1 - \vec{G}_3 - \vec{G}_2}_{\vec{k}}} + \dots}^{\sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}_1 - \vec{G}_3 - \vec{G}}} = 0 \\ & \dots \end{aligned}$$

I have highlighted with an over/underbrace the $\vec{k}$ vector, expressed as $\vec{k}_1 - \vec{G}_i$, which indexes the second and third equations, to make clearer the comparison with the general expression 916. I have also written explicitly the sum over the $\vec{G}$ vectors: note that in such sum *all* the $\vec{G}$ vectors are included, so also $\vec{G}_1$ appears in it.

The first equation above might have been written as:

$$\left(\frac{\hbar^2 \underbrace{|\vec{k}_1 - \vec{G}_1|^2}}{2m} - \epsilon \right) C_{\vec{k}_1 - \vec{G}_1} + U_{\vec{G}_1} C_{\vec{k}_1 - \vec{G}_1 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_1 - \vec{G}_1 - \vec{G}_2} + \dots = 0 \quad (614)$$

but, as already noted, we have assumed $\vec{G}_1 = 0$ and thus, by writing $\vec{k}_1$ instead of $\vec{k}_1 - \vec{G}_1$, I want to better emphasize that $\vec{k}_1$ is inside the $\mathcal{B}_Z$, while all other points $\vec{k}_1 - \vec{G}_i$, $i = 2, \dots, \infty$ are outside it.

325. If we now do the same thing with the remaining $\vec{k}$ points inside the $\mathcal{B}_Z$, $\vec{k}_2, \vec{k}_3, \dots, \vec{k}_N$, we get the N subsystems shown in figure 66.

326. Now comes a fundamental observation.

From figure 66 you see that each subsystem contains only the coefficients corresponding to a $\vec{k}$ point inside the $\mathcal{B}_Z$, say $\vec{k}_j$, and to all the $\vec{k}$ points related to the latter by a $\vec{G}$ translation, i.e. $\vec{k}_j - \vec{G}_i$.

subsystem corresponding to eqs indexed by $\vec{k}_1$ and $\vec{k}_1 - \vec{G}_i$

$$\begin{aligned} & \left(\frac{\hbar^2 k_1^2}{2m} - \epsilon \right) C_{\vec{k}_1} + U_{\vec{G}_1} C_{\vec{k}_1 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_1 - \vec{G}_2} + \cdots = 0 \\ & \left(\frac{\hbar^2 |\vec{k}_1 - \vec{G}_2|^2}{2m} - \epsilon \right) C_{\vec{k}_1 - \vec{G}_2} + U_{\vec{G}_1} C_{\vec{k}_1 - \vec{G}_2 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_1 - \vec{G}_2 - \vec{G}_2} + \cdots = 0 \\ & \left(\frac{\hbar^2 |\vec{k}_1 - \vec{G}_3|^2}{2m} - \epsilon \right) C_{\vec{k}_1 - \vec{G}_3} + U_{\vec{G}_1} C_{\vec{k}_1 - \vec{G}_3 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_1 - \vec{G}_3 - \vec{G}_2} + \cdots = 0 \\ & \cdots (\text{infinite equations indexed by } \vec{k}_1 - \vec{G}_i) \end{aligned}$$

subsystem corresponding to eqs indexed by $\vec{k}_2$ and $\vec{k}_2 - \vec{G}_i$

$$\begin{aligned} & \left(\frac{\hbar^2 k_2^2}{2m} - \epsilon \right) C_{\vec{k}_2} + U_{\vec{G}_1} C_{\vec{k}_2 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_2 - \vec{G}_2} + \cdots = 0 \\ & \left(\frac{\hbar^2 |\vec{k}_2 - \vec{G}_2|^2}{2m} - \epsilon \right) C_{\vec{k}_2 - \vec{G}_2} + U_{\vec{G}_1} C_{\vec{k}_2 - \vec{G}_2 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_2 - \vec{G}_2 - \vec{G}_2} + \cdots = 0 \\ & \left(\frac{\hbar^2 |\vec{k}_2 - \vec{G}_3|^2}{2m} - \epsilon \right) C_{\vec{k}_2 - \vec{G}_3} + U_{\vec{G}_1} C_{\vec{k}_2 - \vec{G}_3 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_2 - \vec{G}_3 - \vec{G}_2} + \cdots = 0 \\ & \cdots (\text{infinite equations indexed by } \vec{k}_2 - \vec{G}_i) \end{aligned}$$

...

subsystem corresponding to eqs indexed by $\vec{k}_N$ and $\vec{k}_N - \vec{G}_i$

$$\begin{aligned} & \left(\frac{\hbar^2 k_N^2}{2m} - \epsilon \right) C_{\vec{k}_N} + U_{\vec{G}_1} C_{\vec{k}_N - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_N - \vec{G}_2} + \cdots = 0 \\ & \left(\frac{\hbar^2 |\vec{k}_N - \vec{G}_2|^2}{2m} - \epsilon \right) C_{\vec{k}_N - \vec{G}_2} + U_{\vec{G}_1} C_{\vec{k}_N - \vec{G}_2 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_N - \vec{G}_2 - \vec{G}_2} + \cdots = 0 \\ & \left(\frac{\hbar^2 |\vec{k}_N - \vec{G}_3|^2}{2m} - \epsilon \right) C_{\vec{k}_N - \vec{G}_3} + U_{\vec{G}_1} C_{\vec{k}_N - \vec{G}_3 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_N - \vec{G}_3 - \vec{G}_2} + \cdots = 0 \\ & \cdots (\text{infinite equations indexed by } \vec{k}_N - \vec{G}_i) \end{aligned}$$

Figure 66: The system 916 can be partitioned into N independent subsystems, each indexed by one of the N $\vec{k}$ points inside the $\mathcal{B}_{\mathcal{Z}}$.

In math notation, the j -th subsystem contains only the coefficients corresponding to the $\vec{k}$ points in the subset S_j , defined by:

$$S_j = \left\{ \vec{k} : \vec{k} = \vec{k}_j - \vec{G}_i, \vec{k}_j \in \mathcal{B}_{\mathcal{Z}}, \vec{G}_i \in \mathcal{R}_{\mu}^* \right\} \quad (615)$$

If you now compare 615 with 274 a blazing glow should explode inside your head: the j -th subsystem contains only the coefficients corresponding to the $\vec{k}$ points of one of the subsets into which the whole set of (infinite) points of $\mathcal{R}_M^*$ can be partitioned.

(beware: do not be confused by the different sign of $\vec{k}_j - \vec{G}_i$ in 615 *versus* $\vec{r}_j + \vec{R}$ in 274: since *all* the infinite $\vec{G}_i$ or $\vec{R}$ vectors are used, summing or subtracting does not make any difference, since for any $\vec{G}_i$ or $\vec{R}$ vector, there will always be its corresponding opposite $-\vec{G}_i$ or $-\vec{R}$)

From the above two crucial remarks immediately follow:

- the N subsystems we have obtained (figure 66) do constitute a partition of the central equation (the original system); in less formal terms: in the N subsystems we did not “leak” any equation
- the coefficients appearing in a given subsystem do *not* appear in any other subsystem: which is to say that each subsystem can be solved independently from the others

327. Each subsystem has infinite solutions. We thus achieved the result of partitioning the original system of equations 916 into N independent linear homogeneous systems, each indexed by one of the N $\vec{k}$ points inside the first Brillouin zone. A single subsystem has still an infinite dimension (the number of equations is equal to the number of $\vec{G}$ vectors) and therefore has infinite solutions: recall that ϵ is an unknown to be found and there will be a solution (i.e. a set of $C_{\vec{k}_j - \vec{G}_i}$ coefficients) for each of the infinite possible ϵ values which satisfy the secular equation. Note that a given solution of a subsystem means a set of $C_{\vec{k}_j - \vec{G}_i}$ coefficients plus the corresponding ϵ eigenvalue. In turn, the set of coefficients means a corresponding $\Psi(\vec{r})$ function given by the expansion 601.

328. An additional integer index is required. Since a given subsystem corresponding to a given $\vec{k}$ point inside the $\mathcal{B}_{\mathcal{Z}}$ has infinite solutions, a single solution with its corresponding eigenvalue cannot be indexed by $\vec{k}$ alone: given $\vec{k} (\in \mathcal{B}_{\mathcal{Z}})$ we need another integer index n which enumerates all the solutions (eigenfunctions) and eigenvalues for the subsystem corresponding to that $\vec{k}$ point. This n index is the same which indexes the $\vec{G}$ vectors, in the sense that for a given subsystem (that is, for a given $\vec{k}$ point inside the $\mathcal{B}_{\mathcal{Z}}$), there are as many solutions as there are vectors of the microscopic reciprocal lattice ($\vec{G}_1, \vec{G}_2, \vec{G}_3, \dots$).

In other words, we label a particular solution of the Schrödinger equation 525 plus its eigenvalue with:

$$\Psi_{\vec{k}n}(\vec{r}) \text{ and } \epsilon_{\vec{k}n}$$

$\Psi_{\vec{k}n}(\vec{r})$ (and its corresponding eigenvalue $\epsilon_{\vec{k}n}$) is the n -th solution of the subsystem corresponding to the point $\vec{k}$ inside the $\mathcal{B}_{\mathcal{Z}}$ (fig. 66).

For quite obvious reasons, the index n is defined in such a way that the eigenvalues $\epsilon_{\vec{k}n}$ are sorted in order of increasing energy, that is:

$$\epsilon_{\vec{k}1} \leq \epsilon_{\vec{k}2} \leq \epsilon_{\vec{k}3} \leq \dots$$

As you can see, the nature of the second index (n) which I anticipated in the statement of Bloch’s theorem on p. 179 has been eventually clarified (note that, indeed, and differently from the wave

vector $\vec{k}$, the index n is not mentioned in any way by Bloch's theorem itself: I just wanted to introduce the symbol of the state function in its complete form from the very beginning).

329. Not all the $\vec{k}$ points of $\mathcal{R}_M^*$ are present in a given solution. A consequence of the above analysis is that a given solution of the central equation 916, corresponding to the allowed $\vec{k}_j$ point inside the $\mathcal{B}_Z$, will contain only the coefficients $C_{\vec{k}_j}$ and $C_{\vec{k}_j - \vec{G}_i}$ (i.e. the coefficients corresponding to only one of the N subsets 615): in other words, in the Fourier expansion of a given solution, not *all* the $\vec{k}$ points of $\mathcal{R}_M^*$ are present, but only those belonging to a single subset among the N subsets into which the whole set of $\vec{k}$ points can be partitioned (in equivalent terms: the coefficients not appearing in the expansion must be, evidently, null). For this reason, the Fourier expansion 601 can be conveniently rewritten as^{vi}:

$$\Psi_{\vec{k}n}(\vec{r}) = \sum_{\vec{G}} C_{(\vec{k}-\vec{G})n} \exp \left(i \left(\vec{k} - \vec{G} \right) \cdot \vec{r} \right) \quad (616)$$

where only the non-null coefficients (and corresponding exponential terms) are explicitly indicated (note that, as already remarked, $\vec{k} - \vec{G}$ is always a point of $\mathcal{R}_M^*$).

In 616 I have omitted the indexes for $\vec{k}$ and $\vec{G}$ for the sake of a lighter notation; on the other hand, I have explicitly added the index n to the coefficients which define the $\Psi_{\vec{k}n}(\vec{r})$; note also that the null $\vec{G}$ vector is included in the sum.

Eq. 616 makes evident the fact that in a particular solution indexed by the point $\vec{k}$ inside the $\mathcal{B}_Z$ and by the index n , not *all* the $\vec{k}$ points are present, but only the images of that particular $\vec{k}$ point which are generated by the infinite $\vec{G}$ translations of $\mathcal{R}_\mu^*$. As already noted, this means that in the Fourier expansion 601 all the coefficients different from $C_{\vec{k}-\vec{G}}$ with $\vec{k} \in \mathcal{B}_Z$ and $\vec{G} \in \mathcal{R}_\mu^*$ are necessarily null.

330. Each single subsystem still has infinite dimension. At this point a clarification is appropriate.

As you might have already realized, the central equation remains almost intractable: it's certainly true that we have partitioned it in a finite number of independent homogeneous linear systems (but note that this finite number is anyway huge: order of magnitude is always Avogadro's number); however, each system of the partition has still an infinite number of equations (equal to the number of all the $\vec{G}$ vectors).

Nonetheless, the central equation has an enormous theoretical value: thanks to it we were able to index and classify the solutions of Schrödinger's equation and discuss some of their properties. Moreover, as we will see in a moment, the central equation and eq. 616 deriving from it offer a second proof of Bloch's theorem.

I can also add that the central equation becomes a useful *practical* tool when it is possible (and properly justifiable):

- $\Rightarrow$ to truncate the Fourier expansions of $U(\vec{r})$ and $\Psi(\vec{r})$ to a *finite* (and manageable) number of terms
- $\Rightarrow$ to limit the number of $\vec{k}$ points to be considered inside the $\mathcal{B}_Z$

Under these conditions, both the number of subsystems to be solved and the dimension of each of them can become computationally manageable in practice.

^{vi}Beware: eqs. 616 and 607 may look very similar, but the " $\vec{k} - \vec{G}$ " term which enters both has a quite different interpretation. Eq. 607 is only an equivalent way to express the *whole* Fourier expansion of $\Psi(\vec{r})$: you can regard the $\vec{k} - \vec{G}$ term in it as a change of origin; the sum in 607 runs over *all* the $\vec{k}$ points and the $\vec{G}$ vector is fixed; at the opposite, in 616, the sum runs over all the $\vec{G}$ vectors and $\vec{k}$ is a fixed point inside the $\mathcal{B}_Z$. In other words: in 607 all the k points are present; in 616 only the k points of a single subset S_j (eq. 615) are present.

4.5 Another, independent, proof of Bloch's theorem

331. The central equation 916 and expression 616 for $\Psi_{\vec{k}n}(\vec{r})$ have been derived *without any reference to Bloch's theorem* (beware: in section 4.3.2 we combined Bloch's theorem and the periodic boundary conditions of Born and von Karman to show that the allowed wave vectors are discrete, eq. 587; but the derivation of the central equation is completely independent on Bloch's theorem); and, indeed, eq. 616 is an equivalent proof of Bloch's theorem.

To see why, rewrite 616 as:

$$\Psi_{\vec{k}n}(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) \overbrace{\sum_{\vec{G}} C_{(\vec{k}-\vec{G})n} \exp(-i\vec{G} \cdot \vec{r})}^{u_{\vec{k}n}(\vec{r})} = \exp(i\vec{k} \cdot \vec{r}) u_{\vec{k}n}(\vec{r}) \quad (617)$$

with:

$$u_{\vec{k}n}(\vec{r}) = \sum_{\vec{G}} C_{(\vec{k}-\vec{G})n} \exp(-i\vec{G} \cdot \vec{r}) \quad (618)$$

It is easy to verify that $u_{\vec{k}n}(\vec{r})$ is periodic on the direct microscopic lattice $\mathcal{R}_\mu$; indeed, for any translation vector $\vec{R} \in \mathcal{R}_\mu$ we have:

$$\begin{aligned} u_{\vec{k}n}(\vec{r} + \vec{R}) &= \sum_{\vec{G}} C_{(\vec{k}-\vec{G})n} \exp(-i\vec{G} \cdot (\vec{r} + \vec{R})) \\ &= \sum_{\vec{G}} C_{(\vec{k}-\vec{G})n} \exp(-i\vec{G} \cdot \vec{R}) \exp(-i\vec{G} \cdot \vec{r}) \\ &= \sum_{\vec{G}} C_{(\vec{k}-\vec{G})n} \exp(-i\vec{G} \cdot \vec{r}) = u_{\vec{k}n}(\vec{r}) \quad \forall \vec{R} \in \mathcal{R}_\mu \end{aligned} \quad (619)$$

because: $\exp(-i\vec{G} \cdot \vec{R}) = 1$ (p. 62).

But then eq. 617 precisely states the first form of Bloch's theorem (eq. 526).

Note that the vector $\vec{k}$ which indexes $\Psi(\vec{r})$ in 526 is the same $\vec{k}$ vector inside the $\mathcal{B}_Z$ which indexes the $\vec{k}$ -th subsystem in the central equation (section 4.4.2).

4.6 Periodicity of $\Psi_{\vec{k}n}(\vec{r})$ and $\epsilon_{\vec{k}n}$ in $\vec{k}$ space

332. From our analysis of the central equation it emerges that all the solutions of the Schrödinger equation 525 with boundary conditions 583 are indexed by the $\vec{k}$ vectors inside the $\mathcal{B}_Z$ (and by the index n , of course). This implicitly suggests that all the remaining points of $\mathcal{R}_M^*$ (i.e. the allowed $\vec{k}$ points *outside* the $\mathcal{B}_Z$) must be somehow “redundant”, that is, that they do not add anything new to what we were already able to obtain by limiting ourselves to the points inside the $\mathcal{B}_Z$ alone.

We can confirm that this is indeed the case in the following way.

Let's take back the expression 616 of the solution of Schrödinger's equation corresponding to a given $\vec{k}$ point inside the $\mathcal{B}_Z$ for a fixed n :

$$\Psi_{\vec{k}n}(\vec{r}) = \sum_{\vec{G}} C_{(\vec{k}-\vec{G})n} \exp\left(i\left(\vec{k}-\vec{G}\right) \cdot \vec{r}\right) \quad (620)$$

and let's ask ourselves what would be the eigenfunction corresponding to the point $\vec{k} + \vec{G}' \in \mathcal{R}_M^*$ (if $\vec{k}$ is inside the $\mathcal{B}_Z$, $\vec{k} + \vec{G}'$ is definitely outside it^{vii}).

By replacing $\vec{k}$ with $\vec{k} + \vec{G}'$ above we get:

$$\Psi_{(\vec{k}+\vec{G}')n}(\vec{r}) = \sum_{\vec{G}} C_{(\vec{k}+\vec{G}'-\vec{G})n} \exp \left(i \left(\vec{k} + \vec{G}' - \vec{G} \right) \cdot \vec{r} \right) \quad (621)$$

But $\vec{G}' - \vec{G}$ is still a translation vector of $\mathcal{R}_\mu^*$; then, letting:

$$\vec{G}'' = \vec{G} - \vec{G}' \quad (622)$$

the sum can be rewritten as:

$$\begin{aligned} \Psi_{(\vec{k}+\vec{G}')n}(\vec{r}) &= \sum_{\vec{G}''+\vec{G}'} C_{(\vec{k}-\vec{G}'')n} \exp \left(i \left(\vec{k} - \vec{G}'' \right) \cdot \vec{r} \right) \\ &= \sum_{\vec{G}''} C_{(\vec{k}-\vec{G}'')n} \exp \left(i \left(\vec{k} - \vec{G}'' \right) \cdot \vec{r} \right) = \Psi_{\vec{k}n}(\vec{r}) \end{aligned}$$

(realize that for reasons similar to those mentioned on p. 197, since $\vec{G}'$ is fixed, running over all the vectors $\vec{G}'' + \vec{G}'$ or $\vec{G}''$ is exactly the same)

As we guessed from the derivation of the central equation, all the $\vec{k}$ points outside the $\mathcal{B}_Z$ (or whatever is the primitive cell of $\mathcal{R}_\mu^*$ which was taken as reference) are redundant: the eigenfunction corresponding to them is exactly the same indexed by a corresponding $\vec{k}$ point inside the $\mathcal{B}_Z$; in equivalent terms, for fixed $\vec{r}$ and n , $\Psi_{\vec{k}n}(\vec{r}) \equiv \Psi_{\vec{r}n}(\vec{k})$ is a periodic function with respect to $\vec{k}$ on $\mathcal{R}_\mu^*$.

In other words: two eigenfunctions whose wave vectors differ by a $\vec{G}$ vector are identical.

This has an immediate implication on the dependence of the eigenvalues on $\vec{k}$.

Since $\Psi_{\vec{k}n}(\vec{r})$ and $\Psi_{(\vec{k}+\vec{G})n}(\vec{r})$ are identical, the two Schrödinger's problems:

$$H\Psi_{\vec{k}n}(\vec{r}) = \epsilon_{\vec{k}n}\Psi_{\vec{k}n}(\vec{r}) \quad (623)$$

and

$$H\Psi_{(\vec{k}+\vec{G})n}(\vec{r}) = \epsilon_{(\vec{k}+\vec{G})n}\Psi_{(\vec{k}+\vec{G})n}(\vec{r}) \quad (624)$$

must necessarily share the same eigenvalue.

But this means:

$$\epsilon_{(\vec{k}+\vec{G})n} = \epsilon_{\vec{k}n} \quad (625)$$

that is: for a fixed n value, $\epsilon(\vec{k})$ is also a periodic function of $\vec{k}$ on the microscopic reciprocal lattice $\mathcal{R}_\mu^*$.

^{vii}Except for the trivial case $\vec{G} = 0$, which we exclude because it would mean that $\vec{k} + \vec{G}'$ is not different from $\vec{k}$.

4.7 The band structure

333. In this section I will introduce for the first time in this course a concept that you have almost certainly already heard of in your coursework: the concept of a *band*.

In the light of all that we have developed until now, you should find the definition of a “band” quite easy and “natural” (at least, this is my hope).

This first introduction is very important, since we will be dealing with bands and band structure during all the remaining part of this course.

334. We have seen that for each of the N $\vec{k}$ points inside the first Brillouin zone the Schrödinger equation 525 admits an infinite set of eigenfunctions and corresponding eigenvalues, indexed by n : $\Psi_{\vec{k}n}(\vec{r})$ and $\epsilon_{\vec{k}n}$.

Given a fixed value of n , the energy $\epsilon_{\vec{k}n}$ of the monoelectronic states is a function of the wave vector $\vec{k}$; in order to better highlight this, let's represent it in the present context with $\epsilon_n(\vec{k})$.

And now the (simple) definition.

Letting ϵ_n^{min} and ϵ_n^{max} be the minimum and maximum value, respectively, that the function $\epsilon_n(\vec{k})$ takes on the $\vec{k}$ points inside the first Brillouin zone (for a fixed n value), we define n -th *band* the energy interval $[\epsilon_n^{min}, \epsilon_n^{max}]$.

The set of bands corresponding to all the consecutive values $n = 1, 2, 3 \dots$ constitutes what is usually called *the band structure of a solid*.

As I said, we will explore the concept of band and band structure in more and more detail in the remaining part of this course: for the time being, it is important that you fix the concept of a band as an interval of energy (a band, precisely) that bounds from below and from above the graph of the function $\epsilon_n(\vec{k})$ in the first Brillouin zone for a particular fixed value of n .

Note: as you will see, in the following I will often use the term “band” to indicate not only the energy interval defined above, but also the graph itself of the function $\epsilon_n(\vec{k})$; it will be always obvious the exact meaning from the context.

The just introduced band definition is illustrated in figure 67 for the case of a monodimensional crystal.

335. Since we already know that $\epsilon_n(\vec{k})$ is periodic on $\mathcal{R}_\mu^*$ (point 332), its graph over the whole $\vec{k}$ space is obtained simply by periodic replication of the first Brillouin zone (which, remember, is just a primitive cell of $\mathcal{R}_\mu^*$); therefore, the concept of band extends without changes to the whole $\vec{k}$ space: if $\epsilon_n(\vec{k})$ takes values inside the interval $[\epsilon_n^{min}, \epsilon_n^{max}]$ in the $\mathcal{B}_Z$, then, due to its periodicity, it will be contained within the same boundaries in all the infinite images of the $\mathcal{B}_Z$, which are obtained by $\vec{G}$ translation, and thus over the whole $\vec{k}$ space, in which $\mathcal{R}_\mu^*$ is “immersed”. Since the bands of a solid are indexed by n , the latter is called *band index*.

336. A clarification is appropriate here. As you have seen, I am treating $\epsilon_n(\vec{k})$ as a *continuous* function of $\vec{k}$ and will do so all over the course; however, you have learned that the allowed $\vec{k}$ points are discrete and this might cause you some perplexity; indeed, mathematically, ϵ enters the Schrödinger equation 525 as a *continuous* parameter: its restriction to discrete values is only a consequence of the periodic boundary conditions (section 4.3.1) which we imposed as a means to take the finite size of the sample into account; equation 525 makes no reference to the size of the sample, leaving the ϵ parameter free to vary with continuity. In other words: *mathematically*, ϵ is perfectly defined over the whole $\vec{k}$ space (review also Bloch's theorem and eq. 575 in particular); only, its *physically* acceptable values are restricted to the ones obtained for the allowed $\vec{k}$ points.

337. The existence of “energy bands” in periodic solids is the reason why the dependence of the energy of the monoelectronic states on the wave vector $\vec{k}$ is called “dispersion relation”.

Just to focus on a particular case, consider the smallest eigenvalue, ϵ_1 , and refer to figure 68. In an isolated system (a single atom or molecule) this eigenvalue is unique (there can be multiple states corresponding to it when degeneracy is present, but ϵ_1 is unique); on the other hand, in a periodic system, we have just seen that the energy of this smallest eigenvalue has an *additional dependence on $\vec{k}$* ($\epsilon_1 \rightarrow \epsilon_1(\vec{k})$) and “disperses” (spreads) itself in the interval $[\epsilon_1^{min}, \epsilon_1^{max}]$ as $\vec{k}$ varies in the $\mathcal{B}_{\mathcal{Z}}$ (and the same holds for all other eigenvalues). The amplitude of the interval $[\epsilon_n^{min}, \epsilon_n^{max}]$, called *band width*, is a measure of this dispersion and the expression relating the energy to the wave vector $\vec{k}$, for a fixed value of the band index n , is called, precisely, the *dispersion relation*.

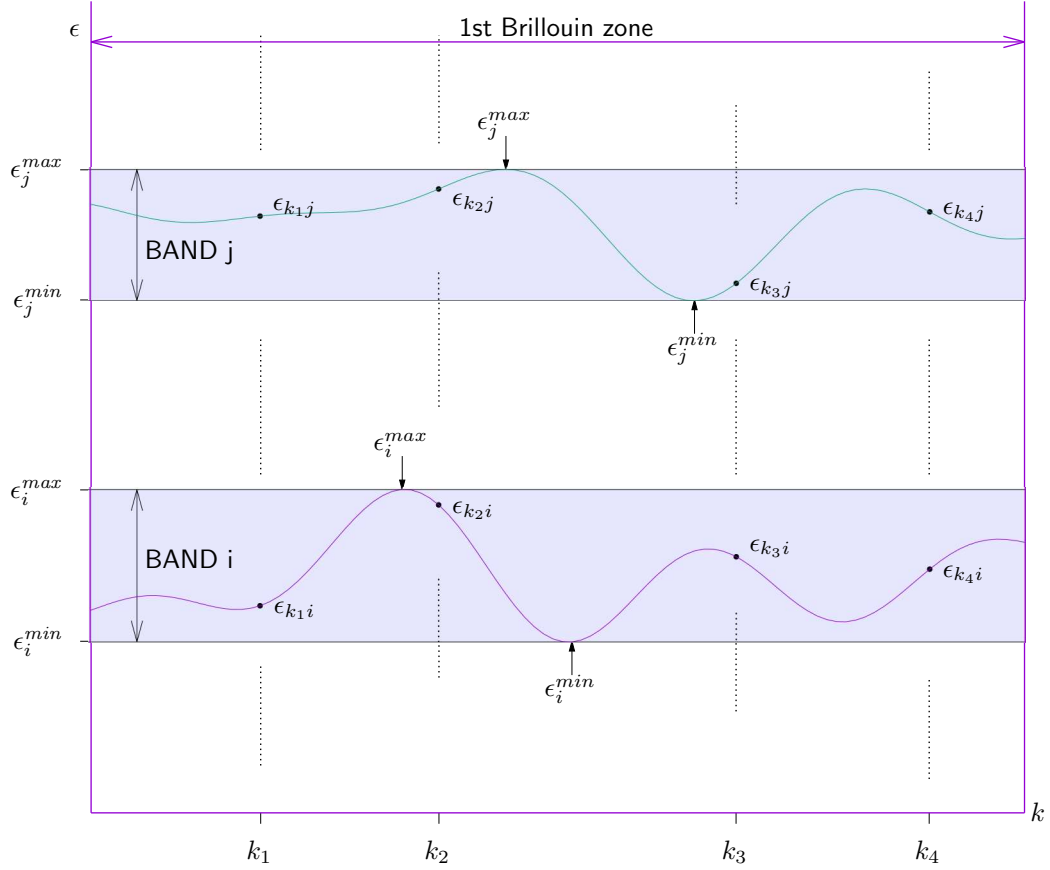


Figure 67: Bands i and j for a monodimensional crystal (in this case the first Brillouin zone reduces to a scalar interval on the k axis). The two solid line plots represent the hypothetical trends of the eigenvalues corresponding to band indexes i and j as k spans the first Brillouin zone, that is, they are the graphs of the two functions $\epsilon_i(k)$ and $\epsilon_j(k)$. For better clarity, four k values and corresponding eigenvalues are explicitly shown on each graph. Bands i and j (evidenced with the transparent solid pattern) are the intervals on the ϵ axis ($[\epsilon_i^{\min}, \epsilon_i^{\max}]$ and $[\epsilon_j^{\min}, \epsilon_j^{\max}]$, respectively) defined by the minimum and maximum eigenvalues of the corresponding graphs.

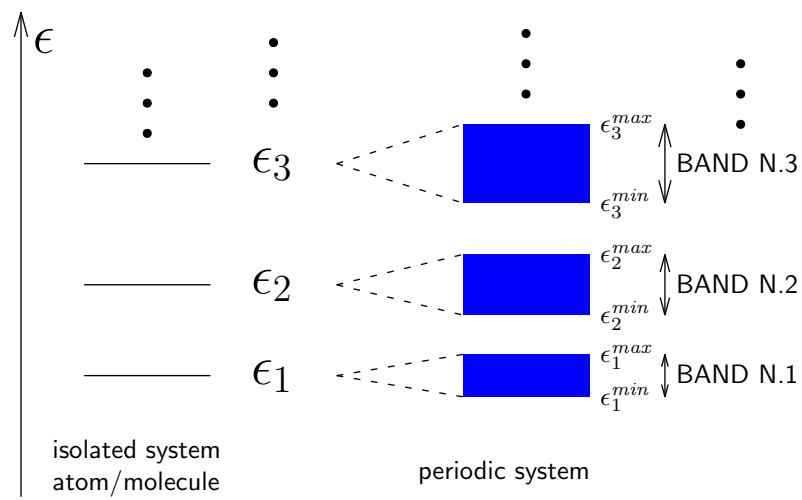


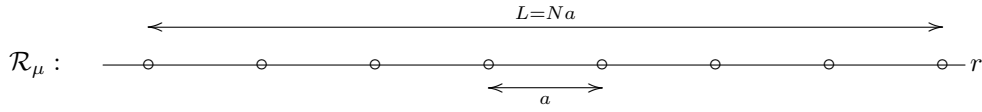
Figure 68: For an isolated system (a single atom or molecule) the energy eigenvalues are unique; for a periodic system, due to the additional dependence on the wave vector $\vec{k}$, each eigenvalue “disperses” into an energy *interval* which is what we call a “band”.

5 The “empty lattice” model

338. In the previous section we introduced the general aspects of the analysis of the electronic structure of crystalline solids. With the aim of better understanding the origin of the band structure, we now consider the simplest possible model of a crystalline solid (from the electronic structure perspective). We will do this in 1D only and extrapolate the results to 2D and 3D without derive them explicitly.

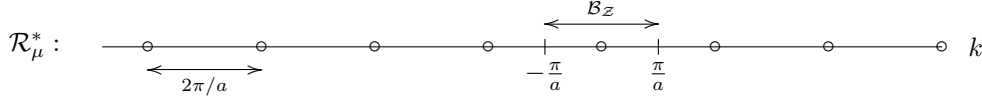
5.1 The definition of the system

339. Let’s focus on a monodimensional “crystal” based on a microscopic Bravais lattice $\mathcal{R}_\mu$ defined by a primitive “cell” of length a (in 1D there is a single cell parameter, point 146). The macroscopic solid sample is a supercell of length L , containing N microscopic primitive cells: $L = Na$.



The assumption of periodic boundary conditions introduces a macroscopic Bravais lattice $\mathcal{R}_M$ of which the supercell of length L is the primitive cell (section 4.3.1).

The microscopic reciprocal lattice $\mathcal{R}_\mu^*$ is a monodimensional grid with spacing $g = 2\pi/a$. The first Brillouin zone $\mathcal{B}_Z$ is the interval $[-\pi/a, \pi/a] = [-g/2, g/2]$ (review figure 40).



The monodimensional version of the Schrödinger equation 525 which gives eigenfunctions and eigenvalues for this system is:

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + U(r) \right) \Psi(r) = \epsilon \Psi(r) \quad (626)$$

and the central equation (eq. 916) which is derived from it in the way we saw in section 4, takes the form:

$$\left(\frac{\hbar^2}{2m} k^2 - \epsilon \right) C_k + \sum_G U_G C_{k-G} = 0 \quad k \in \mathcal{R}_M^* \quad (627)$$

($\mathcal{R}_M^*$ is the macroscopic reciprocal lattice)

The $\vec{k}$ and $\vec{G}$ vectors have turned into simple scalars: k is an allowed wave vector, that is, as we saw in point 307, a point of the macroscopic reciprocal lattice $\mathcal{R}_M^*$ (primitive cell of “volume” $2\pi/L$); G is a vector of the microscopic reciprocal lattice $\mathcal{R}_\mu^*$ which, in this monodimensional case, we can write as:

$$G = j \frac{2\pi}{a} = jg \quad j \in \mathbb{Z} \quad (628)$$

The monodimensional version of the eigenfunction corresponding to the allowed point k inside the $\mathcal{B}_Z$ and to the band index n (eq. 616) becomes:

$$\Psi_{kn}(r) = \sum_j C_{(k-jg)n} \exp(i(k-jg)r) \quad (629)$$

340. As we know, since the solid is a crystal (even if only monodimensional), the potential $U(r)$ which enters Schrödinger's equation is an *a* periodic function of a single variable. You should not have any difficulty in realizing that a *constant* function is periodic: trivially, it satisfies the periodicity condition, eq. 1 or 2, not only for a single particular period T , but for *any* real period:

$$f(x) = \text{constant} \implies f(x+T) = f(x) \quad \forall x \in \mathbb{R}, \forall T \in \mathbb{R} \quad (630)$$

Then, and this is the peculiar feature of the “empty lattice” model we are introducing here, we assume that the potential $U(r)$ is *constant and null*:

$$U(r) = 0 \quad \forall r \in \mathbb{R} \quad (631)$$

The model so defined is called “empty lattice” because it describes a crystalline solid (thus: a *periodic* system) in which, however, the interaction of the electrons with the ions is absent (because $U(r) = 0$).

Physically, you can think of the “empty lattice” model as the limit which a crystalline solid approaches as the electron-ion potential energy approaches 0:

$$\lim_{U(\vec{r}) \rightarrow 0} \boxed{\text{crystalline solid system}} = \boxed{\text{“empty lattice” model}}$$

341. Be careful not to make confusion.

At a first sight, it might look as if the “empty lattice” model is identical to the Fermi gas model (section 3): in both models it is assumed that the electron-ion interaction potential is null.

However, differently from the Fermi gas model, the null potential in the “empty lattice” model is thought of as a *periodic* potential (this is totally admissible, see above) and thus the model is treated with the general approach we developed in section 4.

5.2 The solution of Schrödinger's equation for the “empty lattice” model

342. Let's now see how the solution of Schrödinger's equation for the “empty lattice” model is obtained using the general form of the central equation presented in section 4.4.

343. Let's take back the p -th subsystem of the central equation corresponding to the point $\vec{k}_p \in \mathcal{B}_Z$ (figure 66):

$$\begin{aligned} \left(\frac{\hbar^2 k_p^2}{2m} - \epsilon \right) C_{\vec{k}_p} + U_{\vec{G}_1} C_{\vec{k}_p - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_p - \vec{G}_2} + \dots &= 0 \\ \left(\frac{\hbar^2 |\vec{k}_p - \vec{G}_2|^2}{2m} - \epsilon \right) C_{\vec{k}_p - \vec{G}_2} + U_{\vec{G}_1} C_{\vec{k}_p - \vec{G}_2 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_p - \vec{G}_2 - \vec{G}_2} + \dots &= 0 \quad (632) \\ \left(\frac{\hbar^2 |\vec{k}_p - \vec{G}_3|^2}{2m} - \epsilon \right) C_{\vec{k}_p - \vec{G}_3} + U_{\vec{G}_1} C_{\vec{k}_p - \vec{G}_3 - \vec{G}_1} + U_{\vec{G}_2} C_{\vec{k}_p - \vec{G}_3 - \vec{G}_2} + \dots &= 0 \end{aligned}$$

...

Remember that we numbered the $\vec{G}$ vectors of $\mathcal{R}_\mu^*$ such that $\vec{G}_1$ was the null vector and so $\vec{G}_1$ does not appear in the first term of the first equation.

In the 1D case we are dealing with here, the $\vec{G}$ vectors are simple scalars given by 628. Also the $\vec{k}_p$ point inside the $\mathcal{B}_Z$ is a scalar: $k_p \in [-\frac{\pi}{a}, \frac{\pi}{a}]$.

Then, for what follows, it is convenient to rewrite the whole subsystem in the following compact form:

$$\left(\frac{\hbar^2 (k - jg)^2}{2m} - \epsilon \right) C_{k-jg} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig} = 0 \quad j \in \mathbb{Z} \quad (633)$$

where:

- $\Rightarrow$ we have dropped the index p of point k : it is understood that k is not any point of Fourier space, but it is an allowed wave vector inside the $\mathcal{B}_Z$
- $\Rightarrow$ we have written in a concise form the sum over the Fourier coefficients $U_{ig} C_{k-jg-ig}$
- $\Rightarrow$ as the indexes j and i vary in $\mathbb{Z}$, all the vectors $G \in \mathcal{R}_\mu^*$ are caught
- $\Rightarrow$ note also that in this compact form both j and i can be null and therefore also the origin of $\mathcal{R}_\mu^*$ is taken into account: when $j = 0$ the first equation of the system 632 (in its monodimensional form) is obtained

Please, fully convince yourself that, with the just made clarifications, eq. 633 is a concise, yet complete, representation of the subsystem 632.

344. Since in the “empty lattice” model $U(r) = 0$, all the coefficients of its Fourier expansion must be identically null (p. 195):

$$U(r) = 0 \implies U_{jg} = \frac{1}{a} \int_0^a \overbrace{U(r)}^{=0} \exp(-i(jg)r) dr = 0 \quad \forall j \quad (634)$$

and thus the subsystem 633 reduces to:

$$\left(\frac{\hbar^2 (k - jg)^2}{2m} - \epsilon \right) C_{k-jg} = 0 \quad j \in \mathbb{Z} \quad (635)$$

345. Now our task is to find the possible allowed values of ϵ , that is: the eigenvalues of the Schrödinger equation 626.

When:

$$\epsilon \neq \frac{\hbar^2 (k - jg)^2}{2m} \quad \forall j$$

all the factors which multiply the coefficients C_{k-jg} are $\neq 0$ and this implies that all the C_{k-jg} ’s must be null. In math language:

$$\epsilon \neq \frac{\hbar^2 (k - jg)^2}{2m} \quad \forall j \implies \left(\frac{\hbar^2 (k - jg)^2}{2m} - \epsilon \right) \neq 0 \quad \forall j \implies C_{k-jg} = 0 \quad \forall j$$

But, trivially, if all the coefficients C_{k-jg} are null, the corresponding eigenfunction (given by 629) must be also identically null, and thus not acceptable, because not normalizable:

$$C_{k-jg} = 0 \quad \forall j \implies \Psi(r) = \sum_j C_{k-jg} \exp(i(k-jg)r) = 0 \quad \forall r \quad (636)$$

$$\implies |\Psi|^2 = 0 \implies \int_0^L |\Psi|^2 dr = 0 \neq 1 \quad (637)$$

(equivalently, you can say that a null Ψ is not acceptable because it would give a null probability to find the electron in any point inside the solid sample)

346. From the above it follows that the only acceptable values for ϵ must be of the type:

$$\epsilon = \frac{\hbar^2 (k-jg)^2}{2m} \quad (638)$$

When, for a given $j' \in \mathbb{Z}$:

$$\epsilon = \frac{\hbar^2 (k-j'g)^2}{2m} \quad (639)$$

in the subsystem 633 all the coefficients C_{k-jg} with $j \neq j'$ are null (because the corresponding factors are $\neq 0$), while the coefficient $C_{k-j'g}$ can be $\neq 0$, because the corresponding factor is null. This way, the Fourier expansion of the eigenfunction corresponding to this allowed ϵ value reduces to:

$$\Psi(r) = \sum_j C_{k-jg} \exp(i(k-jg)r) = C_{k-j'g} \exp(i(k-j'g)r) \quad (640)$$

and an acceptable value for $C_{k-j'g}$ is derived from the normalization condition:

$$\int_0^L |\Psi|^2 dr = \int_0^L C_{k-j'g}^2 dr = LC_{k-j'g}^2 = 1 \iff C_{k-j'g} = \frac{1}{\sqrt{L}} \quad (641)$$

347. Since j' was any value of j , eq. 639 tells us that for a given k point inside the $\mathcal{B}_{\mathcal{Z}}$ there are infinite allowed ϵ values, one for each value of j , that is, one for each vector $G = jg \in \mathcal{R}_{\mu}^*$. So, we find again the same result which we deduced in general in point 327.

As said in point 327, it is convenient to index the infinite sequence of allowed eigenvalues (for the particular point $k \in \mathcal{B}_{\mathcal{Z}}$) in ascending order of energy:

$$\epsilon_{k1} \leq \epsilon_{k2} \leq \epsilon_{k3} \leq \dots \leq \epsilon_{kn} \leq \dots \quad (642)$$

The index n is just the band index, which we introduced in general in section 4.7.

Note that, while each eigenvalue is associated with a particular vector $G = jg$, the index of the sequence of eigenvalues cannot be j itself; a first reason for this is that j can become negative (remember that $j \in \mathbb{Z}$), while we want that the band index is a positive integer; a second reason is that, as we shall see (point 353), the relation linking an eigenvalue to its corresponding vector $G = jg$ is not, in general, of monotonic type (in the mathematical sense) (I will come back on this on p. 217).

348. In summary, the solutions of the central equation for the “empty lattice” model (eigenfunctions and eigenvalues) are:

$$\epsilon_{kn} = \frac{\hbar^2 (k - jg)^2}{2m} \quad (643)$$

$$\Psi_{kn}(r) = \frac{1}{\sqrt{L}} \exp(i(k - jg)r) \quad (644)$$

$$k \in \mathcal{B}_{\mathcal{Z}}, \quad j \in \mathbb{Z}$$

where:

- $\Rightarrow$ k is a point inside the first Brillouin zone
- $\Rightarrow$ $j \in \mathbb{Z}$ is an integer which identifies a corresponding vector $G = jg \in \mathcal{R}_{\mu}^*$
- $\Rightarrow$ n is the band index: each value of n corresponds to a value of j and thus to a particular vector $G = jg$ which, when plugged into 639, produces the n -th eigenvalue in order of increasing energy

349. Remarks:

- It is worth comparing and commenting the solutions of Schrödinger's equation found for the Fermi gas (in its monodimensional version) and for the “empty lattice” models.

The expressions for the eigenvalues and corresponding eigenfunctions are very similar:

Fermi gas	“empty lattice”
(eq. 398) $\epsilon_k = \frac{\hbar^2 k^2}{2m}$	(eq. 643) $\epsilon_{kn} = \frac{\hbar^2 (k - jg)^2}{2m}$
(eq. 393) $\Psi_k(r) = \frac{1}{\sqrt{L}} \exp(ikr)$	(eq. 644) $\Psi_{kn}(r) = \frac{1}{\sqrt{L}} \exp(i(k - jg)r)$

In both models the electrons have only kinetic energy and their potential energy is null. However, considering the null (constant) potential as a periodic potential in the “empty lattice” model implies the use of the Fourier methods seen in section 4: the main consequence of this is that, while in the Fermi gas model only a single eigenvalue (and a single eigenfunction) corresponds to each allowed k point inside the first Brillouin zone, in the “empty lattice” model there are infinite eigenvalues (and infinite eigenfunctions), indexed by the band index n , corresponding to a single k point. The band index, in turn, is determined by j , which “scans” all the vectors of the microscopic reciprocal lattice $\mathcal{R}_{\mu}^*$: note that such lattice, which is reciprocal of the Bravais lattice underlying the crystal structure of the solid sample, is completely absent in the Fermi gas model.

- In section 4 we have seen that in the presence of a periodic potential Bloch's theorem must be satisfied. We thus ask ourselves: do the obtained eigenfunctions satisfy Bloch's theorem?

The answer is obviously yes and we can verify it very easily.

In the 1D case we are dealing with, the generic vector of the microscopic direct lattice $\mathcal{R}_{\mu}$ is given by:

$$R = pa \quad p \in \mathbb{Z}$$

a is the primitive direct “vector” (point 339) (in a monodimensional crystal there is only one single primitive vector).

Then:

$$\begin{aligned} \Psi_{kn}(r+R) &= \frac{1}{\sqrt{L}} \exp(i(k-jg)(r+R)) = \overbrace{\frac{1}{\sqrt{L}} \exp(i(k-jg)r) \exp(i(k-jg)R)}^{\Psi_{kn}(r)} \\ &= \exp(i(k-jg)R) \Psi_{kn}(r) = \exp(ikR) \exp(-ijgR) \Psi_{kn}(r) = \exp(ikR) \exp\left(-ij\frac{2\pi}{a}pa\right) \Psi_{kn}(r) \\ &= \exp(ikR) \overbrace{\exp(-ijp2\pi)}^{=1} \Psi_{kn}(r) = \exp(ikR) \Psi_{kn}(r) \end{aligned}$$

which is the monodimensional version of the second statement of Bloch’s theorem (eq. 528).

Alternatively, you can rewrite the eigenfunction 644 in the following way:

$$\Psi_{kn}(r) = \frac{1}{\sqrt{L}} \exp(i(k-jg)r) = \exp(ikr) \overbrace{\frac{1}{\sqrt{L}} \exp(-ijgr)}^{u_{kn}(r)} = \exp(ikr) u_{kn}(r)$$

which is the monodimensional version of the first statement of Bloch’s theorem (eq. 526), after noting that $u_{kn}(r)$, as required by the theorem, is periodic on $\mathcal{R}_\mu$. Indeed, $\forall l \in \mathbb{Z}$ we have:

$$\begin{aligned} u_{kn}(r+la) &= \frac{1}{\sqrt{L}} \exp(-ijg(r+la)) = \exp\left(-ij\frac{2\pi}{a}la\right) \overbrace{\frac{1}{\sqrt{L}} \exp(-ijgr)}^{u_{kn}(r)} \\ &= \overbrace{\exp(-ijl2\pi)}^{=1} u_{kn}(r) = u_{kn}(r) \end{aligned}$$

5.3 The dispersion relation

350. The dispersion relation for the “empty lattice” model, that is, the relation which links the energy ϵ to the allowed wave vectors k , is eq. 643 written above. In order to highlight that we are now interested to the dependence of ϵ on k , let’s rewrite it as:

$$\epsilon(k) = \frac{\hbar^2 (k-jg)^2}{2m} \quad k \in \mathcal{B}_Z, \quad j \in \mathbb{Z} \quad (645)$$

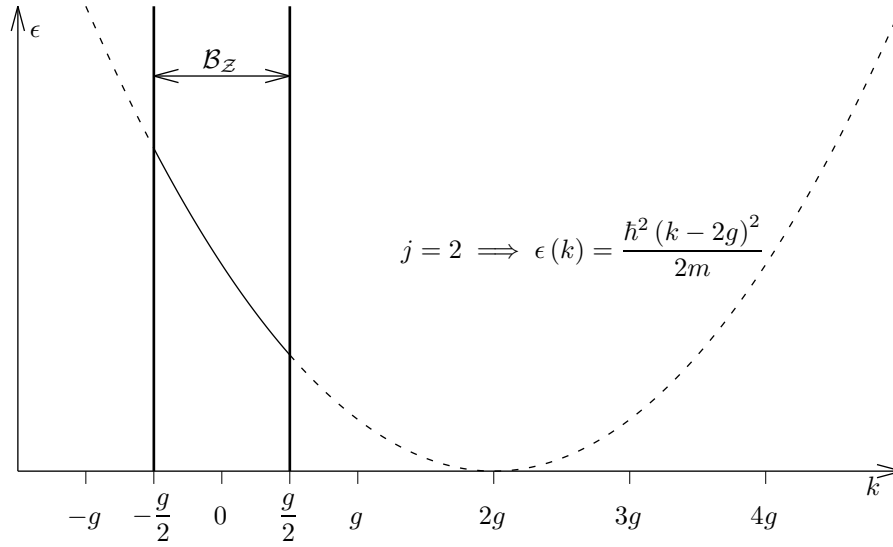


Figure 69: The graph of the dispersion relation 643 in the first Brillouin zone for $j = 2$ is the portion of the Fermi gas parabola translated by $2g = 2 \times 2\pi/a$ in the positive direction of the k axis.

(to alleviate notation, I have omitted the band index n , being understood that it is uniquely determined by j)

351. First of all, note that, in rigorous mathematical terms, $\epsilon(k)$ in 645 is not a function. In mathematics, we say that:

$$y = f(x) \quad (646)$$

is a function if *one and only one* value of the dependent variable y is associated with each value of the independent variable x .

In 645, for a given value of the independent variable k there are *infinite* possible values of the dependent variable ϵ : one for each $j \in \mathbb{Z}$.

352. For fixed j (and thus for a fixed band index n) eq. 645 defines the dependence of the energy on k in the first Brillouin zone.

The trend of ϵ as a function of k (for fixed j) in the first Brillouin zone is easy to be figured out. The RHS of 645 is nothing but the parabolic dispersion relation for the Fermi gas (eq. 398), *translated* by $G = jg \in \mathcal{R}_\mu^*$ (to the right when $j > 0$, to the left when $j < 0$).

Therefore, for a given j , the graph of 645 in the first Brillouin zone is the portion of the Fermi gas parabola translated such that its vertex is on the point $G = jg$ of the k axis (the parabola 398 with no translation has its vertex at the origin of the k axis, $k = 0$).

Figure 69 graphically illustrates this aspect for a single value of j .

Figure 70 shows the graph of $\epsilon(k)$ in the first Brillouin zone for the first 7 G vectors of smallest modulus: $G = jg$, with $j = 0, \pm 1, \pm 2, \pm 3$.

From this figure it should not be difficult to imagine what the graph of $\epsilon(k)$ should look like to when plotted for all the infinite values of j .

At the web site of this course you can find an animated version of figure 70 (but limited to $j = 0, \pm 1, \pm 2$) which further clarifies the origin of the graph of the dispersion relation in the first Brillouin zone.

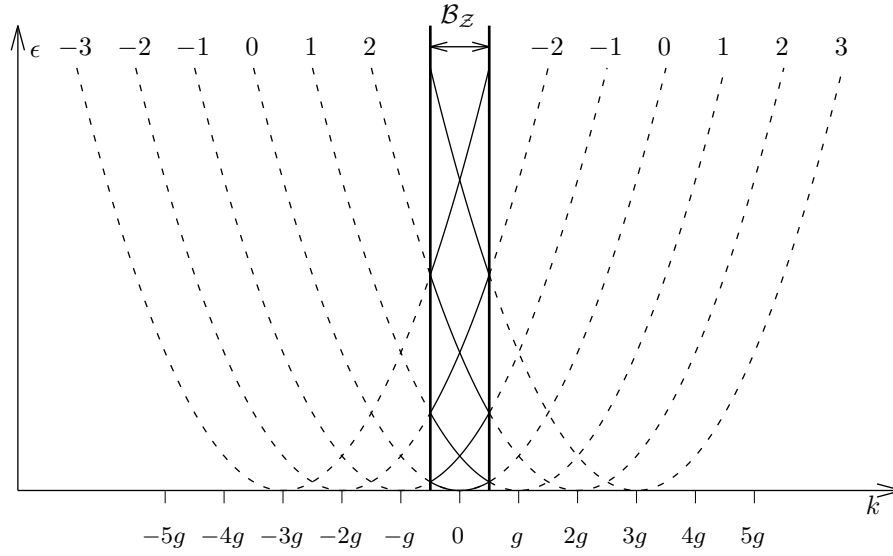


Figure 70: The graph of the dispersion relation 643 for $j = 0, \pm 1, \pm 2, \pm 3$. The j values are shown on the corresponding Fermi gas parabolas, whose “clipped” portions inside the first Brillouin zone constitute the graph of relation 643.

353. Some remarks:

- Sequence of the eigenvalues.

For a fixed k , the sequence of its eigenvalues (eq. 642) can be graphically obtained moving vertically from k : each intersection of the vertical line with the portion of a parabola is an eigenvalue corresponding to that k point. The procedure is shown in figure 71.

- Band index and G vectors.

As I already mentioned in point 347, the relation linking the band index n to the index j of the corresponding vector $G = jg$ is not simple.

Refer to figures 70 and 71.

In any case, the lowest eigenvalue corresponds always to the null vector $G = 0$, that is $j = 0$.

The $n \iff j$ map for the following eigenvalues depends also on the k point.

In particular, it should not be difficult to realize that the following holds:

$n :$	1	2	3	4	5	6	7	...
$k \leq 0 : j :$	0	-1	1	-2	2	-3	3	...
$k \geq 0 : j :$	0	1	-1	2	-2	3	-3	...

The cases where $k = 0$ or $k = \pm g/2$ are “special” and we will come back to them in a moment.

In section 5.1 of the extracurricular part I show you a possible way to represent analytically the dependence of the band index n on the index j which identifies a particular vector

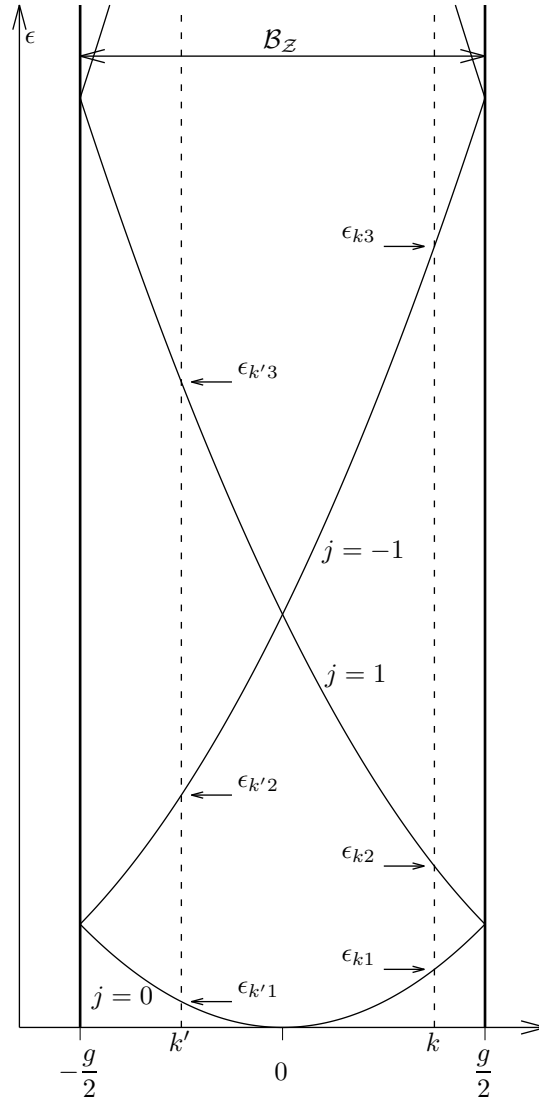


Figure 71: For the two points k and k' inside the first Brillouin zone the first three eigenvalues in order of increasing energy are indicated: ϵ_{k1} , ϵ_{k2} , ϵ_{k3} and $\epsilon_{k'1}$, $\epsilon_{k'2}$, $\epsilon_{k'3}$. These eigenvalues are obtained from the intersection of the vertical line passing through the considered k point with all the portions of the Fermi gas parabolas which, taken all together, constitute the dispersion relation for the “empty lattice” model. In the figure only the first three parabolic portions, for $j = 0, 1, -1$, are shown (review also figure 70).

$\vec{G} \in \mathcal{R}_\mu^*$ (and thus a corresponding portion of Fermi gas parabola inside the first Brillouin zone).

Leaving aside the details, the important aspects to be retained here are:

- ▷ for any j value there is always one and only one vector $G = jg \in \mathcal{R}_\mu^*$ and (thus) one and only one portion of a Fermi gas parabola inside the first Brillouin zone corresponding to it
- ▷ the smallest eigenvalue ($n = 1$) always corresponds to $j = 0$, that is, to the null G vector. Thus we always have:

$$\epsilon_{k1} = \frac{\hbar^2 k^2}{2m} \quad -\frac{g}{2} \leq k \leq \frac{g}{2}$$

- ▷ for a fixed k point, for each parabola portion there is always one and only one eigenvalue (identified by a particular j value) corresponding to it
- ▷ given a k point, j indexes of greater absolute value always correspond to greater eigenvalues (that is, greater n values). For instance, independently of the k point inside the $\mathcal{B}_Z$, the eigenvalues corresponding to $|j| = 2$ are always less than those corresponding to $|j| = 3$ (fig. 70). In other words: eigenvalues corresponding to reciprocal vectors of smaller modulus (length) are always smaller.
The relation between two eigenvalues corresponding to j values of equal absolute value, but opposite sign depends on the sign of the k vector, as mentioned above.

- Degeneracy.

If you look at figure 70 or 71 you will notice that for $k = 0, \pm g/2$ two parabola portions share a common point (for example: for $k = g/2$ the pairs of parabola portions $j = 0, 1, j = -1, 2, j = -2, 3$ etc. do share a common point).

Sharing a common point means that the two eigenvalues of the two parabola portions coincide: that is, the corresponding electronic states are degenerate.

So, the “empty lattice” model gives a double degeneracy (i.e. two states having the same energy) when $k = 0$ and $k = \pm g/2$ (note: the latter values define the left and right boundary of the first Brillouin zone).

The existence of this double degeneracy (two different j values giving the same eigenvalue) when $k = 0, \pm g/2$ can also be seen analytically, and if you are interested I show it in section 5.2 of the extracurricular part.

5.4 Periodicity in k space

354. In section 4.6 we have seen in general that for a periodic system eigenfunctions and eigenvalues are periodic functions of k with the periodicity of the microscopic reciprocal lattice $\mathcal{R}_\mu^*$. Therefore, the trend of the dispersion relation on the whole k axis for the monodimensional “empty lattice” model is obtained by indefinitely replicating the first Brillouin zone to the left and to the right.

This is shown in figure 72.

From the figure you can also realize that a simple way of visualizing the trend of the dispersion relation over the whole k axis is that of imagining infinite Fermi gas parabolas, each centered on a point $G = jg$ of $\mathcal{R}_\mu^*$.

In fact: think of the first Brillouin zone simply as one of the infinite primitive cells which make up the microscopic reciprocal lattice. Now consider any three consecutive primitive cells (refer

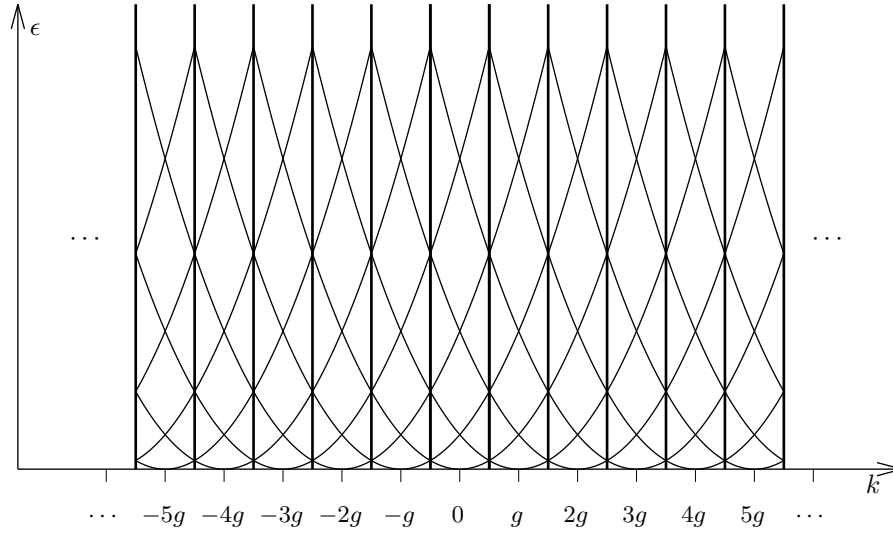


Figure 72: The dispersion relation for the “empty lattice” model on the whole k space is obtained by replicating the graph inside the first Brillouin zone.

to figure 72). The parabola which gives the $j = 0$ portion in the central cell is the same which gives the $j = -1$ portion in the cell on the right and the $j = 1$ portion in the cell on the left. And so on and so forth for all other cells to the left and to the right.

In other words, the portions of the parabolas in a given cell connect with continuity with those of the cells adjacent to it and the final result of this continuous connection is that by indefinitely replicating a primitive cell (the first Brillouin zone) we obtain an infinite sequence of complete Fermi gas parabolas each with its vertex on a reciprocal lattice point, as said above.

An equivalent way of realizing the same thing is that of considering the expression for the dispersion relation 645:

$$\epsilon(k) = \frac{\hbar^2 (k - jg)^2}{2m} \quad j \in \mathbb{Z}$$

Due to the way we derived it in section 5.2, the k values are limited to those inside the first Brillouin zone; however, nothing prevents us from extending it to the whole k axis. But doing so for all j values precisely means to plot infinite Fermi gas parabolas, each with its vertex on a reciprocal lattice point.

Accurately note the following remark: for the “empty lattice” model the dispersion relation on the whole k space is *not a single* Fermi gas parabola (as was the case for the Fermi gas model); in this case, the dependence of the energy upon k is represented by the *infinite* parabolas of figure 72 *taken as a whole*.

5.5 The band structure in the “empty lattice” model

355. In order to make the connection between the band structure as we introduced it in point 334 and the dispersion relation we have obtained for the “empty lattice” model, look at figure 73, which is an enlarged portion of figure 72.

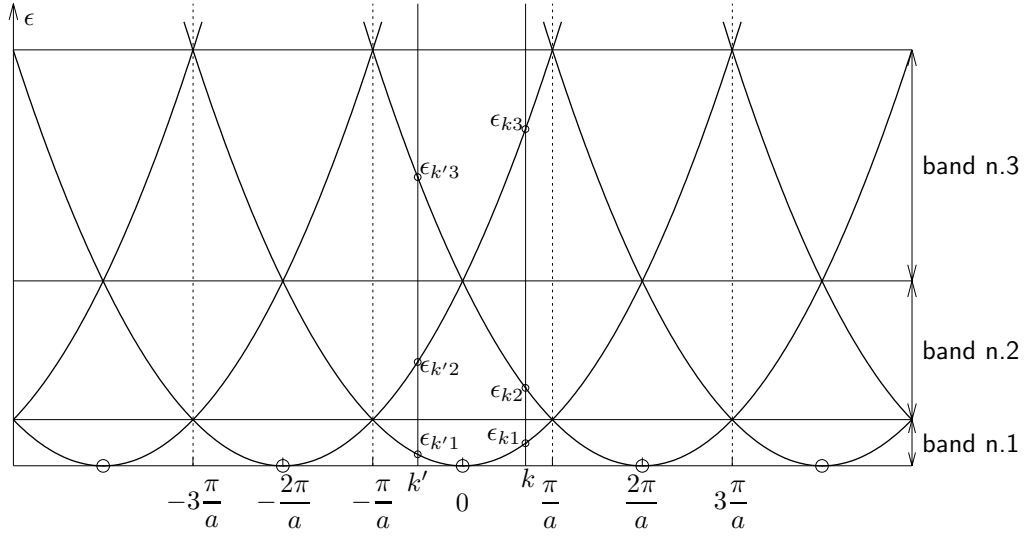


Figure 73: “Repeated zone” representation of the first three bands for the monodimensional “empty lattice” model.

Remember that, given a particular k point inside the first Brillouin zone, the subsystem of the central equation corresponding to it admits infinite eigenvalues ϵ_{kn} indexed by the band index n in order of increasing energy (points 327 and 353): $\epsilon_{k1}, \epsilon_{k2}, \epsilon_{k3}, \dots$

In figure 73 a point $k \in \mathcal{B}_Z$ is shown; as said in point 353 and shown in detail in figure 71, if you proceed along the vertical through k you will intersect first the parabola with vertex in the origin: this intersection identifies ϵ_{k1} , the smallest eigenvalue. If you continue moving upwards you will intersect the parabola with vertex at $g = 2\pi/a$: this intersection gives ϵ_{k2} , the second eigenvalue; the next intersection, which gives the third eigenvalue ϵ_{k3} , will be with the parabola having its vertex at $-g = -2\pi/a$ and so on, according to the relation of p. 217 which maps the j values (in $G = jg$) to the values of the band index n (in ϵ_{kn}) (the additional intersections are not shown in the figure).

In a similar way, moving along the vertical through another point $k' \in \mathcal{B}_Z$, you will obtain the corresponding eigenvalues $\epsilon_{k'1}, \epsilon_{k'2}, \epsilon_{k'3}, \dots$

If you now imagine repeating this process for all the k points of the first Brillouin zone, it should be clear that the first band, that is, the energy interval which bounds the graph of $\epsilon_1(\vec{k})$ inside the first Brillouin zone, is determined by the lowest portion of the parabola with its vertex at the origin; such parabola portion is then replicated by periodicity in all the primitive cells of the microscopic reciprocal lattice (as we saw in general in point 332, eq. 625, and in particular for the “empty lattice” model in section 5.4). The first band, that is, the energy interval into which the lowest eigenvalue is contained for all the allowed k points inside the first Brillouin zone, is indicated as “band n.1” in figure 73.

In a similar way, if you locate for all the k points inside the $\mathcal{B}_Z$ the second eigenvalue (i.e. the second lowest one, like, for example, ϵ_{k2} and $\epsilon_{k'2}$) you should realize that the second band, indicated as “band n.2” in the figure, is determined:

- by the portion of the parabola with its vertex at $-2\pi/a$ and delimited by the interval $[-\pi/a, 0]$
- and by the portion of the parabola with its vertex at $2\pi/a$ and delimited by the interval $[0, \pi/a]$

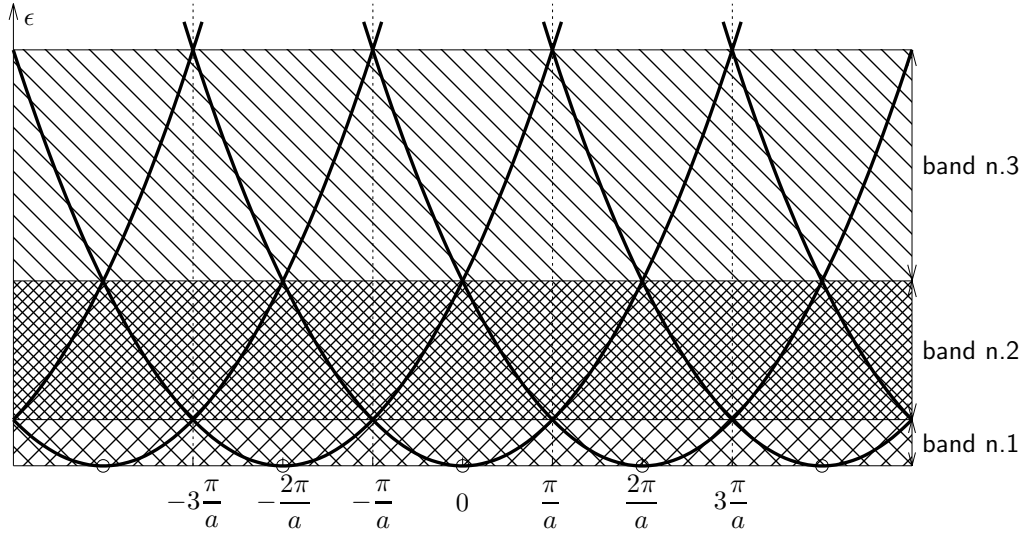


Figure 74: The same first three bands of figure 73 for the monodimensional “empty lattice” model; but now each band is highlighted with a different pattern.

As in the case of the first band, also in this case the graph inside the first Brillouin zone is repeated indefinitely by periodicity to the left and to the right.

Finally, with an identical procedure, you can locate the third band (“band n.3” in the figure). Also this one has a periodic trend along the whole k axis and its graph inside the first Brillouin zone is obtained:

- by the portion of the parabola with its vertex at $2\pi/a$ and delimited by the interval $[-\pi/a, 0]$
- and by the portion of the parabola with its vertex at $-2\pi/a$ and delimited by the interval $[0, \pi/a]$

At this point you should be able to imagine how all the other (infinite) bands after the third one are originated (these are not shown in figure 73).

To further clarify, I have tried to better evidence the trend of each of the three bands of figure 73 in figure 74, where each band is highlighted with a different pattern.

5.5.1 The general expression for the branches of the bands

356. The procedure by which we have described the formation of the first three bands for the monodimensional “empty lattice” model can be generalized. Refer back to figure 73.

The first band is simply given by the lowest portion of the Fermi gas parabola centered at the origin. The equation of this band is thus:

$$\text{BAND N. 1: } \epsilon_1(k) = \frac{\hbar^2}{2m} k^2 \quad k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right] \quad (647)$$

The second band is composed by two so called “branches”, which are obtained from the parabolas centered on the reciprocal points to the left and to the right of the origin:

$$\text{BAND N. 2: } \epsilon_2(k) = \begin{cases} \frac{\hbar^2}{2m} \left(k + \frac{2\pi}{a}\right)^2 & k \in \left[-\frac{\pi}{a}, 0\right] \\ \frac{\hbar^2}{2m} \left(k - \frac{2\pi}{a}\right)^2 & k \in \left[0, \frac{\pi}{a}\right] \end{cases} \quad (648)$$

The same holds for the two branches of the third band, but in this case the “right” branch comes from the parabola which originated the “left” branch of band n.2, and viceversa.

$$\text{BAND N. 3: } \epsilon_3(k) = \begin{cases} \frac{\hbar^2}{2m} \left(k - \frac{2\pi}{a}\right)^2 & k \in \left[-\frac{\pi}{a}, 0\right] \\ \frac{\hbar^2}{2m} \left(k + \frac{2\pi}{a}\right)^2 & k \in \left[0, \frac{\pi}{a}\right] \end{cases} \quad (649)$$

You should have no difficulties in realizing that the branches of the subsequent bands (n.4, n.5, n.6 ...) are obtained from parabolas which are centered on reciprocal points gradually farther (both to the left and to the right) from the origin. As already seen (eq. 645) the general equation of one of these parabolas is:

$$\frac{\hbar^2}{2m} (k - jg)^2 = \frac{\hbar^2}{2m} \left(k - j \frac{2\pi}{a}\right)^2 \quad j \in \mathbb{Z} \quad (650)$$

or, since $jg = j \, 2\pi/a$ is the generic vector G of the microscopic reciprocal lattice:

$$\frac{\hbar^2}{2m} (k - G)^2 \quad G \in \mathcal{R}_\mu^* \quad (651)$$

This procedure is completely general and keeps its validity also for 2D or 3D systems and for any form of the dispersion relation (not only the parabolic one characterizing the “empty lattice” model) (we will not “prove” this claim in a rigorous way, but it should be rather intuitive in the light of what we have just seen above).

The final message of this section is the following.

The band structure of *any* system with *any* type of dispersion relation $\epsilon = \epsilon(\vec{k})$ can be generated by calculating:

$$\epsilon(\vec{k} - \vec{G}) \quad (652)$$

for $\vec{k} \in \mathcal{B}_Z$ and $\forall \vec{G} \in \mathcal{R}_\mu^*$.

Equivalently, we can say that it *always* exists an appropriate reciprocal vector $\vec{G}$ such that any branch of any band can be obtained from 652 evaluated in the first Brillouin zone, or in a region contained in the first Brillouin zone.

5.5.2 The branches of the bands are delimited by the boundaries of the Brillouin zones

357. Another useful observation which can be done for the “empty lattice” model, but which is of completely general scope (and thus holds also for 2D/3D systems) is the following.

The branches of the bands shown in figure 73 are delimited on the k axis by the points:

$$\dots -\frac{3\pi}{a}, -\frac{2\pi}{a}, -\frac{\pi}{a}, 0, \frac{\pi}{a}, \frac{2\pi}{a}, \frac{3\pi}{a} \dots \quad (653)$$

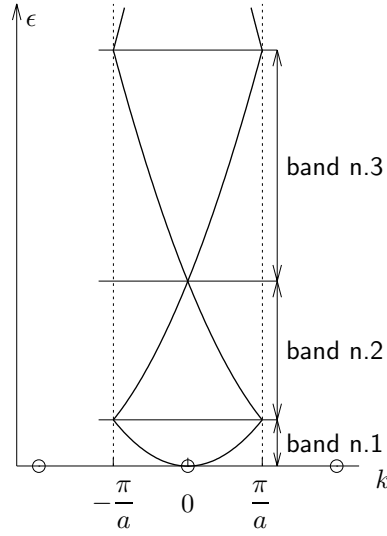


Figure 75: Reduced zone representation of the first three bands of the monodimensional “empty lattice” model.

These are also the boundaries of all the Brillouin zones for a monodimensional system (with the additional point $k = 0$) (review figure 40): the boundaries of Brillouin zones are thus the “connection points” between the different branches of the bands of the system.

As mentioned above, also this observation keeps its validity for any band and also in systems with higher dimensionality (2D/3D) (of course, for 2D/3D systems, the boundaries of the Brillouin zones are not points, but lines for 2D or planes for 3D systems).

5.5.3 Different representations of the band structure

358. The representation of the bands shown in figure 73 is referred to as *repeated zone representation*, since the periodic trend of the bands is repeated, precisely, over the whole k axis (look also at figure 74). Of course, the repeated zone representation is highly redundant since the content of all the primitive cells of $\mathcal{R}_\mu^*$ is always the same (this is so, as we have seen, because $\epsilon(\vec{k})$ is periodic on $\mathcal{R}_\mu^*$ in $\vec{k}$ space).

For this reason often the so called *reduced zone representation* is used instead. This consists in showing the content of only the first Brillouin zone (which is obtained in the way we have seen in section 5.3). The reduced zone representation corresponding to figure 73 is shown in figure 75.

359. You can notice that figure 75 is symmetric with respect to the ordinate axis. This is a consequence of the quadratic analytical form of the dispersion relation for the “empty lattice” model (which, as we saw, is identical to the dispersion relation for the Fermi gas model; the difference between the two models is that, let’s repeat it, in the Fermi gas model the dispersion relation is fully represented by a single parabola centered at the origin, while in the “empty lattice” model the dispersion relation is made up by the infinite parabolas having exactly the same form as the one for the Fermi gas, but each being centered on a point of the microscopic reciprocal lattice $\mathcal{R}_\mu^*$).

For band n.1 the parity is self evident (see eq. 647).

For the subsequent bands, for example band n.2, the parity can be formally seen in the following

way. We know that the function describing band n.2 in the first Brillouin zone is (eq. 648):

$$\epsilon_2(k) = \begin{cases} \frac{\hbar^2}{2m} \left(k + \frac{2\pi}{a}\right)^2 & k \in \left[-\frac{\pi}{a}, 0\right] \\ \frac{\hbar^2}{2m} \left(k - \frac{2\pi}{a}\right)^2 & k \in \left[0, \frac{\pi}{a}\right] \end{cases} \quad (654)$$

(review also figure 73)

The parity of $\epsilon_2(k)$ is evident if you notice that in its two forms the content of the parentheses only changes sign, and so, raising to the second power, the result is unchanged; that is:

$$\forall k \in \left[0, \frac{\pi}{a}\right] : \epsilon_2(k) = \frac{\hbar^2}{2m} \left(k - \frac{2\pi}{a}\right)^2 = \frac{\hbar^2}{2m} \left((-k) + \frac{2\pi}{a}\right)^2 = \epsilon_2(-k)$$

which is the condition for parity.

An even more formal way to see the same thing is presented in the extracurricular part (section 5.3).

360. Yet a third way of representing the band structure is called *extended zone representation*. Since any branch of the reduced zone representation is obtained via an appropriate $\vec{G}$ translation of the dispersion relation (eq. 652):

$$\epsilon(\vec{k} - \vec{G})$$

in this representation the branches of the reduced representation are translated back to their original location. That is, each branch inside the first Brillouin zone is translated outside by $-\vec{G}$.

I have tried to illustrate this idea in figure 76 for the “empty lattice” model.

As you can see in the figure, in the case of a monodimensional crystal containing free electrons (the “empty lattice” model, precisely) the end result of this procedure is the single Fermi gas parabola centered at the origin: $\epsilon = \hbar^2 k^2 / (2m)$. In the general case (i.e. for any dispersion relation and for any dimensionality) one obtains the *unshifted* dispersion relation centered at the origin, that is: $\epsilon(\vec{k})$ (or, if you prefer, $\epsilon(\vec{k} - \vec{G})$ with $\vec{G} = 0$).

361. In point 357 we already noticed that the boundaries of the Brillouin zones delimit the different branches of the bands. Indeed, the relation between bands and Brillouin zones is stricter than this. From figure 76 it also appears that in the extended zone representation each band “occupies” “its own” Brillouin zone. Looking at the figure, you can see that band n.1 is located in the first Brillouin zone, the two branches of band n.2 are located in the second Brillouin zone and the two branches of band n.3 are located in the third Brillouin zone. If you extend both the parabola and the Brillouin zones, you will find that this correspondence is maintained without exceptions.

So, while there is not a simple map between band index and $\vec{G}$ vectors (as we have seen on p. 353), band index and Brillouin zone index do coincide (when the extended zone representation is considered):

band n. i is fully contained in the i -th Brillouin zone

We have derived this result from the analysis of figure 76 in a purely phenomenological way; nevertheless (no formal proof of this claim), its scope is completely general and holds for any dimensionality and/or any form of the dispersion relation.

This suggests another way of identifying the bands for a given system (alternative to the way I described in section 5.5). In the extended zone representation, draw the boundaries of the

Brillouin zones: the intersections of these latter with the (unshifted) dispersion relation identify the bands of the system (to realize this, refer again to figure 76).

362. The three equivalent representations of the band structure are summarized in the following table:

reduced zone: all band branches are plotted inside the first Brillouin zone with:

$$\epsilon(\vec{k} - \vec{G}) \quad \vec{k} \in \mathcal{B}_Z, \quad \vec{G} \in \mathcal{R}_\mu^*$$

No redundancy, but the picture of the whole dispersion relation is somehow lost (figure 75).

repeated zone: all the replicas of the dispersion relation are plotted on the whole $\vec{k}$ space with:

$$\epsilon(\vec{k} - \vec{G}) \quad \vec{k} \in \mathcal{R}_M^*, \quad \vec{G} \in \mathcal{R}_\mu^*$$

Highly redundant, but shows well the periodicity of the dispersion relation in $\vec{k}$ space (figure 73).

extended zone: the *unshifted* dispersion relation (centered at the origin) is plotted with:

$$\epsilon(\vec{k}) \quad \vec{k} \in \mathcal{R}_M^*$$

No redundancy, only a single replica of the dispersion relation; it is easy to identify the different branches of the bands based on the boundaries of the Brillouin zones (figure 76).

5.6 The representation of the band structure for 2D and 3D systems

363. The concept of a band structure as we have introduced it in general terms in section 4.7 is independent on the dimensionality of the system (that is, it holds unchanged for 1D/2D/3D systems).

However, from a purely mathematical standpoint, increasing the dimensionality makes the description of the band structure more complex.

5.6.1 2D system with square Bravais lattice

364. As an example, let's see the first bands in a bidimensional crystal with a square Bravais lattice (cell constant a) in the “empty lattice” model.

As I said at the beginning of this section (point 338) we will not derive in detail the extension of the “empty lattice” model to 2D or 3D systems; if you retrace the steps of section 5.2, you will easily find that the dispersion relation for a periodic system in 2D or 3D is the natural extension of what we did find for the 1D case (eq. 645):

$$\epsilon(\vec{k}) = \frac{\hbar^2 |\vec{k} - \vec{G}|^2}{2m} \quad \vec{G} \in \mathcal{R}_\mu^* \quad (655)$$

Note that, since now the dimension of the system is > 1 , the generic vector $\vec{G} \in \mathcal{R}_\mu^*$ is not a simple scalar, but will be of the form:

$$\vec{G} = \sum_{i=1}^D n_i \vec{b}_i \quad D \in \{2, 3\}, \quad n_i \in \mathbb{Z} \quad (656)$$

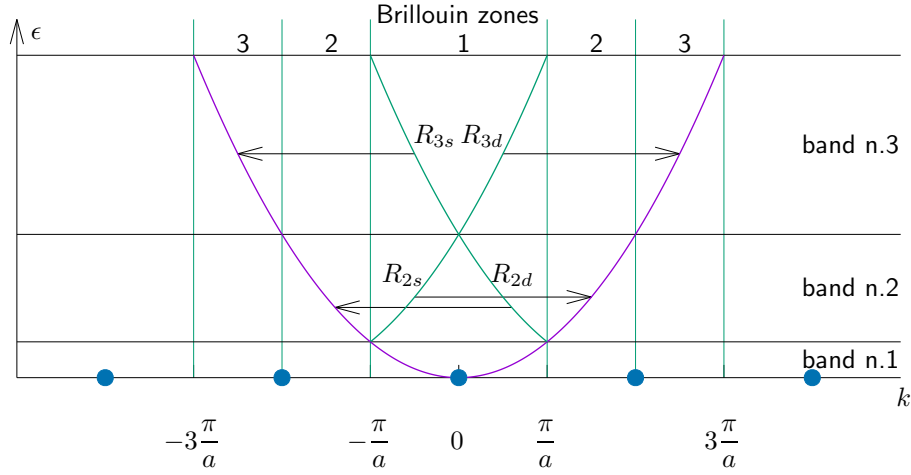


Figure 76: Extended zone representation of the first three bands for a monodimensional crystal containing free electrons. The arrows show how this representation is obtained from the reduced zone representation of figure 75. For instance, the left branch of band n.2 in the first Brillouin zone (R_{2s}) is obtained by translating the Fermi gas parabola by the vector $-2\pi/a$:

$$\epsilon(\vec{k} - \vec{G}) \equiv \epsilon(k - (-2\pi/a)) = \epsilon(k + 2\pi/a)$$

So, in the extended zone representation this branch is translated by the same vector, but in the opposite direction ($+2\pi/a$). Convince yourself that the same procedure is applied to the remaining branches in the figure (R_{2d} , R_{3s} , R_{3d})

where the $\vec{b}_i$'s are the primitive vectors of the microscopic reciprocal lattice.

All the infinite bands of the system are obtained by evaluating expression 655 for all the allowed $\vec{k}$ points inside the first Brillouin zone and for all possible $\vec{G}$ vectors.

365. Let's apply the general method presented in point 356.

The reciprocal lattice of a square lattice is itself a square lattice with cell constant $2\pi/a$ (so: the two primitive vectors of $\mathcal{R}_\mu^*$ can be chosen as $\vec{b}_1 = (2\pi/a, 0)$ and $\vec{b}_2 = (0, 2\pi/a)$); the first Brillouin zone is a square of side $2\pi/a$ centered at the origin. The generic vector of the reciprocal lattice is:

$$\vec{G} = n_x \vec{b}_1 + n_y \vec{b}_2 = n_x \left(\frac{2\pi}{a}, 0 \right) + n_y \left(0, \frac{2\pi}{a} \right) = \frac{2\pi}{a} (n_x, n_y) \quad n_x, n_y \in \mathbb{Z} \quad (657)$$

Since we limit ourselves to the first bands only, that is, those at lowest energy, we consider only a small number of $\vec{G}$ vectors with smallest modulus (p. 219).

Refer to figure 77, where I have drawn the first Brillouin zone and the first 8 cells surrounding it. Including the first Brillouin zone there are 9 cells in total, each identified by a distinct $\vec{G}$ vector: I have used the integers n_x and n_y defined above to label the 9 primitive cells (and thus their corresponding $\vec{G}$ vectors).

We have:

$$\epsilon(\vec{k}) = \frac{\hbar^2}{2m} |\vec{k} - \vec{G}|^2 = \frac{\hbar^2}{2m} \left| (k_x, k_y) - \frac{2\pi}{a} (n_x, n_y) \right|^2$$

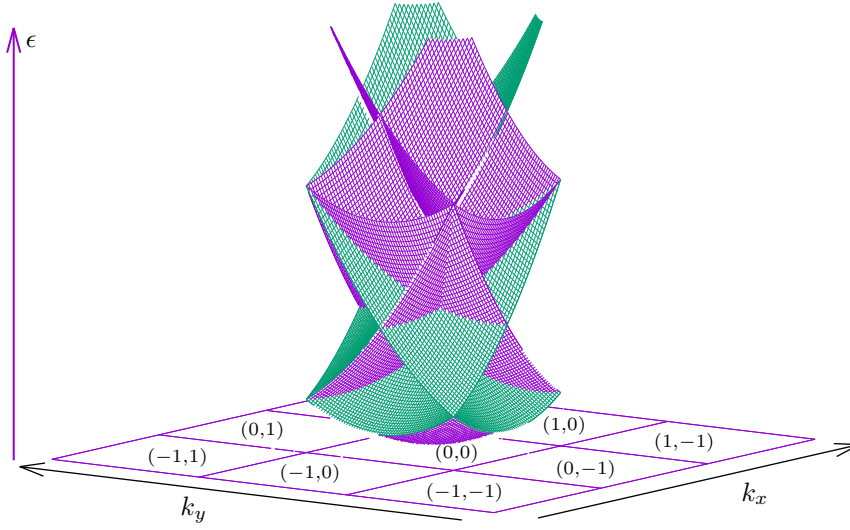


Figure 77: Reduced zone representation of the band structure (first 9 bands only) for a bidimensional crystal with square Bravais lattice in the “empty lattice” model. The explanation of this figure is detailed in the text.

$$= \frac{\hbar^2}{2m} \left(\left(k_x - \frac{2\pi}{a} n_x \right)^2 + \left(k_y - \frac{2\pi}{a} n_y \right)^2 \right) \quad (658)$$

I obtained the figure by evaluating the branches of the parabolas (note: now they are 2D parabolas, see above) on a grid of $\vec{k}$ points spanning the first Brillouin zone (the (0, 0) cell). The parabolas were calculated for the values of n_x and n_y shown in figure 77. The actual used expressions for the calculations are reported in figure 78: it would be a nice exercise if you try to reproduce the graph.

366. An equivalent (more “geometric”) way to understand the graph in figure 77 is the following. In section 5.4 we have seen that the dispersion relation for the 1D “empty lattice” model is given by all the infinite Fermi gas parabolas, each centered on a reciprocal lattice point. The reduced zone representation is obtained by “clipping” those parabolas inside the first Brillouin zone (review also figs. 72 and 70).

Now: this argument extends without any conceptual change also to the 2D (or 3D) cases, the only change being the increased dimensionality. So you can view the reduced zone representation in figure 77 as obtained in the following way:

- there is a $\mathcal{R}_\mu^*$ lattice point at the center of each of the 9 cells shown in the figure (the lattice points are not shown, to avoid overcrowding) (note: since now we are in 2D, the cells are not intervals on a single axis, but squares defined on 2 axes: k_x and k_y)
- plot a (2D!) Fermi gas parabola with the vertex on each reciprocal lattice point (so, you plot 9 parabolas)
- clip the drawn parabolas inside the first Brillouin zone
- the result is figure 77

In the hope of clarifying this further, I have prepared also figure 79, which aims at showing how the reduced zone representation in figure 77 originates in the way just described in this point. To

n_x	n_y	$\epsilon(\vec{k}) = \frac{\hbar^2}{2m} \vec{k} - \vec{G} ^2$
-1	-1	$\frac{\hbar^2}{2m} \left(\left(k_x + \frac{2\pi}{a} \right)^2 + \left(k_y + \frac{2\pi}{a} \right)^2 \right)$
-1	0	$\frac{\hbar^2}{2m} \left(\left(k_x + \frac{2\pi}{a} \right)^2 + k_y^2 \right)$
-1	1	$\frac{\hbar^2}{2m} \left(\left(k_x + \frac{2\pi}{a} \right)^2 + \left(k_y - \frac{2\pi}{a} \right)^2 \right)$
0	-1	$\frac{\hbar^2}{2m} \left(k_x^2 + \left(k_y + \frac{2\pi}{a} \right)^2 \right)$
0	0	$\frac{\hbar^2}{2m} (k_x^2 + k_y^2)$
0	1	$\frac{\hbar^2}{2m} \left(k_x^2 + \left(k_y - \frac{2\pi}{a} \right)^2 \right)$
1	-1	$\frac{\hbar^2}{2m} \left(\left(k_x - \frac{2\pi}{a} \right)^2 + \left(k_y + \frac{2\pi}{a} \right)^2 \right)$
1	0	$\frac{\hbar^2}{2m} \left(\left(k_x - \frac{2\pi}{a} \right)^2 + k_y^2 \right)$
1	1	$\frac{\hbar^2}{2m} \left(\left(k_x - \frac{2\pi}{a} \right)^2 + \left(k_y - \frac{2\pi}{a} \right)^2 \right)$

Figure 78: The expressions used for calculating on a k_x, k_y grid built on the first Brillouin zone the portions of the 9 parabolas corresponding to the 9 $\vec{G}$ vectors which, in turn, correspond to the 9 n_x, n_y pairs of integers (eq. 657).

avoid overcrowding, only 5 parabolas are shown: the unshifted one (i.e. the one centered at the origin, (0, 0)) plus the 4 parabolas centered on the lattice points (0, 1), (-1, 0), (0, -1), (1, 0). For each of the 4 parabolas around the (0, 0) cell only the portion inside the corresponding cell plus the portion extending into the first Brillouin zone have been drawn. It should be clear that the portion of the graph clipped inside the first Brillouin zone is identical to the graph shown in figure 77 (actually, only the lower part of that graph, because I did not plot all the 9 parabolas). Can you see it?

Note: on moving from 1D to 2D there is absolutely nothing new from a conceptual standpoint, but visualizing and calculating things in 2D becomes much more complicated and cumbersome. **367.** In the 2D case we can still represent graphically the band structure in a complete way, but, as you have seen in figures 77 and 78, the representation becomes more complicated than the 1D case.

For this reason, in “real life” (i.e. multidimensional) systems, the band structure is represented only “partially”; that is, instead of considering all the $\vec{k}$ points inside the first Brillouin zone, only a section of the complete graph is plotted. The section is calculated along a *trajectory* (almost always consisting of one or more linear segments) inside the first Brillouin zone.

In figure 80 a section of the bidimensional graph along the $[k_x, 0]$ segment inside the first Brillouin zone is shown: this is the panel with bold lines.

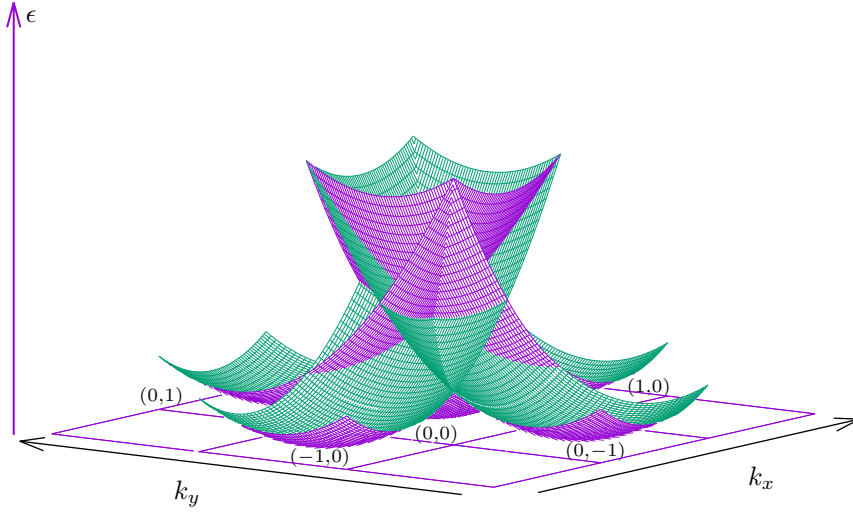


Figure 79: This figure shows an equivalent way in which the reduced representation in figure 78 can be thought to have been derived. See text for the detailed explanation.

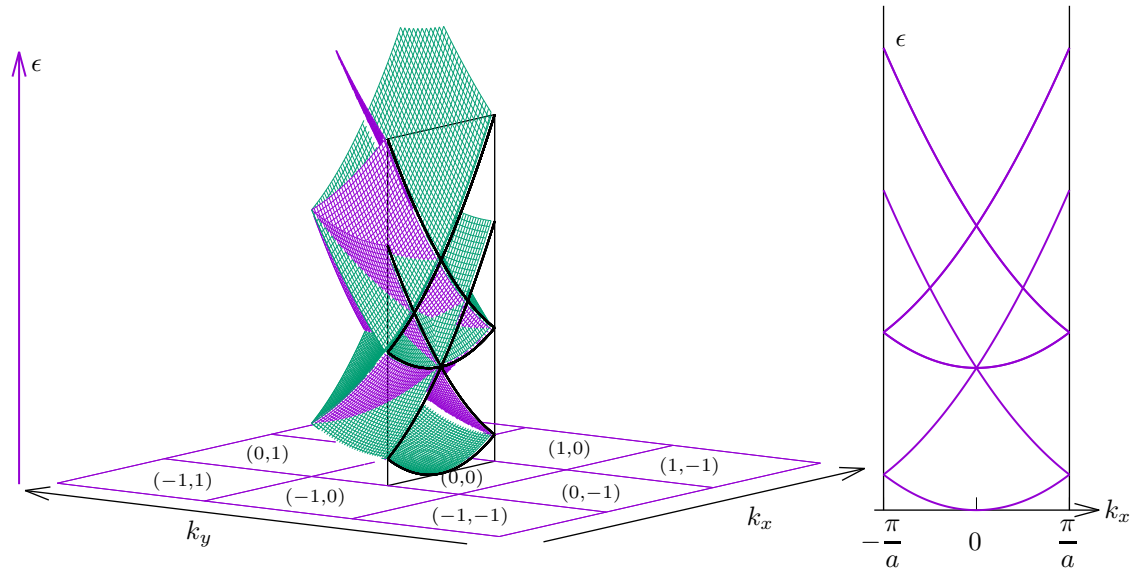


Figure 80: Left: the graph of figure 77 is vertically “cut” by the plane $k_y = 0$: the trace left by the graph on such plane (the black bold lines) is the reduced zone representation of the band structure along the $(k_x, 0)$ segment of the first Brillouin zone. Right: the panel with the bold lines from the left is represented as a “regular” 2D graph of energy (ϵ) versus k_x , for $-\pi/a \leq k_x \leq \pi/a$.

The calculation is always the same (i.e. evaluate the branches of the 9 parabolas inside the first Brillouin zone), but now $k_y = 0$ and thus $\epsilon(\vec{k})$ becomes a simple function of the single variable k_x :

$$\begin{aligned}\epsilon(\vec{k}) &= \frac{\hbar^2}{2m} |\vec{k} - \vec{G}|^2 = \frac{\hbar^2}{2m} \left| (k_x, 0) - \frac{2\pi}{a} (n_x, n_y) \right|^2 \\ &= \frac{\hbar^2}{2m} \left| \left(k_x - \frac{2\pi}{a} n_x, -\frac{2\pi}{a} n_y \right) \right|^2 \\ &= \frac{\hbar^2}{2m} \left(\left(k_x - \frac{2\pi}{a} n_x \right)^2 + \left(-\frac{2\pi}{a} n_y \right)^2 \right) = \epsilon(k_x) \quad (n_x, n_y \in \mathbb{Z})\end{aligned}\quad (659)$$

So: the bold lines in the section shown in figure 77 were calculated for the 9 (n_x, n_y) pairs with the same expressions shown in figure 78, but with $k_y = 0$ (try it!).

With respect to the 1D case, the 2D system introduces two “new” and important aspects.

5.6.1.1 The bands can overlap

368. The first new feature is that bands can overlap, only partially or completely. I have tried to illustrate this in figure 81.

Figure 81 is just the repeated zone version of the section shown in figure 80 (convince yourself that the content of the first Brillouin zone in figure 81 is identical to the content of the section shown in figure 80). In order to better distinguish consecutive bands, I have alternated the use of filled and dashed lines in the plot; the bandwidth of each band is also indicated on the sides of the plot.

To understand the trend of each band in the figure start from a point on the abscissa axis (different from the boundary of a Brillouin zone, where different branches share a common point) and locate the eigenvalues by proceeding vertically: the first eigenvalue will identify band n. 1, the second eigenvalue will identify band n. 2 and so on. If you repeat this procedure for several points on the abscissa axis you should easily realize “who is who”.

From the figure you can see that:

- ⇒ bands 1 and 2 overlap neither any other band nor each other
- ⇒ instead, band 3 completely overlaps band 4; the latter has a greater bandwidth (band 3 is plotted with a filled line, band 4 with a dashed line)
- ⇒ bands 5 and 6 overlap only partially: the upper part of band 5 overlaps the lower part of band 6

As we will see, the nature of electrical insulator or conductor of a crystal is crucially determined by band overlapping (point 528).

In simple terms, and based on what we already know, when two consecutive bands n and $n + 1$ overlap, that means that there can be electronic states of band n at *higher* energy than states of band $n + 1$. Of course, this can happen *only* in correspondence with *different* $\vec{k}$ points: that is, $\epsilon_{\vec{k}_1 n}$ can be greater than $\epsilon_{\vec{k}_2 (n+1)}$ only if $\vec{k}_1 \neq \vec{k}_2$. This should be clear if you look at figure 81 and if you also remember that, for a *fixed* wave vector, i.e. a given single point inside the first Brillouin zone, the band index enumerates the eigenvalues in order of increasing energy, and so, if $\vec{k}$ is the same, it must always be: $\epsilon_n(\vec{k}) \leq \epsilon_{n+1}(\vec{k})$.

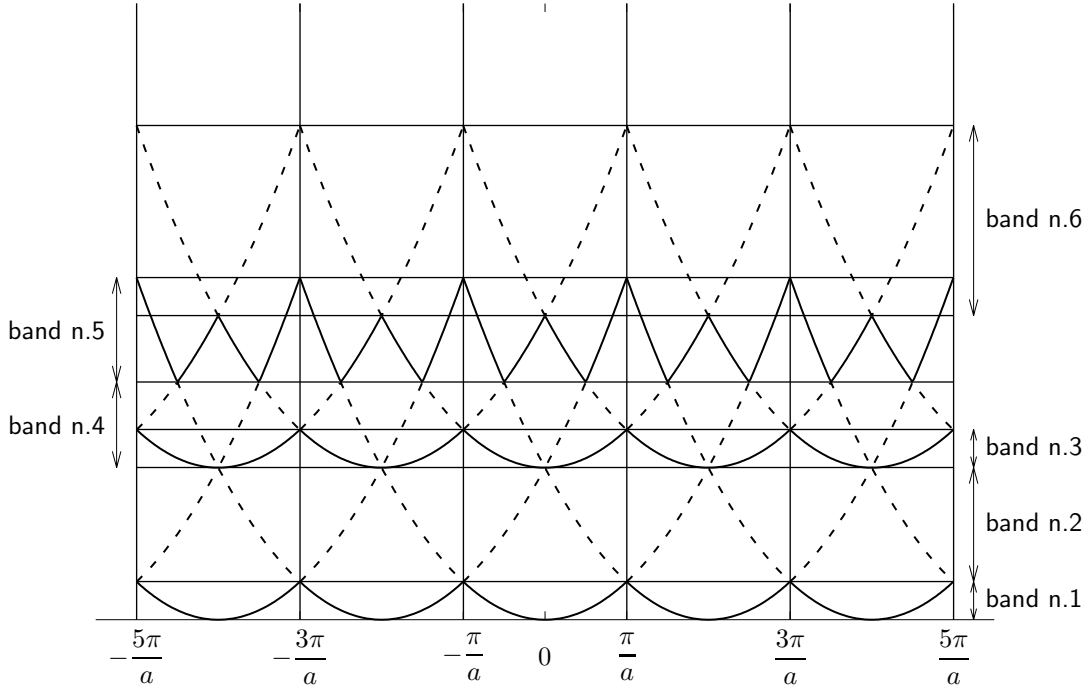


Figure 81: Band structure (repeated zone representation) along the segment $[k_x, 0]$ inside the first Brillouin zone for a bidimensional crystal with a square Bravais lattice (cell constant: a) in the “empty lattice” model. The different bands are rendered with alternating filled and dashed lines to facilitate identifying them; the energy interval corresponding to each band is shown on the sides of the graph.

5.6.1.2 More degeneracy

369. The second important effect of the increased dimensionality is the degeneracy of the energy levels. In the monodimensional case we already noted that there are doubly degenerate eigenvalues for k values corresponding to the boundaries of the Brillouin zones (p. 219).

This effect is amplified in systems with dimension 2 or 3.

If you look at figure 81 you can see that, for example, there is a triple degeneracy for $k_x = i2\pi/a$, $i = 0, \pm 1, \pm 2 \dots$ with respect to the band index: the bands 2, 3 and 4 share a common point.

Moreover, along the section $k_y = 0$ of the first Brillouin zone (that is, still in figure 81), band 3 is given by the Fermi gas parabola unshifted horizontally but translated vertically, that is eq. 659 in the form:

$$\epsilon(k_x) = \frac{\hbar^2}{2m} \left(k_x^2 + \left(\frac{2\pi}{a} \right)^2 \right) = \frac{\hbar^2}{2m} k_x^2 + \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} \right)^2 \quad (660)$$

The above form of eq. 659 is obtained for *both* $(n_x, n_y) = (0, -1)$ and $(n_x, n_y) = (0, 1)$:

$$\frac{\hbar^2}{2m} k_x^2 + \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} \right)^2 =$$

$$\frac{\hbar^2}{2m} \left(\left(k_x - \frac{2\pi}{a} \times 0 \right)^2 + \left(-\frac{2\pi}{a} \times (-1) \right)^2 \right) = \quad [(n_x, n_y) = (0, -1)]$$

$$\frac{\hbar^2}{2m} \left(\left(k_x - \frac{2\pi}{a} \times 0 \right)^2 + \left(-\frac{2\pi}{a} \times 1 \right)^2 \right) \quad [(n_x, n_y) = (0, 1)]$$

But this means that in figure 81 the band n. 3 is actually given by *two* degenerate, perfectly overlapped bands corresponding to the two pairs $(n_x, n_y) = (0, \pm 1)$ (that is, two distinct $\vec{G}$ vectors, $\vec{G} = 0\vec{b}_1 \pm 1\vec{b}_2$, eq. 657).

As a further example let's consider band 4 in figure 81. This is composed by 4 branches, each of which is obtained with eq. 659 for appropriate values of n_x and n_y , according to the following table:

in the interval:	eq. 659 becomes:	possible (n_x, n_y) values
$-\frac{\pi}{a} \leq k_x \leq -\frac{1}{2} \frac{\pi}{a}$	$\frac{\hbar^2}{2m} \left(\left(k_x + \frac{2\pi}{a} \right)^2 + \left(\frac{2\pi}{a} \right)^2 \right)$	$(-1, 1), (-1, -1)$
$-\frac{1}{2} \frac{\pi}{a} \leq k_x \leq 0$	$\frac{\hbar^2}{2m} \left(k_x - \frac{2\pi}{a} \right)^2$	$(1, 0)$
$0 \leq k_x \leq \frac{1}{2} \frac{\pi}{a}$	$\frac{\hbar^2}{2m} \left(k_x + \frac{2\pi}{a} \right)^2$	$(-1, 0)$
$\frac{1}{2} \frac{\pi}{a} \leq k_x \leq \frac{\pi}{a}$	$\frac{\hbar^2}{2m} \left(\left(k_x - \frac{2\pi}{a} \right)^2 + \left(\frac{2\pi}{a} \right)^2 \right)$	$(1, 1), (1, -1)$

For example: the first branch is obtained for the Fermi gas parabola shifted to the right by $2\pi/a$ and vertically by $(\hbar^2/(2m)) (2\pi/a)^2$, and so on. From the above table you can see that the outermost branches of band n. 4 are actually given by the perfect overlap of two degenerate bands corresponding to two different $\vec{G}$ vectors: $(-1, 1), (-1, -1)$ and $(1, 1), (1, -1)$, respectively.

Consider that in this example we limited ourselves to only 9 $\vec{G}$ vectors. Band degeneracy (partial or total) becomes more and more frequent as the number of the involved $\vec{G}$ vectors increases, and this number is theoretically infinite.

Finally note that, like in the monodimensional case, the quadratic form of the dispersion relation for the “empty lattice” induces mirror symmetry with respect to the ordinate axis.

5.6.2 3D system with simple cubic Bravais lattice

370. As already noted, the complete representation of the dispersion relation for a 3D system is simply not possible (the “graph” would be fourdimensional); therefore, in this case, it is mandatory to set up partial representations on sections or trajectories inside the first Brillouin zone.

In this regard it is worth mentioning that for each of the Brillouin zones corresponding to the 14 Bravais lattices there exists a traditional nomenclature which identifies “special” points (of high symmetry) in the interior or on the faces of it. For instance, in all cases the origin, that is, the central point of the first Brillouin zone, is labeled with Γ . In the case of the first Brillouin zone of a simple cubic Bravais lattice the symbols M , X and R are used to indicate the points corresponding to the intersection with the cube faces (you remember: the first Brillouin zone for a simple cubic lattice is itself a cube) of the directions given by the reciprocal vectors with

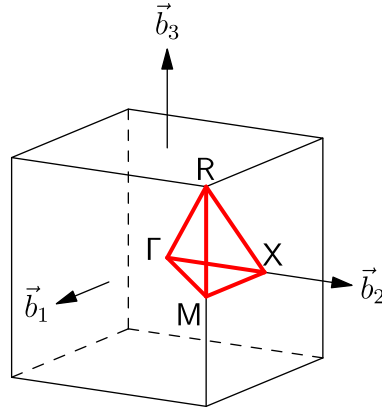


Figure 82: The first Brillouin zone for a simple cubic lattice with the indication of the special points Γ , X , M , R .

integer coefficients $(1, 1, 0)$, $(0, 1, 0)$ and $(1, 1, 1)$, respectivelyⁱ(figure 82).

So, for example, you might find the band structure for a real crystal calculated along the trajectory $\Gamma X M \Gamma R X$ and so on.

371. As an example of a band calculation for a 3D system, let's see the extension of what we already did in the 2D case to a three-dimensional crystal with a simple cubic Bravais lattice (cell parameter: a) in the “empty lattice” model.

Let's build the reduced zone representation of the “empty lattice” bands along the linear segment $k(1, 1, 1)$ ⁱⁱ of the first Brillouin zone (in terms of special points, this is the ΓR segment, fig. 82) (a similar example, but for the $k(1, 0, 0)$ segment, is presented in the books by Kittel²⁴ and by Ibach e Lüth²⁵).

Also in this case we consider only the set of $\vec{G}$ vectors corresponding to the cells “surrounding” the first Brillouin zone. Realize that the number of these vectors is 26: there are 9 primitive cells “above” and “below” the first Brillouin zone, plus 8 cells “around” it: $9 + 9 + 8 = 26$; so we consider 26 vectors of type:

$$2\pi/a (n_x, n_y, n_z) \quad \text{with: } n_x, n_y, n_z = 0, \pm 1 \quad (\text{excluding } (n_x, n_y, n_z) = (0, 0, 0))$$

(you can equivalently think of these 26 vectors as given by the 6 nearest neighbors, plus the 12 second neighbors, plus the 8 third neighbors of the origin). Counting also the null vector (which corresponds to the first Brillouin zone itself: $(n_x, n_y, n_z) = (0, 0, 0)$) our band calculation is to be done with 27 $\vec{G}$ vectors.

The calculation is always the same: evaluate expression 652:

$$\begin{aligned} & \epsilon \left(\vec{k} - \vec{G} \right) \\ &= \frac{\hbar^2}{2m} \left| \vec{k} - \vec{G} \right|^2 = \frac{\hbar^2}{2m} \left| k(1, 1, 1) - \frac{2\pi}{a} (n_x, n_y, n_z) \right|^2 \end{aligned}$$

ⁱYou can find the representation of all the first Brillouin zones with the notation for their special points at this URI https://en.wikipedia.org/wiki/Brillouin_zone

ⁱⁱThe notation $k(1, 1, 1)$ means “ k times the vector $(1, 1, 1)$ ”; so, as k (a scalar) varies in $\mathbb{R}$, $k(1, 1, 1)$ is the set of points of the straight line (in 3D space) having the same direction as the $(1, 1, 1)$ vector.

$$\begin{aligned}
&= \frac{\hbar^2}{2m} \left| \left(k - \frac{2\pi}{a}n_x, k - \frac{2\pi}{a}n_y, k - \frac{2\pi}{a}n_z \right) \right|^2 \\
&= \frac{\hbar^2}{2m} \left(\left(k - \frac{2\pi}{a}n_x \right)^2 + \left(k - \frac{2\pi}{a}n_y \right)^2 + \left(k - \frac{2\pi}{a}n_z \right)^2 \right) \tag{661}
\end{aligned}$$

on all the points of the $k(1, 1, 1)$ linear segment inside the first Brillouin zone, for $n_x, n_y, n_z = 0, \pm 1$.

In order to perform the calculation, we also need to sort out the lower and upper limits of k which determine the start and end point, respectively, along the straight line $k(1, 1, 1)$.

This is done in the following way.

The linear segment along which we want to make the calculation is the body diagonal of the first Brillouin zone (a cube of side $2\pi/a$ and centered on the origin: see figure 82). The coordinates of the two vertices connected by the segment are:

$$\frac{2\pi}{a} \left(-\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2} \right) = -\frac{\pi}{a} (1, 1, 1) \tag{662}$$

and

$$\frac{2\pi}{a} \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right) = \frac{\pi}{a} (1, 1, 1) \tag{663}$$

Thus, the points of the segment $k(1, 1, 1)$ inside the first Brillouin zone are obtained when k varies in the interval:

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a} \tag{664}$$

The 27 explicit forms which takes eq. 661 for the 27 considered $\vec{G}$ vectors are shown in figure 83 (I suggest you to verify with pencil and paper some of the expressions).

By calculating the expressions of figure 83 for $-\pi/a \leq k \leq \pi/a$, figure 84 is obtained.

Besides the mirror symmetry with respect to the energy axis, as in the previous cases, note that there are only 10 bands (how to count them: start from a generic point on the k axis and count how many times you intersect the curves while going up vertically). Since we made the calculation for 27 $\vec{G}$ vectors, we would expect 27 bands; we find only 10 because the remaining are perfectly overlapped (degenerate) with one or the other of the visible bands.

For example, in figure 83 you can see that the three $\vec{G}$ vectors corresponding to the three triplets of coefficients:

$$\begin{aligned}
(n_x, n_y, n_z) &= (1, 0, 0) \\
(n_x, n_y, n_z) &= (0, 1, 0) \\
(n_x, n_y, n_z) &= (0, 0, 1)
\end{aligned}$$

lead to the same expression:

$$\frac{\hbar^2}{2m} \left(\left(k - \frac{2\pi}{a} \right)^2 + 2k^2 \right)$$

n_x	n_y	n_z	$\epsilon(\vec{k} - \vec{G}) = \frac{\hbar^2}{2m} \left((k - \frac{2\pi}{a}n_x)^2 + (k - \frac{2\pi}{a}n_y)^2 + (k - \frac{2\pi}{a}n_z)^2 \right)$
-1	-1	-1	$3 \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} + k \right)^2$
-1	-1	0	$\frac{\hbar^2}{2m} \left(2 \left(\frac{2\pi}{a} + k \right)^2 + k^2 \right)$
-1	-1	1	$\frac{\hbar^2}{2m} \left(2 \left(\frac{2\pi}{a} + k \right)^2 + \left(k - \frac{2\pi}{a} \right)^2 \right)$
-1	0	-1	$\frac{\hbar^2}{2m} \left(2 \left(\frac{2\pi}{a} + k \right)^2 + k^2 \right)$
-1	0	0	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + 2 k^2 \right)$
-1	0	1	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + \left(k - \frac{2\pi}{a} \right)^2 + k^2 \right)$
-1	1	-1	$\frac{\hbar^2}{2m} \left(2 \left(\frac{2\pi}{a} + k \right)^2 + \left(k - \frac{2\pi}{a} \right)^2 \right)$
-1	1	0	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + \left(k - \frac{2\pi}{a} \right)^2 + k^2 \right)$
-1	1	1	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + 2 \left(k - \frac{2\pi}{a} \right)^2 \right)$
0	-1	-1	$\frac{\hbar^2}{2m} \left(2 \left(\frac{2\pi}{a} + k \right)^2 + k^2 \right)$
0	-1	0	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + 2 k^2 \right)$
0	-1	1	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + \left(k - \frac{2\pi}{a} \right)^2 + k^2 \right)$
0	0	-1	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + 2 k^2 \right)$
0	0	0	$3 \frac{\hbar^2}{2m} k^2$
0	0	1	$\frac{\hbar^2}{2m} \left(\left(k - \frac{2\pi}{a} \right)^2 + 2 k^2 \right)$
0	1	-1	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + \left(k - \frac{2\pi}{a} \right)^2 + k^2 \right)$
0	1	0	$\frac{\hbar^2}{2m} \left(\left(k - \frac{2\pi}{a} \right)^2 + 2 k^2 \right)$
0	1	1	$\frac{\hbar^2}{2m} \left(2 \left(k - \frac{2\pi}{a} \right)^2 + k^2 \right)$
1	-1	-1	$\frac{\hbar^2}{2m} \left(2 \left(\frac{2\pi}{a} + k \right)^2 + \left(k - \frac{2\pi}{a} \right)^2 \right)$
1	-1	0	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + \left(k - \frac{2\pi}{a} \right)^2 + k^2 \right)$
1	-1	1	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + 2 \left(k - \frac{2\pi}{a} \right)^2 \right)$
1	0	-1	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + \left(k - \frac{2\pi}{a} \right)^2 + k^2 \right)$
1	0	0	$\frac{\hbar^2}{2m} \left(\left(k - \frac{2\pi}{a} \right)^2 + 2 k^2 \right)$
1	0	1	$\frac{\hbar^2}{2m} \left(2 \left(k - \frac{2\pi}{a} \right)^2 + k^2 \right)$
1	1	-1	$\frac{\hbar^2}{2m} \left(\left(\frac{2\pi}{a} + k \right)^2 + 2 \left(k - \frac{2\pi}{a} \right)^2 \right)$
1	1	0	$\frac{\hbar^2}{2m} \left(2 \left(k - \frac{2\pi}{a} \right)^2 + k^2 \right)$
1	1	1	$3 \frac{\hbar^2}{2m} \left(k - \frac{2\pi}{a} \right)^2$

Figure 83: By plugging the 27 integer triplets n_x, n_y, n_z corresponding to the 27 $\vec{G}$ vectors considered for the band calculation described in the text, eq. 661 assumes the 27 explicit forms shown in this figure.

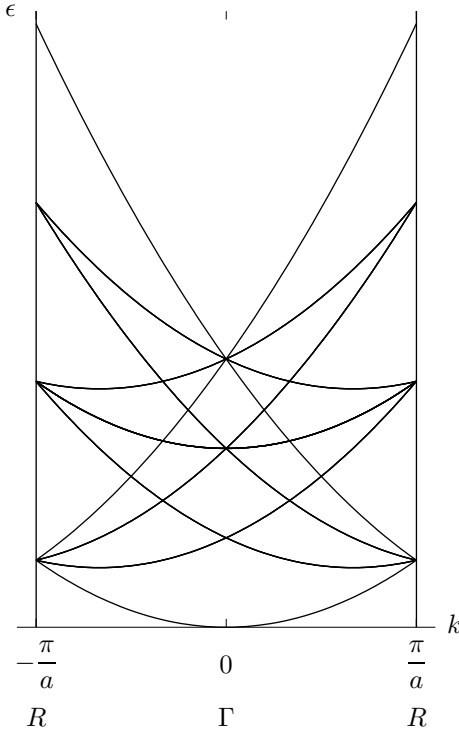


Figure 84: Band structure calculated along the segment $k(1, 1, 1)$ for a 3D crystal with simple cubic Bravais lattice (cell constant: a) in the “empty lattice” model.

5.6.3 The Fermi surface

372. Another way to get information about the band structure is to build the Fermi surface. We introduced the general definitions of the Fermi energy and the Fermi surface in section 3.12. The Fermi surface encloses all and only the $\vec{k}$ points corresponding to occupied states, and this is a very useful piece of information.

373. In the case of a periodic potential we have seen that the energy of the electronic states is partitioned into bands. The position of the bands with respect to the Fermi energy ϵ_F can generate at least three different scenarios:

1. if the minimum ϵ_n^{min} of band n is *greater* than ϵ_F :

$$\epsilon_F < \epsilon_n^{min} \quad (665)$$

then all the band states are obviously unoccupied: we say that the band is *empty*.

2. if the maximum ϵ_n^{max} of band n is *less* than ϵ_F :

$$\epsilon_n^{max} < \epsilon_F \quad (666)$$

then all the band states are occupied: we say that the band is *full* or *completely occupied*.

3. finally, if ϵ_F is inside the energy interval which defines band n :

$$\epsilon_n^{min} < \epsilon_F < \epsilon_n^{max} \quad (667)$$

then the states of the band at energy less than ϵ_F will be occupied, while those at energy greater than ϵ_F will be empty. We say that the band is *partially occupied*.

374. For each partially occupied band it is possible to plot in $\vec{k}$ space the surface defined by:

$$\epsilon_n(\vec{k}) = \epsilon_F \quad (668)$$

(obviously, for an empty or full band it is not possible to plot such a surface because in these cases eq. 668 has no solutions)

The set of surfaces obtained for all the partially occupied bands is the Fermi surface for the case of a crystal (i.e. periodic potential). The parts of the Fermi surface originated by each partially occupied band are called *the branches* of the Fermi surface.

By definition, branch n of the Fermi surface encloses the $\vec{k}$ points corresponding to occupied states in band n .

We already know that the function $\epsilon_n(\vec{k})$ is periodic in $\vec{k}$ space and therefore the Fermi surface will exhibit the same periodicity. For this reason, the Fermi surface can be represented in one of the three modes that we already discussed for the band structure, namely “reduced zone”, “extended zone” or “repeated zone”.

375. In order to better understand the relation between the different bands and the Fermi surface in a periodic system let’s analyze the 2D system of section 5.6.1.

As already noted in general (section 3.12), the Fermi “surface” for a 2D system isn’t actually a surface, but rather a trajectory on the k_x, k_y plane.

5.6.3.1 Reduced zone representation

376. The reduced zone representation of the *whole* Fermi surface can be obtained in a single step by solving eq. 409 inside the first Brillouin zone. In section 5.6.1 we already derived the reduced zone representation of the dispersion relation for this system (figure 77), that is, $\epsilon(k_x, k_y)$ in eq. 409 (keep in mind here that in this 2D case the dispersion relation is a function of the two independent variables k_x and k_y and thus its graph is represented in $\mathbb{R}^3$ with respect to the ϵ, k_x, k_y cartesian reference system).

Now: realize that, *geometrically*, the solution of equation 409 inside the first Brillouin zone is obtained as the trace left on the plane $\epsilon = \epsilon_F$ by the dispersion relation; $\epsilon = \epsilon_F$ is a plane which is parallel to the k_x, k_y plane and “cuts” the ϵ axis at ϵ_F .

This is explicitly shown in figure 85.

You can see that, for $\epsilon = \epsilon_{F1}$ in the figure, the Fermi surface reduces to a circle centered at the origin: indeed, for that low value of the Fermi energy, the plane $\epsilon = \epsilon_{F1}$ intersects the dispersion relation in its lowest part, where its plot is simply that of the 2D parabola centered at the origin (see also figure 77).

As you can see in figure 85, for greater values of the Fermi energy, the Fermi surface becomes more complicated.

5.6.3.2 Repeated zone representation

377. The repeated zone representation can be obtained in the following way.

The dispersion relation for a bidimensional crystal in the “empty lattice” model is given by the set of infinite 2D parabolas each centered on a point of the microscopic reciprocal lattice $\mathcal{R}_\mu^*$ (point 366 and figure 79).

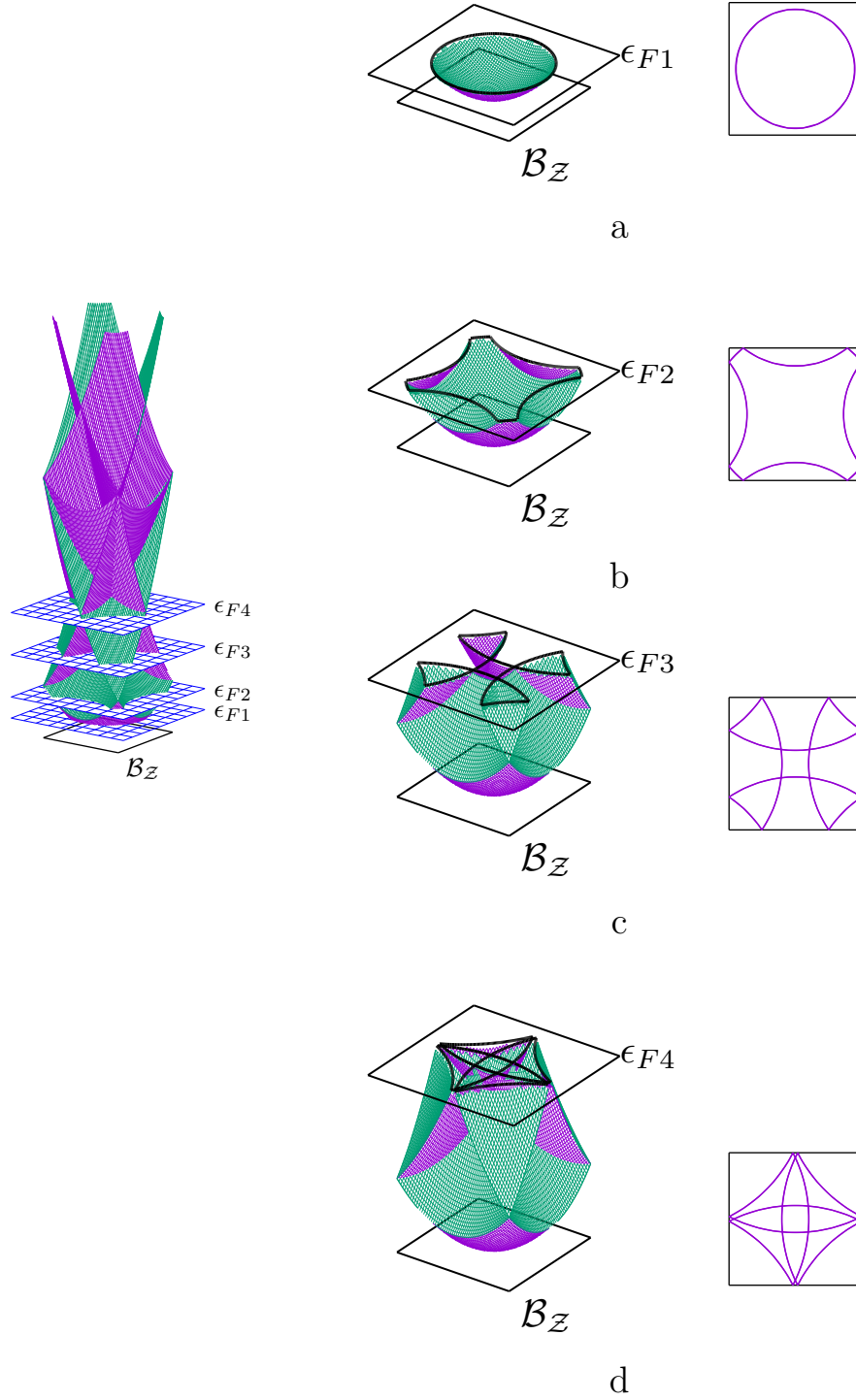


Figure 85: The reduced zone representation of the dispersion relation for a bidimensional crystal with square Bravais lattice in the "empty lattice" model is reproduced from figure 77 on the left. Four planes of equation $\epsilon = \epsilon_{Fi}$ $i = 1, 2, 3, 4$, at increasing values of the Fermi energy ϵ_{Fi} are also shown. The portion of the dispersion relation "cut" by each plane is represented on the right (panels a-d), together with its trace on the sectioning plane evidenced as a black bold trajectory. For more clarity, the section trace in the first Brillouin zone is also plotted separately on the right: such trace is the reduced zone representation of the Fermi "surface" for the corresponding value of the Fermi energy.

Out of the infinite set, consider the single parabola centered on the $n_x \vec{b}_1 + n_y \vec{b}_2$ point of $\mathcal{R}_\mu^*$. Its equation is (eq. 658):

$$\epsilon(k_x, k_y) = \frac{\hbar^2}{2m} \left(\left(k_x - \frac{2\pi}{a} n_x \right)^2 + \left(k_y - \frac{2\pi}{a} n_y \right)^2 \right) \quad (669)$$

The equation defining the Fermi surface for this single parabola is (eq. 409):

$$\frac{\hbar^2}{2m} \left(\left(k_x - \frac{2\pi}{a} n_x \right)^2 + \left(k_y - \frac{2\pi}{a} n_y \right)^2 \right) = \epsilon_F \quad (670)$$

or:

$$\left(k_x - \frac{2\pi}{a} n_x \right)^2 + \left(k_y - \frac{2\pi}{a} n_y \right)^2 = \frac{2m}{\hbar^2} \epsilon_F \quad (671)$$

As you might have guessed, this is a circle of radius $\sqrt{(2m/\hbar^2)\epsilon_F}$ with center on $(n_x, n_y) 2\pi/a$. So: the part of the Fermi surface originated by a *single* parabola of the dispersion relation is a circle with center on a reciprocal lattice point and with a radius directly proportional to the square root of the Fermi energy.

The complete repeated zone representation of the Fermi surface will thus be given by the set of infinite circles originated by all the parabolas.

The appearance of the Fermi surface depends on the Fermi energy; for sufficiently small values of the latter, the radius of the circles will be small enough so that each circle will be fully confined into its own primitive cell; however, as the Fermi energy exceeds the threshold which makes the radius greater than π/a (half side of the square primitive cell), the circles will intersect each other and the Fermi surface becomes more complex.

378. In figure 86 I have drawn with this procedure the Fermi surfaces for the same values of the Fermi energy used in figure 85 (sequence *a, b, c, d*). Each panel of the figure shows the first Brillouin zone (central cell) together with its eight nearest surrounding cells (like in figure 77). In each panel I have evaluated the circles defined by eq. 670 for the given Fermi energy value. So each panel is the repeated zone representation of the Fermi surface for that Fermi energy value. As we already know from the dispersion relation, the reduced zone representation of the Fermi surface is obtained by simply “clipping” all the circles inside the first Brillouin zone, and this is shown as the red plot in the first Brillouin zone of each panel: the red plots in figure 86 are identical to the plots in figure 85.

As already noted in figure 85, the value ϵ_{F1} of the Fermi energy is sufficiently small that the horizontal section of the Fermi gas parabola is a circle fully contained in its reciprocal cell. This is the simplest case: the infinite circles have no intersections; the red circle inside the first Brillouin zone encloses the $\vec{k}$ points corresponding to occupied states. The points of the first Brillouin zone outside the red circle correspond to unoccupied states (at 0 K and for $\epsilon_F = \epsilon_{F1}$).

In panels *b, c, d* the Fermi energy increases and the circles do intersect each other: as a result, the reduced zone representation of the Fermi surface (the red plot inside the first Brillouin zone) becomes increasingly complex.

5.6.3.3 Extended zone representation

379. Figures 85 and 86 show the “whole” Fermi surface, but we have seen that for a periodic system the Fermi surface is composed by branches, each branch being originated by a corresponding partially occupied band (eq. 668).

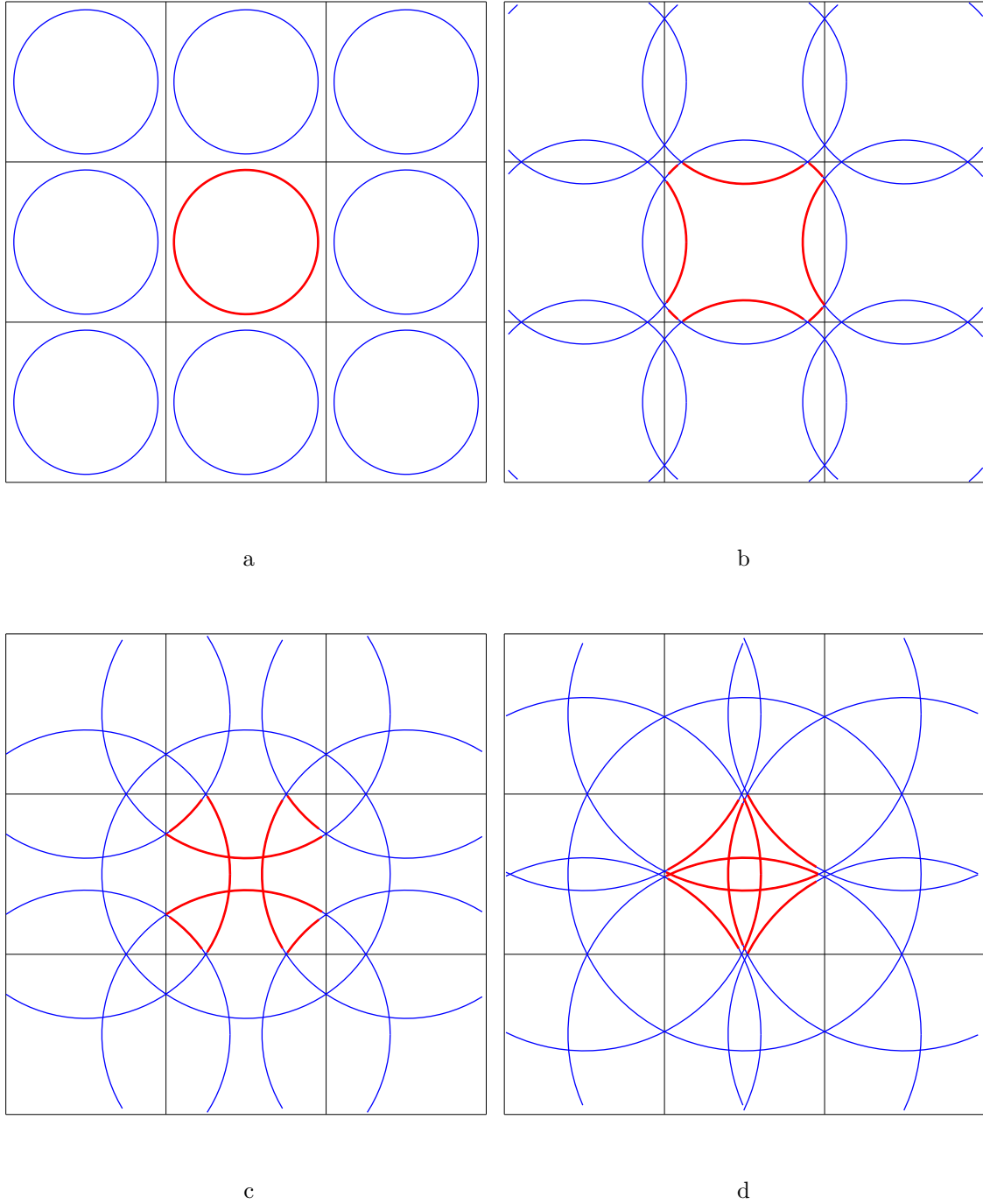


Figure 86: The Fermi surface (actually, not a surface, but rather a periodically repeating trajectory on the plane) for the 2D system of section 5.6.1. The a , b , c , d panels refer to increasing values of the Fermi energy. In each panel the repeated zone representation is shown; the reduced zone representation is also shown as the red plot inside the first Brillouin zone (i.e. the central primitive cell of $\mathcal{R}_\mu^*$).

So how can we partition the “whole” surface into its component branches (that is, the contributions from each partially occupied band)?

The answer to this question comes from the extended zone representation. In point 361 we have seen that in this representation the i –th band corresponds to the content of the i –th Brillouin zone. This continues to be true also for the extended zone representation of the Fermi surface: plot the single circle centered on the first Brillouin zone and overlay the grid of all the Brillouin zones onto the plot. The portion(s) of the circle contained in the i –th Brillouin zone constitute the branch of the Fermi surface originated by the i –th band.

380. Let’s see how this works in practice.

Go back to figure 86.

Interpreting the Fermi surface in panel a is very simple: the circle is fully contained into the first Brillouin zone: realize that this means that the red circle is both the reduced zone and the extended zone representation of the Fermi surface. So, in this simplest case, the Fermi surface intersects only the first Brillouin zone and thus is composed by only the single branch coming from the first band. All the $\vec{k}$ points inside the circle correspond to occupied states in the first band; the $\vec{k}$ points outside the circle correspond to unoccupied states in the first band. Of course, all the states of the second, third etc bands are unoccupied for the given value of the Fermi energy.

On passing to panels b, c and d of figure 86, the situation is not so simple: in these cases the circle representing the Fermi surface for this system “overflows” the first Brillouin zone; as you can see, now the reduced zone representation of the Fermi surface becomes complicated: understanding what are its different branches and which bands they come from is not immediately obvious.

As I mentioned above, the analysis of the Fermi surface is greatly simplified if we consider its extended zone representation. We have introduced and discussed the extended zone representation of the dispersion relation in section 5.5.3. In this case we are considering a different quantity (the Fermi surface, precisely, although the two are strictly related, as you have seen), but conceptually there is no difference: basically, the extended zone representation of the Fermi surface (which, just because it is derived from the dispersion relation, is periodic on $\mathcal{R}_\mu^*$) is simply obtained by plotting the single circle centered at the origin. If we then overlay onto the plot the Brillouin zones, we immediately see which parts of the Fermi surface intersect which Brillouin zones, and, in turn, this allows us to identify its different branches.

In figure 87 I show you how this works in practice, taking panel d of figure 86 as an example.

Panel a of figure 87 is the extended zone representation of the Fermi surface from panel d of figure 86: the single circle at the origin (in blue). Onto the plot of the circle I have superimposed the diagram of the Brillouin zones for this bidimensional system (it is just figure 39 with few more zones added). We immediately see that the circle only intersects zones 4 and 5ⁱⁱⁱ and this means that the Fermi surface is made of only two branches: one from band 4 and one from band 5.

Zones 1, 2 and 3 are fully contained within the circle: this means that bands 1, 2 and 3 are fully occupied (you remember: in general, all the $\vec{k}$ points inside the Fermi surface correspond to occupied states).

Panels b/c and d/e of figure 87 show how we can characterize the two branches of the Fermi surface.

In panel b I have replotted only Brillouin zone 4 and the portion of the circle inside it. The portions of zone 4 within the circle correspond to occupied states in band 4. Now: we know that the Fermi surface, being derived from the dispersion relation, is periodic on $\mathcal{R}_\mu^*$; this means that any portion of the Fermi surface *outside* the first Brillouin zone (which is a primitive cell of

ⁱⁱⁱActually, if you zoom a lot, you will notice that the circle has also a tiny intersection with Brillouin zone 3, but we ignore that for the sake of simplifying this example.

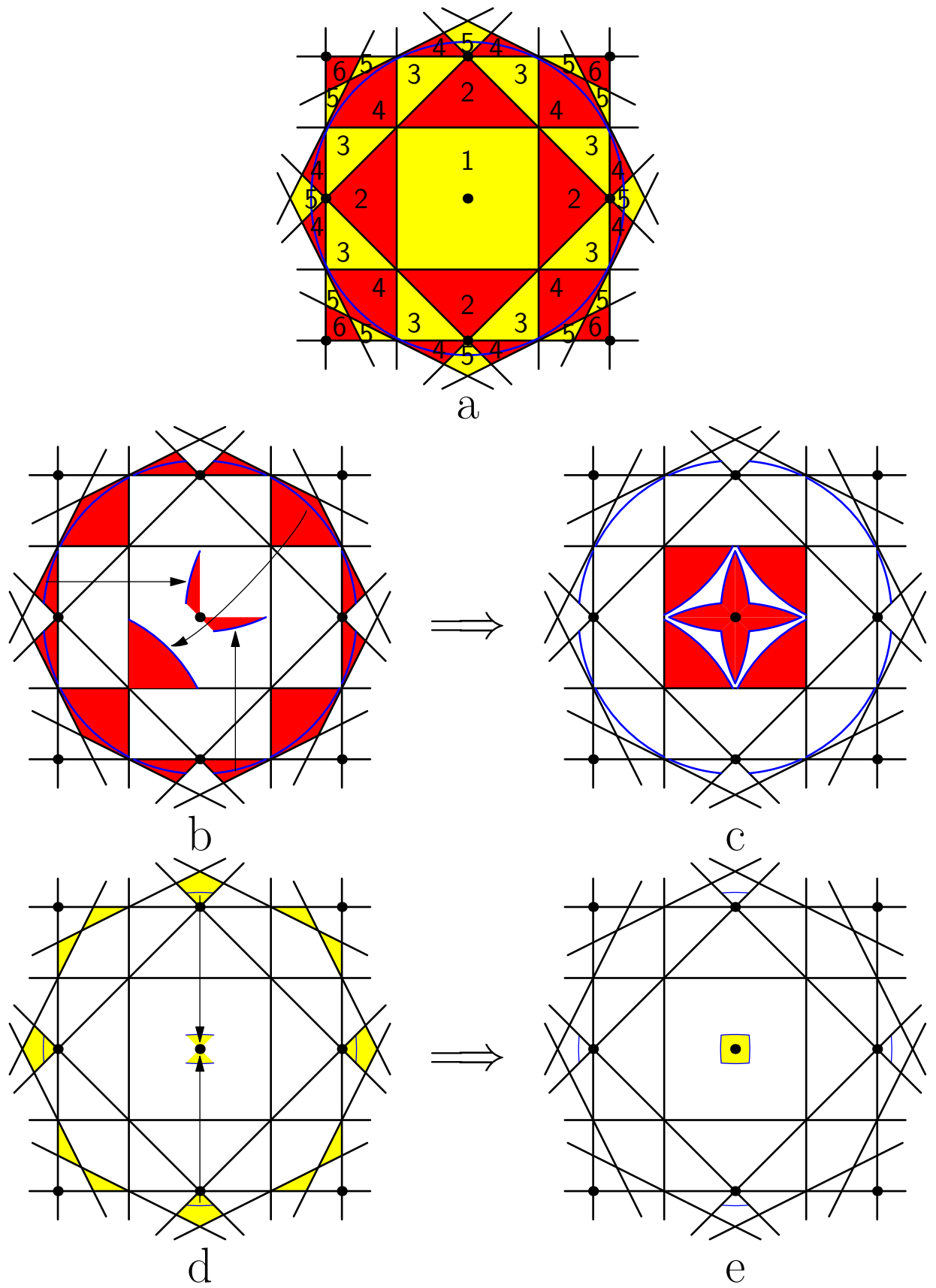


Figure 87: The reduced zone representation of the Fermi surface in figure 86d has been resolved into the different branches (actually only two) originated by corresponding bands. Detailed explanation is in the text.

$\mathcal{R}_\mu^*$) must have a corresponding image *inside* it. So, in order to recover branch 4 of the reduced zone representation in figure 86d (or 85) we have to “refold” the portions of the Fermi surface in zone 4 back into the first Brillouin zone. This is shown by the arrows in panel b: in order to avoid overcrowding the figure, I have shown how to refold only three portions of the Fermi surface (but, please, make sure you would be able to complete the process for all the portions of the Fermi surface!). Note also that we refold not only the portion of the circle, but also the region of $\vec{k}$ space corresponding to occupied states delimited by it (still due to the periodicity, any $\vec{k}$ point corresponding to an occupied state in zone 4 must have its image in the first Brillouin zone, right?).

When all the portions of the circle (and the respective regions of zone 4 corresponding to occupied states) are taken back into the first Brillouin zone, panel c is obtained.

Now compare panel c with figure 86d (or 85d): we have clearly identified branch 4 of the reduced zone representation and the regions of the first Brillouin zone that correspond to occupied states in band 4. Please note: *all* the $\vec{k}$ points in the first Brillouin zone do correspond to occupied states in bands 1 2 and 3, but only those $\vec{k}$ points in the red regions of figure 87c identify occupied states in band 4; in other words: there are $\vec{k}$ points in the first Brillouin zone that correspond to occupied states in bands 1 2 and 3 and to unoccupied states in band 4 (the $\vec{k}$ points in the uncolored regions of figure 87c). Realize that this is definitely what we would expect: panel 87a clearly shows that, for the fixed value of the Fermi energy, only bands 4 and 5 are partially occupied: bands 1 2 and 3 are full and bands ≥ 6 are empty (recall that for a given $\vec{k}$ point there are infinite eigenvalues and corresponding states, see, for example, figure 71).

Panels d/e of figure 87 show the same procedure for zone 5. In panel d I have reproduced only Brillouin zone 5 together with its intersecting portions of the circle: you see that only four small portions of the circle do intersect zone 5. For two of these portions, I show how they can be folded back inside the first Brillouin zone. Panel c shows the final result of the refolding process: this is branch 5 of the Fermi surface and now we immediately identify it in the reduced zone representation of figure 86d (or 85d). As you can see by comparing branches 4 and 5, only a small fraction of the $\vec{k}$ points in band 5 correspond to occupied states.

381. The above procedure can be applied for any value of the Fermi energy in order to recover the branches of the Fermi surface originated by each band (try to obtain the branches of the Fermi surfaces in panels b and c of figure 86).

The construction of the branches of the Fermi surface for the same system discussed above (although based on a slightly different procedure) is presented in the book by Kittel²⁶).

At this web address:

http://lampx.tugraz.at/~hadley/ss2/fermisurface/2d_fermisurface/2dsquare.php

you can find a nice interactive interface which allows you to see, for the same 2D system discussed here, how the Fermi surface and its individual branches change as the Fermi energy changes: try to reproduce what you have seen in this section by using that interface.

5.6.3.4 3D systems

382. What we have just seen about the Fermi surface for 2D systems extends with no conceptual differences also to 3D systems: it only becomes more complicated to treat and represent. One additional complication (among others) is that the dispersion relation, from which the Fermi surface is derived, is now a 4D object (that is, a function of the three independent variables k_x, k_y, k_z) and thus its graph is non representable. On the other hand, the Fermi surface, defined implicitly by eq. 408, is a surface in space and thus still representable in a three-dimensional reference system.

Similar to the 2D case, the 3D dispersion relation is given by the set of infinite hyperparabolas, each centered on a point of $\mathcal{R}_\mu^*$. The Fermi surface for a single hyperparabola will be a sphere. In the simplest case, when the Fermi energy is less than ϵ_1^{max} , the maximum energy value in the first band, each sphere will be completely confined inside its primitive cell; for greater values of the Fermi energy the spheres will overflow their respective primitive cells and intersect each other, originating more complicated Fermi surfaces.

5.7 Density of states

383. The concept of density of states, which we introduced in the section about the Fermi gas model (p. 158) is of completely general scope and thus extends straightforwardly to the case of a periodic potential. Similar to the Fermi surface and for the same reason (that in a periodic system the electronic states are organized into bands) it makes sense to define the density of states $g_n(\epsilon(\vec{k}'))$ for the single band n . That is, using the general definition 506:

$$g_n(\epsilon(\vec{k}')) = \frac{1}{V} \sum_{\vec{k}} \delta(\epsilon(\vec{k}') - \epsilon_n(\vec{k})) \quad (672)$$

where $\epsilon_n(\vec{k})$ is the energy of the state corresponding to the allowed wave vector $\vec{k}$ in band n (i.e. the n -th eigenvalue of the subsystem of the central equation labelled by point $\vec{k}$).

Clearly, the total density of states is obtained as:

$$g(\epsilon(\vec{k}')) = \sum_n g_n(\epsilon(\vec{k}')) = \frac{1}{V} \sum_n \sum_{\vec{k}} \delta(\epsilon(\vec{k}') - \epsilon_n(\vec{k})) \quad (673)$$

Since in presence of a periodic potential the energy of the electronic states is periodic on $\mathcal{R}_\mu^*$, the calculation of the density of states can be restricted to the first Brillouin zone only. We know that the states corresponding to $\vec{k}$ points outside the first Brillouin zone are exact replicas of those inside it (point 332).

In other words, eq. 672 can be equivalently rewritten as:

$$g_n(\epsilon(\vec{k}')) = \frac{1}{V} \sum_{\vec{k} \in \mathcal{B}_Z} \delta(\epsilon(\vec{k}') - \epsilon(\vec{k} - \vec{G}_{\vec{k},n})) \quad (674)$$

where $\mathcal{B}_Z$ stands for the first Brillouin zone and $\vec{G}_{\vec{k},n}$ is the vector of $\mathcal{R}_\mu^*$ which we must add to (or subtract from) $\vec{k}$ to obtain the energy value of the corresponding state in band n ($\vec{G}_{\vec{k},n}$ depends on both the band index n and the $\vec{k}$ point inside the first Brillouin zone: review the contents of p. 353 and figure 71).

In the case of the simple “empty lattice” model, the total density of states is exactly the same as the one we obtained for the free electron model, that is, in the absence of a periodic potential (actually, in the absence of a potential altogether) (eq. 487).

Indeed, if you review figure 73 (the figure is for the 1D case, but everything still holds for the 2D or 3D cases), you realize that the energy values for which the δ function of 673 “shoots its shots” are exactly the same as those for the Fermi gas, and thus the density of states must be the same either. The difference between the “empty lattice” and the Fermi gas models is conceptual: in the former, differently from the latter, the eigenvalues are partitioned into bands and because of this you can imagine the graph of figure 60b as made into “slices”, each slice being the density of states for a single band (eq. 672); I have illustrated the concept in figure 88.

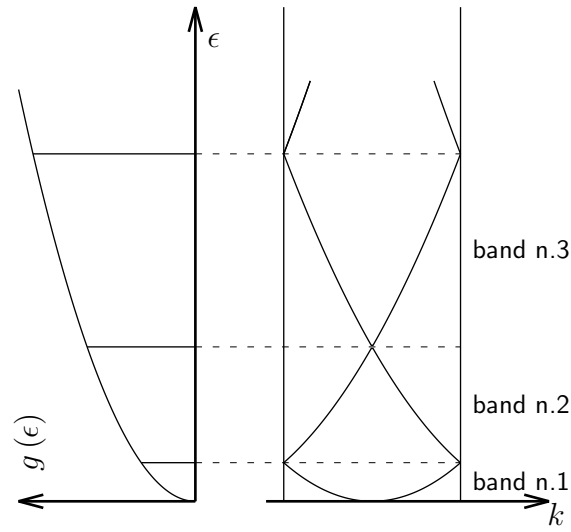


Figure 88: The first three bands in the “empty lattice” model (on the right) and the corresponding density of states $g(\epsilon)$ (on the left): I have emphasized that the total density of states (identical to that of the Fermi gas) can be thought of as made in “slices”, each slice corresponding to a single band (attention: the band structure is the same as figure 75, that is, for a 1D system, but the density of states is that for a 3D system; actually, as I mentioned in point 267, the density of states for a 1D system does not exhibit the trend shown in this figure: I just wanted to illustrate the idea presented in the text. It would have been more appropriate to use the band structure in figure 84, but the end result would have been (uselessly) more complicated).

6 The “nearly free electron” model and the band gap

384. In the previous section we analyzed the “empty lattice” model and we saw what the bands for this system look like in practice (figure 73).

However, in this model the potential energy operator $U(\vec{r})$ in Schrödinger’s equation is actually the null operator, which is a rather peculiar and special feature.

In this section we will see that when the potential is $\neq 0$ (which, of course, is the norm for any physically significant system) a new feature, absent in the “empty lattice” model, enters the game; this new feature plays a fundamental role in determining the properties of crystalline solids.

In figure 73 you may have noticed that the energy bands for the “empty lattice” model are *contiguous*, that is: as energy increases, we pass from any band to the following one with continuity.

In the present section you will see that if the potential is not null, then the energy bands become separated: in between two consecutive bands an energy region appears where *no allowed eigenvalues are present*. These forbidden energy intervals are called *band gaps* and, as we will see, they are of fundamental importance in the discussion of the properties of crystalline materials.

385. It is possible to justify both mathematically and physically the formation of the band gap by using a model which is somehow more realistic than the “empty lattice” model; it is called the “nearly free electron” model and is characterized by the introduction of a non null potential, which, however, is sufficiently small that the following two assumptions always hold:

1. the coefficients of the Fourier expansion of the potential:

$$U(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r})$$

are negligibly small, that is, mathematically:

$$U_{\vec{G}} \rightarrow 0 \quad \forall \vec{G} \quad (675)$$

2. just because the potential is *almost* null, the electronic energy levels (the eigenvalues of Schrödinger’s equation) differ from those which we found for the “empty lattice” model only by an infinitesimal amount; that is:

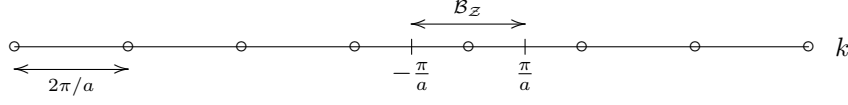
$$\epsilon(\vec{k} - \vec{G}) = \overbrace{\frac{\hbar^2 |\vec{k} - \vec{G}|^2}{2m}}^{\text{empty lattice model}} + \alpha \quad \text{with: } |\alpha| \rightarrow 0 \quad (676)$$

6.1 A mathematical justification for the band gap ⁱ

386. We will now derive the formation of the band gap in the “nearly free electron” model from a purely mathematical standpoint. To keep the derivation at a manageable level we consider a monodimensional crystal with a primitive cell of length a (and thus a reciprocal primitive cell of “length” $2\pi/a$).

So, the “physical” system is identical to the one we considered when we studied the band structure in the “empty lattice” model in point 338: the reciprocal lattice is just a monodimensional grid and the first Brillouin zone is the interval $[-\pi/a, \pi/a]$:

ⁱThe material of this part is based on the books by Kittel,²⁷ Ibach and Lüth,²⁸ and Ashcroft and Mermin.²⁹



Identically to what we already did for the “empty lattice” model, we rewrite the subsystem of the central equation corresponding to the allowed point k inside the first Brillouin zone as:

$$\left(\frac{\hbar^2 (k - jg)^2}{2m} - \epsilon \right) C_{k-jg} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig} = 0 \quad j \in \mathbb{Z} \quad (677)$$

387. Eq. 677 is identical to 633 and the meaning of the symbols is the same.

k is an allowed wave “vector” inside the first Brillouin zone; the U ’s are the coefficients of the Fourier expansion of the potential; the C ’s are the coefficients of the Fourier expansion of the eigenfunction corresponding to (i.e. indexed by) k : they are our unknowns to be found, together with their corresponding eigenvalues ϵ .

Recall that the subsystem 677 (for which k is fixed) has infinite solutions (that is, infinite sets of C coefficients, each with its own eigenvalue) indexed by the band index n (point 327 and eq. 616):

$$\epsilon_{kn}, \quad \Psi_{kn}(r) = \sum_{p=-\infty}^{\infty} C_{(k-pg)n} \exp(i(k-pg)r)$$

The term g is defined by:

$$g = \frac{2\pi}{a} \quad (678)$$

and it is the spacing of the microscopic reciprocal lattice $\mathcal{R}_\mu^*$, or, in equivalent terms, its primitive vector (since we are in 1D, there is a single primitive “vector”).

All the infinite vectors of the microscopic reciprocal lattice have the form:

$$G = pg \quad p \in \mathbb{Z} \quad (679)$$

As said, the difference between the “empty lattice” and the “nearly free electron” models is in the Fourier coefficients U_{ig} of the potential: these are *exactly null* in the former, while they are very small, *but non-null*, in the latter.

6.1.1 The solutions of the k -th subsystem when $k \neq 0, \pm\pi/a$

388. As the first thing we will show that for all the k points of the first Brillouin zone which are farⁱⁱ from $k = 0$ and $k = \pm\pi/a = \pm g/2$, the solutions of the system 677 are, to a good approximationⁱⁱⁱ, those that we already found for the “empty lattice” model.

The points $k = 0$ and $k = \pm\pi/a = \pm g/2$ are special and we will see that when k is precisely close to one of them the presence of a non null potential produces solutions which are *different* from those of the “empty lattice” model, with the creation of a band gap.

Let’s rewrite the system 677 in the following way:

ⁱⁱI realize that “far” means nothing in mathematchese, but we are not doing math; the meaning of “far” will be clarified by what comes in the following.

ⁱⁱⁱAlso these words might be made more precise; this is done by Ashcroft and Mermin in their book, p. 152-156.

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\left(\epsilon - \frac{\hbar^2 (k-jg)^2}{2m} \right)} \quad j \in \mathbb{Z} \quad (680)$$

You can see this as an expression for the generic coefficient C_{k-jg} of the subsystem. Obviously there is a catch, for on the RHS there are unknown quantities, namely all the $C_{k-jg-ig}$ coefficients and the energy ϵ .

However, thanks to the assumptions implicit in the “nearly free electron” model (p. 247), we will now see that it is possible to obtain a good approximation for the RHS and thus for the C_{k-jg} on the LHS.

6.1.1.1 Band n.1

389. Let’s begin with considering band n.1, that is the band at lowest energy.

Thanks to 2 on p. 247 and to the expression that we derived for band n.1 in the “empty lattice” model (eq. 647) we can set:

$$\epsilon = \epsilon_1(k) = \frac{\hbar^2 k^2}{2m} + \alpha \quad (|\alpha| \rightarrow 0) \quad (681)$$

(don’t get lost: k is the point inside the first Brillouin zone which identifies a whole subsystem of the central equation; eq. 680 is just the j -th equation of such subsystem)

Eq. 680 thus becomes:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\left(\frac{\hbar^2 k^2}{2m} + \alpha - \frac{\hbar^2 (k-jg)^2}{2m} \right)} \quad j \in \mathbb{Z} \quad (682)$$

Thanks to the assumption 1 on p. 247 the whole sum on the numerator tends to zero (because $U_{ig} \rightarrow 0$).

Then, when k is far from $\pm g/2 = \pm \pi/a$, there are only two possibilities:^{iv}

$\forall j \neq 0$ the numerator is small ($\rightarrow 0$); the denominator is finite (i.e. not small) because the difference $\left(\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 (k-jg)^2}{2m} \right)$ is finite (its absolute value is the greater the greater is that of j) and $|\alpha| \rightarrow 0$; therefore we have:

$$C_{k-jg} = \frac{\overbrace{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}^{\rightarrow 0}}{\underbrace{\left(\frac{\hbar^2 k^2}{2m} + \alpha - \frac{\hbar^2 (k-jg)^2}{2m} \right)}_{\text{finite}}} \approx 0 \quad (683)$$

^{iv}What follows is very unformal. More mathematical rigour could be achieved by the use of perturbation theory, but that appears to me an unnecessary complication; the meaning of the message I want to pass on should be clear anyway.

$j = 0$ the numerator remains small ($\rightarrow 0$), but now also the denominator tends to zero (it becomes equal to α) and thus the ratio is finite:

$$C_{k-jg} = C_k = \frac{\overbrace{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}^{\rightarrow 0}}{\alpha \rightarrow 0} \neq 0 \quad (684)$$

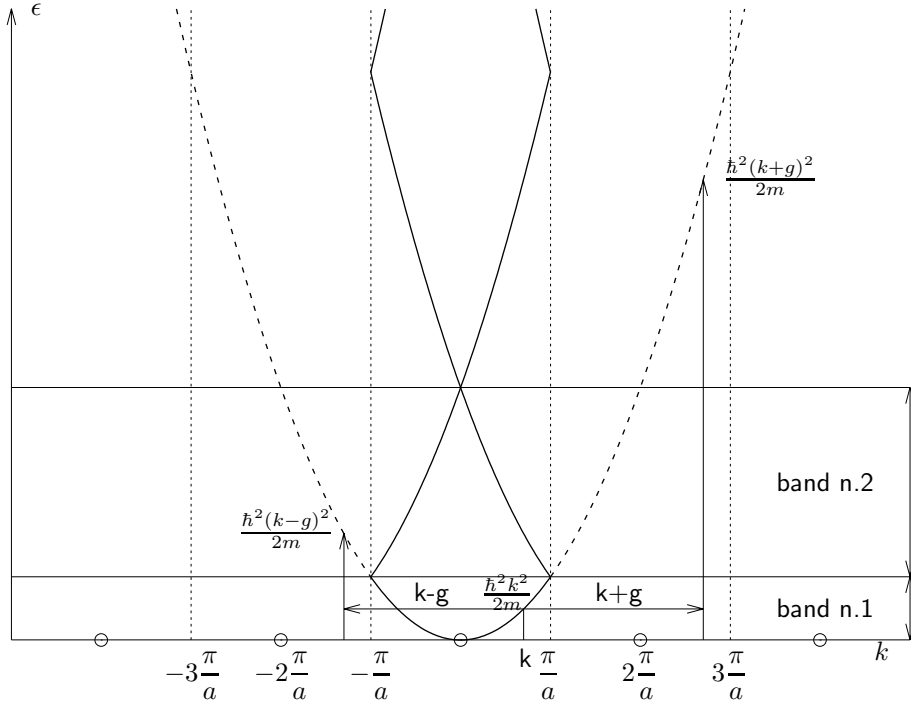


Figure 89: In the “nearly free electron” model the eigenvalue corresponding to point k in band n.1 (when such point is far from $k = \pm g/2$) is, to a good approximation, $\frac{\hbar^2 k^2}{2m}$. The values $\frac{\hbar^2 (k-jg)^2}{2m}$ with $j \neq 0$, for example $\frac{\hbar^2 (k-g)^2}{2m}$ and $\frac{\hbar^2 (k+g)^2}{2m}$ shown in the figure, will differ from the former by a *finite* amount.

390. I have depicted the situation in figure 89. The figure shows the “empty lattice” bands and the Fermi gas parabola. A point k is taken inside the first Brillouin zone ($[-\pi/a, \pi/a]$); the lowest eigenvalue ($n = 1$) corresponding to such k point is equal (to a good approximation, thanks to assumption 2 on p. 247) to the one that can be picked on the parabola: $\hbar^2 k^2/2m$. In the figure are also shown the two values:

$$\frac{\hbar^2 (k+g)^2}{2m} \quad \text{and} \quad \frac{\hbar^2 (k-g)^2}{2m}$$

that is, the values that the term:

$$\frac{\hbar^2 (k-jg)^2}{2m}$$

takes in the denominator of 682 for the two shortest G vectors ($\pm g$, i.e. $j = \pm 1$). These two values differ by a *finite* amount from the one corresponding to k . From the figure you can also easily understand that the difference:

$$\left(\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 (k - jg)^2}{2m} \right) \quad (685)$$

becomes greater (in absolute value) as j increases (and thus 683 is all the more justified).

391. In summary, for band n.1 and for any point of the first Brillouin zone far from $k = \pm\pi/a = \pm g/2$, the subsystem 680 becomes, to a very good approximation:

$$\begin{aligned} C_k &\neq 0 \\ C_{k-g} &\approx 0 \\ C_{k-2g} &\approx 0 \\ &\dots \\ C_{k+g} &\approx 0 \\ C_{k+2g} &\approx 0 \\ &\dots \end{aligned}$$

which means that all the coefficients of the Fourier expansion of the solution of Schrödinger's equation tend to zero, *but* for coefficient C_k (that is, C_{k-jg} with $j = 0$). Moreover, the corresponding eigenvalue is equal (up to an error $\alpha \rightarrow 0$) to that of the “empty lattice” model:

$$\Psi_{k1}(r) = \sum_{j=-\infty}^{\infty} C_{(k-jg)1} \exp(i(k-jg)r) \approx C_{k1} \exp(ikr) \quad (686)$$

$$\epsilon_1(k) \approx \frac{\hbar^2 k^2}{2m} \quad (687)$$

(I have emphasized that the result refers to band n.1)

This is precisely what we already found for the “empty lattice” model (p. 214) (the coefficient C_k is to be redetermined anyway due to the normalization condition) and is definitely reasonable: we are assuming that the periodic potential is very small and thus we expect everything to work very closely to the case when the potential was exactly null.

392. Note how the result we have just found for band n.1 (that is: that only a single coefficient among all the C_{k-jg} 's is different from zero) holds only when k is appreciably different from $\pm g/2 = \pm\pi/a$. For example, if k was equal (or very close) to $g/2$, then the denominator of 682 would become equal (or very close) to zero for *two* possible j values, namely:

$$k \approx \frac{g}{2} \implies C_{k-jg} \approx \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\left(\frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} + \alpha - \frac{\hbar^2 \left(\frac{g}{2} - jg\right)^2}{2m} \right)}$$

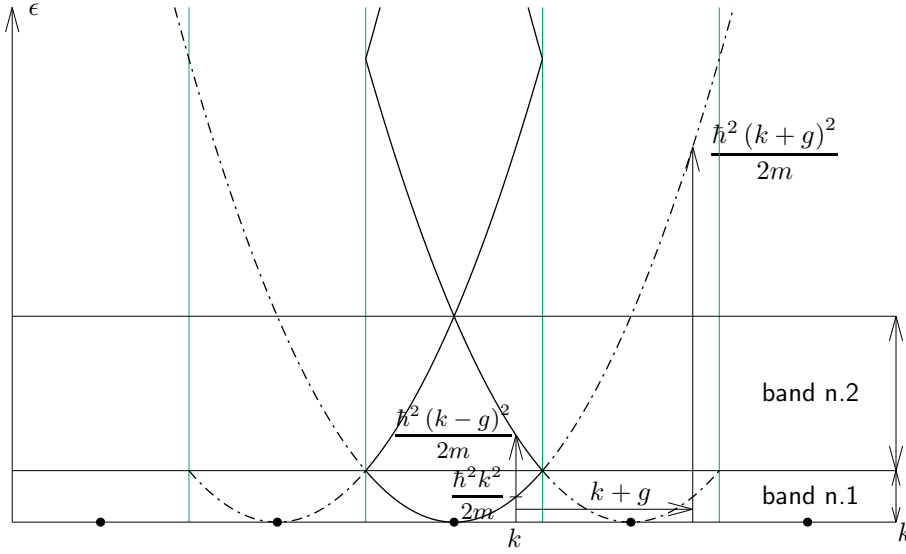


Figure 90: In the “nearly free electron” model the eigenvalue corresponding to the point k inside the first Brillouin zone (and far from $k = 0$) for band n.2 is, to a good approximation, $\frac{\hbar^2 (k-g)^2}{2m}$. The values $\frac{\hbar^2 (k-jg)^2}{2m}$ with $j \neq 1$ (for example $\frac{\hbar^2 k^2}{2m}$ and $\frac{\hbar^2 (k+g)^2}{2m}$ in the figure) differ from it by a *finite* amount.

$$= \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\alpha} \iff j = 0, 1$$

We will see that it is precisely this that makes the two points $k = \pm g/2$ special.

6.1.1.2 Band n.2

393. For the bands after the first ($n > 1$) the procedure is similar; the only difference is that the eigenvalue corresponding to the k point inside the first Brillouin zone is obtained from the Fermi gas parabola shifted by an appropriate G vector, as said in point 356 (eq. 652).

Apart from that, the math is identical to that for band n.1.

For example, situation for band n.2 and a given k point (far from 0) is shown in figure 90.

Thanks to assumption 2 on p. 247 and to the expression we derived for band n.2 in the “empty lattice” model (eq. 648), for the point k shown in the figure we can set:

$$\epsilon = \epsilon_2(k) = \frac{\hbar^2 (k-g)^2}{2m} + \alpha \quad \text{with: } |\alpha| \rightarrow 0 \quad (688)$$

Similarly to the case of band n.1 eq. 680 becomes:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\left(\frac{\hbar^2 (k-g)^2}{2m} + \alpha - \frac{\hbar^2 (k-jg)^2}{2m} \right)} \quad (689)$$

Again, only two possibilities can occur:

$\forall j \neq 1$ the numerator is small ($\rightarrow 0$) (assumption 1 on p. 247); the denominator is finite (that is, not small) because the difference:

$$\frac{\hbar^2 (k - g)^2}{2m} - \frac{\hbar^2 (k - jg)^2}{2m} \quad (690)$$

is finite and $|\alpha| \rightarrow 0$ (the absolute value of such difference is the greater the greater is that of j , look at figure 90); therefore we have:

$$C_{k-jg} = \frac{\overbrace{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}^{\rightarrow 0}}{\underbrace{\left(\frac{\hbar^2 (k - g)^2}{2m} + \alpha - \frac{\hbar^2 (k - jg)^2}{2m} \right)}_{\text{finite}}} \approx 0 \quad (691)$$

$j = 1$ the numerator stays small ($\rightarrow 0$), but now also the denominator is small (since it becomes equal to α) and thus the ratio is finite:

$$C_{k-g} = \frac{\overbrace{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}^{\rightarrow 0}}{\alpha \quad (\rightarrow 0)} \neq 0 \quad (692)$$

394. In conclusion, for band n.2 and for any point inside the first Brillouin zone and far from $k = 0$ the subsystem 680 becomes, to a good approximation:

$$\begin{aligned} C_k &\approx 0 \\ C_{k-g} &\neq 0 \\ C_{k-2g} &\approx 0 \\ &\dots \\ C_{k+g} &\approx 0 \\ C_{k+2g} &\approx 0 \\ &\dots \end{aligned}$$

which means that all the coefficients of the Fourier expansion of the solution of Schrödinger's equation are negligibly small, *but for* the coefficient C_{k-g} (that is, C_{k-jg} with $j = 1$). Moreover, the corresponding eigenvalue is equal, up to a negligible error, to that of the “empty lattice” model:

$$\Psi_{k2}(r) = \sum_{j=-\infty}^{\infty} C_{(k-jg)2} \exp(i(k-jg)r) \approx C_{(k-g)2} \exp(i(k-g)r) \quad (693)$$

$$\epsilon_2(k) \approx \frac{\hbar^2 (k - g)^2}{2m} \quad (694)$$

Again, the result is identical to what can be obtained for an exactly null potential (“empty lattice” model, eq. 644 with $j = 1$).

Verify by yourself that the same conclusion is reached when in figure 90 a point $k \in [-\frac{\pi}{a}, 0]$ is considered: in this case the only non null coefficient will be C_{k+g} .

395. As already noted for band n.1, also for band n.2 I make you notice that the obtained result only holds when k is appreciably different from 0 and $\pm g/2 = \pm\pi/a$. For example, if k was equal (or very close) to 0, then there would be *two* possible j values which would make the denominator of 689 infinitesimal:

$$\begin{aligned} k \approx 0 &\implies C_{k-jg} \approx \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\left(\frac{\hbar^2 (-g)^2}{2m} + \alpha - \frac{\hbar^2 (-jg)^2}{2m} \right)} \\ &= \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\alpha} \iff j = 1, -1 \end{aligned}$$

Thus, also $k = 0$ is special, and we will analyze it in a moment.

6.1.1.3 n-th band

396. In general, when k is far from 0 and $\pm g/2$ and for any band n , the subsystem 680 takes the form:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\left(\frac{\hbar^2 (k - pg)^2}{2m} + \alpha - \frac{\hbar^2 (k - jg)^2}{2m} \right)} \quad j \in \mathbb{Z} \quad (695)$$

where $p \in \mathbb{Z}$ is an appropriate integer number which, given a k point inside the first Brillouin zone, defines the n -th eigenvalue through:

$$\epsilon_n(k) = \frac{\hbar^2 (k - pg)^2}{2m} + \alpha \quad (696)$$

Note that, as already mentioned on p. 217, the integer p is a function of both k and the band index n . For instance, with reference to figure 89, for the point k shown in the figure and band n.3 we would have:

$$p(k, 3) = -1 \quad (697)$$

that is:

$$\epsilon_3(k) = \frac{\hbar^2 (k + g)^2}{2m} + \alpha \quad (698)$$

While if we considered the point k' , symmetric image with respect to the origin of the one shown, we would have:

$$p(k', 3) = 1 \quad (699)$$

that is:

$$\epsilon_3(k') = \frac{\hbar^2 (k - g)^2}{2m} + \alpha \quad (700)$$

Here the important message is that, in any case, the denominator of eq. 695 is always *finite*, but for *the single case* when $j = p$, and thus the subsystem 680 becomes to a good approximation:

$$\begin{aligned} C_k &\approx 0 \\ C_{k-g} &\approx 0 \\ C_{k-2g} &\approx 0 \\ &\dots \\ C_{k-pg} &\neq 0 \\ &\dots \\ C_{k+g} &\approx 0 \\ C_{k+2g} &\approx 0 \\ &\dots \end{aligned}$$

That is: for k values far from $0 \pm g/2$ and for any band n , only *a single coefficient* of the Fourier expansion of the $\Psi_{kn}(\vec{r})$ “survives” and we fall back on the solution for the “empty lattice” model (p. 214):

$$\Psi_{kn}(r) \approx C_{(k-pg)n} \exp(i(k - pg)r) \quad (701)$$

$$\epsilon_n(k) \approx \frac{\hbar^2 (k - pg)^2}{2m} \quad (702)$$

6.1.2 The solutions of the k -th subsystem when $k \approx \pi/a$

397. Until now it looks like there is nothing new with respect to what we already knew from the “empty lattice” model, right?

But we will now see that when the potential is not exactly null (though very small), the dispersion relation of the “empty lattice” model ($\epsilon(k)$) when k is close to those “special” points in the first Brillouin zone ($0, \pm\pi/a$) is only the lowest level of approximation.

In this section we will derive with a better degree of approximation the relation between ϵ and k close to $g/2 = \pi/a$.

Let’s see what happens to bands n.1 and n.2 when we consider a point k within a small interval on the left of $k = g/2 = \pi/a$: $k \in [g/2 - \delta, g/2]$.

As the first thing note that in the “empty lattice” model when $k = g/2 = \pi/a$ bands n.1 and n.2 (as well as bands n.3 and n.4 etc) do “touch” each other (look, for example, figure 90); this means that in the “empty lattice” model the energy level corresponding to the boundary of the first Brillouin zone is doubly degenerate with respect to the band index:

$$\epsilon_1\left(\frac{g}{2}\right) = \epsilon_2\left(\frac{g}{2}\right) \quad (703)$$

We will now see that if the periodic potential is slightly increased with respect to the null value (i.e. for the transition from the “empty lattice” to the “nearly free electron” model) this degeneracy is removed.

398. Like previous cases, the starting point is still subsystem 680:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\left(\epsilon - \frac{\hbar^2 (k-jg)^2}{2m}\right)} \quad j \in \mathbb{Z}$$

We focus on the small energy interval:

$$\frac{\hbar^2}{2m} \left(\frac{g}{2}\right)^2 - \gamma_1 \leq \epsilon \leq \frac{\hbar^2}{2m} \left(\frac{g}{2}\right)^2 + \gamma_2 \quad (704)$$

determined by the interval $[g/2 - \delta, g/2]$ on the k axis (look at figure 91^v)
Since the interval $[g/2 - \delta, g/2]$ is small, also the interval:

$$\left[\frac{\hbar^2}{2m} \left(\frac{g}{2}\right)^2 - \gamma_1, \frac{\hbar^2}{2m} \left(\frac{g}{2}\right)^2 + \gamma_2 \right]$$

will be correspondingly small and thus, in such interval, we have:

$$\overbrace{\frac{\hbar^2}{2m} \left(\frac{g}{2}\right)^2}^{\text{empty lattice value}} \approx \epsilon = \frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} + \alpha \quad \text{with } |\alpha| \rightarrow 0 \quad (705)$$

In the previous cases we saw that the denominator of 680 became infinitesimal only for *a single* coefficient which, therefore, was the only “survivor” in the Fourier expansion of the eigenfunction, solution of Schrödinger’s equation.

399. The present case is different precisely in this respect.

Since:

$$k \approx \frac{g}{2} \quad (706)$$

$$\epsilon = \frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} + \alpha \quad (707)$$

eq. 680 can be rewritten as:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\left(\frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} + \alpha - \frac{\hbar^2 \left(\frac{g}{2} - jg\right)^2}{2m} \right)}$$

^vDespite what the figure might suggest, the interval on the ϵ axis is *not* symmetric with respect to the common energy value of the two bands, that is $\frac{\hbar^2}{2m} \left(\frac{g}{2}\right)^2$: can you see why?

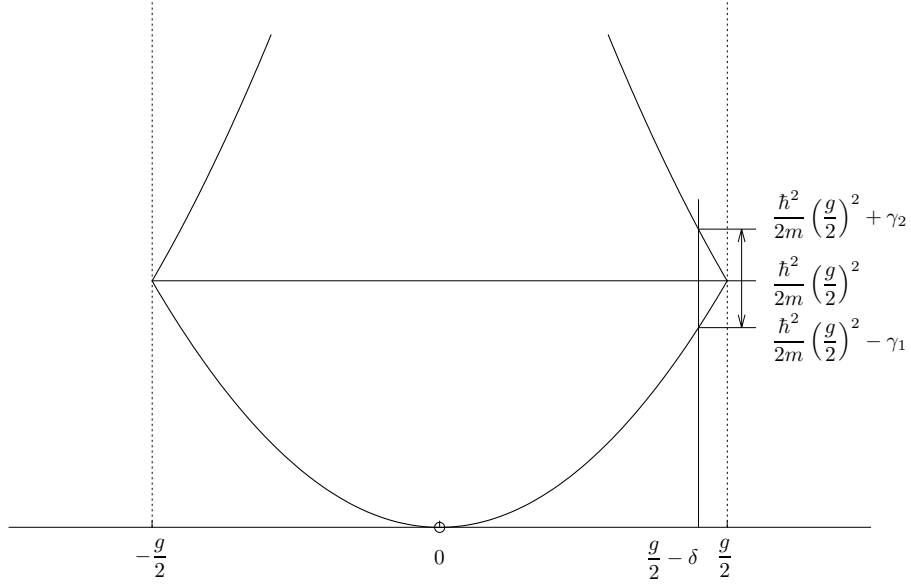


Figure 91: The small interval $[g/2 - \delta, g/2]$ to the left of the boundary of the first Brillouin zone defines a corresponding small energy interval $\left[\frac{\hbar^2}{2m} \left(\frac{g}{2}\right)^2 - \gamma_1, \frac{\hbar^2}{2m} \left(\frac{g}{2}\right)^2 + \gamma_2\right]$.

where I have replaced ϵ and k in the denominator with the respective values they take under the conditions we are considering.

This time, as I anticipated in point 392 and differently from the previous case when k was “far” from $g/2$, the situation is the following:

$\forall j \neq 0, 1$ the numerator is small ($\rightarrow 0$) (assumption 1 on p. 247); the denominator is finite (i.e. not small), because the difference:

$$\frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} - \frac{\hbar^2 \left(\frac{g}{2} - jg\right)^2}{2m} \quad (708)$$

is finite and $|\alpha| \rightarrow 0$; we therefore have:

$$C_{k-jg} = \frac{\overbrace{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}^{\rightarrow 0}}{\underbrace{\left(\frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} + \alpha - \frac{\hbar^2 \left(\frac{g}{2} - jg\right)^2}{2m} \right)}_{\text{finite}}} \approx 0 \quad (709)$$

$j = 0, 1$ the numerator is still small ($\rightarrow 0$), but now the denominator is also infinitesimally small (it becomes equal to α) and thus the ratio is finite:

$$C_{k-jg} = \frac{\overbrace{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}^{\rightarrow 0}}{\alpha \quad (\rightarrow 0)} \neq 0 \quad (710)$$

So: now there are *two* j values for which the denominator of 680 becomes infinitesimal. In summary, under the conditions we are considering, that is, when k is close to the (right) boundary of the first Brillouin zone, the subsystem 680 becomes, to a good approximation:

$$\begin{aligned} C_k &\neq 0 \\ C_{k-g} &\neq 0 \\ C_{k-2g} &\approx 0 \\ &\dots \\ C_{k+g} &\approx 0 \\ C_{k+2g} &\approx 0 \\ &\dots \end{aligned}$$

which means that all the coefficients of the Fourier expansion of the solutions of Schrödinger's equation corresponding to eigenvalues included in the interval shown in figure 91 (thus belonging to bands n.1 and n.2), are negligibly small, but for C_k and C_{k-g} (or: C_{k-jg} with $j = 0$ and $j = 1$).

400. We are now in the position to derive the relation between ϵ and k in the small interval $[g/2 - \delta, g/2]$.

To begin with, let's rewrite the two "surviving" equations (those for C_k and C_{k-g}) holding for $k \in [g/2 - \delta, g/2]$ and go back indicating ϵ and k as variables.

Don't forget that the validity of what follows is restricted to the interval $[g/2 - \delta, g/2]$, for it is in such interval that the above derived results do hold for true.

We rewrite the two equations for $j = 0, 1$ in the form 677:

$$\begin{aligned} j = 1 : \quad & \left(\frac{\hbar^2 (k-g)^2}{2m} - \epsilon \right) C_{k-g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-g-ig} = 0 \\ j = 0 : \quad & \left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) C_k + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} = 0 \end{aligned}$$

First of all, since only the C_k and C_{k-g} coefficients are significantly different from zero the two sums over i can be approximated to the only terms containing the two coefficients.

But careful: these two terms occur for *different* values of i in the two sums, because the index of C is $k - g - ig$ in the sum for $j = 1$, but it is $k - ig$ in the sum for $j = 0$.

In order to find the values of i for which the C_k and C_{k-g} terms occur in each of the two sums, we must equate the subscript expression of C to k and $k - g$ separately for the two cases $j = 1$ and $j = 0$, that is:

$$\begin{aligned}
j = 1 : \quad & \begin{cases} C_{k-g-ig} = C_k & \Longleftrightarrow & i = -1 \\ C_{k-g-ig} = C_{k-g} & \Longleftrightarrow & i = 0 \end{cases} \implies \sum_{i=-\infty}^{\infty} U_{ig} C_{k-g-ig} \approx U_{-g} C_k + U_0 C_{k-g} \\
j = 0 : \quad & \begin{cases} C_{k-ig} = C_k & \Longleftrightarrow & i = 0 \\ C_{k-ig} = C_{k-g} & \Longleftrightarrow & i = 1 \end{cases} \implies \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} \approx U_0 C_k + U_g C_{k-g}
\end{aligned}$$

We thus obtain a homogeneous system of two equations in the two unknowns C_k and C_{k-g} :

$$\begin{aligned}
\left(\frac{\hbar^2 (k-g)^2}{2m} - \epsilon \right) C_{k-g} + U_{-g} C_k + U_0 C_{k-g} &= 0 \\
\left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) C_k + U_0 C_k + U_g C_{k-g} &= 0
\end{aligned} \tag{711}$$

401. To make our life even easier we make two more assumptions related to the periodic potential $U(r)$.

1. In general it is always possible to introduce an additive constant into the hamiltonian without changing its solution.

If Ψ is an eigenfunction of the Schrödinger equation:

$$H\Psi = \epsilon\Psi \tag{712}$$

then for an arbitrary constant C :

$$(H + C)\Psi = H\Psi + C\Psi = \epsilon\Psi + C\Psi = (\epsilon + C)\Psi \tag{713}$$

That is: Ψ is also an eigenfunction of the hamiltonian $H + C$; the only additional effect is the shift of the energy of all states by the same amount: but this is never a problem, since the energy of the states is always defined up to a constant.

On this basis, we can introduce into our hamiltonian a constant $-U_0$, U_0 being the coefficient of the Fourier expansion of the potential for $G = 0$ (i.e. for $i = 0$ in the sum of 677).

This “trick” allows us to assume $U_0 = 0$ in the expansion of the potential:

$$\begin{aligned}
& -\frac{\hbar^2}{2m} \nabla^2 - U_0 + U(\vec{r}) \\
&= -\frac{\hbar^2}{2m} \nabla^2 - U_0 + \sum_{\vec{G}} U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}) \\
&= -\frac{\hbar^2}{2m} \nabla^2 - U_0 + U_0 + \sum_{\vec{G} \neq 0} U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r})
\end{aligned}$$

$$= -\frac{\hbar^2}{2m} \nabla^2 + \sum_{\vec{G} \neq 0} U_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}) \quad (714)$$

The two terms containing U_0 can thus be deleted from the system 711:

$$\begin{aligned} \left(\frac{\hbar^2 (k-g)^2}{2m} - \epsilon \right) C_{k-g} + U_{-g} C_k &= 0 \\ U_g C_{k-g} + \left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) C_k &= 0 \end{aligned} \quad (715)$$

2. We additionally assume that the potential $U(r)$ is a real and even function, that is:

$$U(r) = U(-r) \quad (716)$$

(in the three-dimensional case this would be equivalent to assume that the crystalline structure of the sample has an inversion point of symmetry and thus: $U(\vec{r}) = U(-\vec{r})$; realize that this always holds for true when the base associated with each lattice point of the structure is monoatomic, and, as I already remarked more than once, this is the only case which we consider in all this course)

Under this assumption, thanks to the general property which enjoy the Fourier coefficients of a real and even function (point 104), we have:

$$U_{ig} = U_{-ig} \quad (717)$$

(in the 3D case: $U_{\vec{G}} = U_{-\vec{G}}$)

and thus, in particular:

$$U_g = U_{-g} \quad (718)$$

In conclusion, we can rewrite the system as:

$$\begin{aligned} \left(\frac{\hbar^2 (k-g)^2}{2m} - \epsilon \right) C_{k-g} + U_g C_k &= 0 \\ U_g C_{k-g} + \left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) C_k &= 0 \end{aligned} \quad (719)$$

402. The unknowns to be found are the two coefficients C_k and C_{k-g} and the energy ϵ ; the latter is approximately given by the value of the Fermi gas $\frac{\hbar^2 (g/2)^2}{2m}$ (eq. 707); however, we are now in the position to obtain it at a higher precision level.

In fact, if you review the steps in point 388 where we derived the energy and the eigenfunctions for k points far from the boundary of the first Brillouin zone, you should realize that, in practice, the key point was to assume that the sum:

$$\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}$$

was negligible ($\rightarrow 0$). In the present case, on the other hand, we do not neglect the sum *completely*, because we take the terms containing U_g e U_{-g} into account; this is why the level of precision is higher here.

403. The homogeneous system 719 has a non trivial solution if and only if the determinant of the coefficients is null, or:

$$\det \begin{pmatrix} \left(\frac{\hbar^2 (k-g)^2}{2m} - \epsilon \right) & U_g \\ U_g & \left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) \end{pmatrix} = 0 \quad (720)$$

For the sake of a lighter notation, let's set:

$$\lambda_{k-g} = \frac{\hbar^2 (k-g)^2}{2m} \quad (721)$$

$$\lambda_k = \frac{\hbar^2 k^2}{2m} \quad (722)$$

We then have:

$$\begin{aligned} (\lambda_{k-g} - \epsilon)(\lambda_k - \epsilon) - U_g^2 &= 0 \\ \epsilon^2 - \epsilon(\lambda_k + \lambda_{k-g}) + \lambda_k \lambda_{k-g} - U_g^2 &= 0 \\ \epsilon &= \frac{\lambda_k + \lambda_{k-g} \pm \sqrt{(\lambda_k + \lambda_{k-g})^2 - 4(\lambda_k \lambda_{k-g} - U_g^2)}}{2} \\ \epsilon &= \frac{1}{2}(\lambda_k + \lambda_{k-g}) \pm \left\{ \frac{1}{4}(\lambda_k - \lambda_{k-g})^2 + U_g^2 \right\}^{1/2} \end{aligned} \quad (723)$$

The just obtained expression gives us the dependence of the energy ϵ of the electronic states from the wave vector k in the small left interval of $k = g/2$, where the approximations on which it is based are valid.

For each value of $k \in [\frac{g}{2} - \delta, \frac{g}{2}]$ there are two allowed values of energy, given by 723. These two values correspond to bands n.1 and n.2, respectively.

Since λ_k and λ_{k-g} depend quadratically on k , the same must be true for ϵ ; that is: the dependence of ϵ on k in a small interval to the left of $k = g/2$ is of quadratic type.

404. Note that when $U_g = 0$ ("empty lattice" model) the two solutions of the quadratic equation become:

$$\epsilon = \frac{1}{2}(\lambda_k + \lambda_{k-g}) \pm \frac{1}{2}(\lambda_k - \lambda_{k-g}) = \begin{cases} \lambda_{k-g} &= \frac{\hbar^2 (k-g)^2}{2m} \\ \lambda_k &= \frac{\hbar^2 k^2}{2m} \end{cases} \quad (724)$$

which are the expressions for bands n.1 and n.2 in the “empty lattice” model (eq. 647 and 648). Moreover, under these conditions, the two bands are degenerate for $k = g/2$, as it is to be expected for the “empty lattice” model.

405. As anticipated, the degeneracy of the energy for $k = g/2$ has been removed, because now there are two distinct values of ϵ for such value of k . Indeed, when k is exactly equal to $g/2$, we have:

$$k = \frac{g}{2} \implies \lambda_k = \lambda_{k-g} = \frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} \quad (725)$$

$$\epsilon = \overbrace{\frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m}}^{\text{free electron}} \pm |U_g| \quad (726)$$

The term evidenced by the overbrace is the Fermi gas (or “empty lattice”) energy value (for $k = g/2 = \pi/a$): therefore you see that switching on a non null potential splits the energy on the boundary of the first Brillouin zone in two values which lay above and below the Fermi gas value by an amount which is equal to the absolute value of the first Fourier coefficient U_g of the potential. The difference between the two non degenerate values is thus $2|U_g|$:

$$\epsilon_+ - \epsilon_- = \lambda_{\frac{g}{2}} + |U_g| - \left(\lambda_{\frac{g}{2}} - |U_g|\right) = 2|U_g| \quad (727)$$

Now bands n.1 and n.2 are no more contiguous; they are separated by the energy interval $[\epsilon_-, \epsilon_+]$; an electron moving in the crystal *cannot* have an energy within such forbidden interval, which is thus what we have called *the band gap*.

406. The eigenvalue ϵ_- is the maximum of band n.1, while the eigenvalue ϵ_+ is the minimum of band n.2; the two bands are now detached.

As already said, the change in the eigenvalues with respect to the “empty lattice” model (= potential exactly null) represented by 723 holds not only when k is exactly equal to $g/2$, but also when k is sufficiently close to $g/2$ such that the arguments we used to obtain 723 are still valid. Basically, the main assumptions were:

$$\begin{aligned} k &\approx \frac{g}{2} \\ \epsilon &\approx \frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} = \frac{\hbar^2 \left(-\frac{g}{2}\right)^2}{2m} \end{aligned} \quad (728)$$

Therefore, we expect that the branches of the parabola which describe band n.1 and n.2 in the “empty lattice” model modify themselves in the immediate neighborings of the boundary of the first Brillouin zone “repelling” each other, and we expect this effect to be maximum at $k = g/2$.

407. Note also that the two modified branches of the parabola “enter” orthogonally into the vertical line passing through the first Brillouin zone boundary. In equivalent terms, the derivative of the two bands is null for $k = g/2$. This is easily verified by taking the derivative with respect to k of 723:

$$\frac{d\epsilon}{dk} = \frac{d}{dk} \left(\frac{1}{2} (\lambda_k + \lambda_{k-g}) \pm \left\{ \frac{1}{4} (\lambda_k - \lambda_{k-g})^2 + U_g^2 \right\}^{1/2} \right)$$

$$\begin{aligned}
&= \frac{1}{2} \left(\frac{d\lambda_k}{dk} + \frac{d\lambda_{k-g}}{dk} \right) \pm \frac{1}{2} \left\{ \frac{1}{4} (\lambda_k - \lambda_{k-g})^2 + U_g^2 \right\}^{-1/2} \\
&\times \left(\frac{1}{2} (\lambda_k - \lambda_{k-g}) \right) \left(\frac{d\lambda_k}{dk} - \frac{d\lambda_{k-g}}{dk} \right)
\end{aligned} \tag{729}$$

We have:

$$\begin{aligned}
\left[\frac{d\lambda_k}{dk} + \frac{d\lambda_{k-g}}{dk} \right]_{k=g/2} &= \left[\frac{\hbar^2}{2m} \left(\frac{dk^2}{dk} + \frac{d}{dk} (k-g)^2 \right) \right]_{k=g/2} \\
&= \left[\frac{\hbar^2}{2m} (2k + 2(k-g)) \right]_{k=g/2} = \left[\frac{\hbar^2}{2m} (4k - 2g) \right]_{k=g/2} = \frac{\hbar^2}{2m} (2g - 2g) = 0
\end{aligned}$$

Moreover, we already know (eq. 725) that:

$$k = \frac{g}{2} \implies \lambda_k = \lambda_{k-g} \tag{730}$$

and thus:

$$\left(\frac{d\epsilon}{dk} \right)_{k=g/2} = 0 \tag{731}$$

The graphical representation of the results we have obtained here is shown in figure 92, with bands n.1 and n.2 before and after the creation of the band gap: the dashed lines are the prediction of the “empty lattice” model; the continuous lines are the prediction of the “nearly free electron” model and show the two functions $\epsilon_{\pm}$, eq. 723, in the interval $[g/2 - \delta, g/2]$.

6.1.3 The solutions of the k -th subsystem when $k \approx -\pi/a$

As you will have noticed, figure 92 is symmetric, in that the changes which take place in an interval to the left of $k = g/2$ also occur in an interval to the right of $k = -g/2$.^{vi}

At this point it should be easy to realize that, indeed, things must be like that.

If you repeat the steps we performed from point 397 on for $k \in [-g/2, -g/2 + \delta]$ (that is, for k within a small interval to the right of $k = -g/2$), then you will find that there are again only two Fourier coefficients of the eigenfunction being significantly different from 0:

$$C_k \text{ and } C_{k+g} \tag{732}$$

(that is: C_{k-jg} , for $j = 0$ and $j = -1$)

The two “surviving” equations of the subsystem corresponding to a k point belonging to $[-g/2, -g/2 + \delta]$ are:

$$j = -1 : \left(\frac{\hbar^2 (k+g)^2}{2m} - \epsilon \right) C_{k+g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k+g-ig} = 0$$

^{vi}Note that this is *not* a consequence of the periodicity of the function $\epsilon_n(k)$ in reciprocal space (point 332); if anything, such periodicity would replicate the left interval of $k = g/2$ into a *left* interval of $k = -g/2$; we will come back on this aspect in a moment.

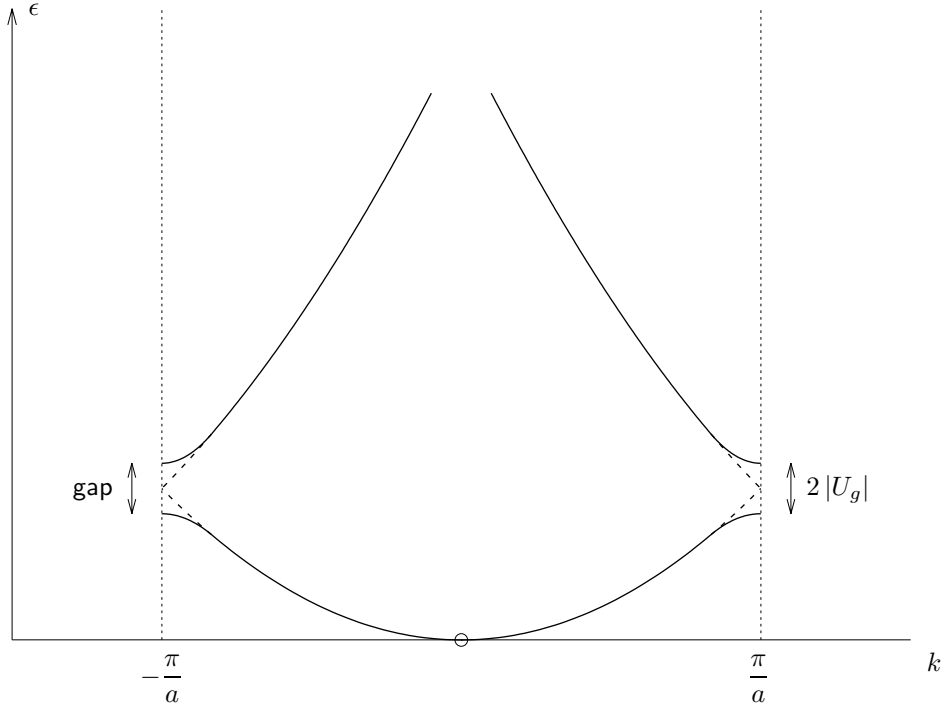


Figure 92: Bands n.1 and n.2, which are degenerate for $k = \pi/a = g/2$ in the “empty lattice” model (dashed lines) become detached in the “nearly free electron” model when k is within a small interval to the left of the first Brillouin zone boundary (continuous lines). Everything works as if the two involved bands were “repelling” each other in proximity of the Brillouin zone boundary.

$$j = 0 : \quad \left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) C_k + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} = 0$$

The two sums can be approximated to the only two terms containing C_k and C_{k+g} , or:

$$j = -1 \quad \left\{ \begin{array}{l} C_{k+g-ig} = C_k \\ C_{k+g-ig} = C_{k+g} \end{array} \right. \begin{array}{l} \Longleftrightarrow i = 1 \\ \Longleftrightarrow i = 0 \end{array} \Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k+g-ig} \approx U_g C_k + U_0 C_{k+g}$$

$$j = 0 \quad \left\{ \begin{array}{l} C_{k-ig} = C_k \\ C_{k-ig} = C_{k+g} \end{array} \right. \begin{array}{l} \Longleftrightarrow i = 0 \\ \Longleftrightarrow i = -1 \end{array} \Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} \approx U_0 C_k + U_{-g} C_{k+g}$$

By assuming the same simplifications discussed in point 401 we arrive at:

$$\left(\frac{\hbar^2 (k+g)^2}{2m} - \epsilon \right) C_{k+g} + U_g C_k = 0$$

$$U_g C_{k+g} + \left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) C_k = 0$$

This system is identical to 719, the only difference being $k + g$ in place of $k - g$. All the remarks we did in point 402 and following hold unchanged (apart from trivial adjustments): I suggest you to verify this.

6.1.4 The solutions of the k -th subsystem when $k \approx 0$

408. In previous points we have described the formation of a band gap between bands n.1 and n.2 in a monodimensional crystal containing “nearly free” electrons. Of course, this phenomenon is not restricted to only those two bands: switching on a non null potential (even if appropriately small) determines the opening of band gaps between all the bands of the system.

Based on what we already saw it is not difficult to explain the formation of a band gap between bands n.2 and n.3.

To this end, let's focus on the k points within a small interval centered around $k = 0$: $k \in [-\delta, \delta]$. In the “nearly free electron” model, for such k points, we have:

$$\epsilon_2(k) = \frac{\hbar^2 g^2}{2m} + \alpha \quad \text{with } |\alpha| \rightarrow 0 \quad (733)$$

Note: given k , $\epsilon_2(k)$ is the *second* eigenvalue, i.e. the energy value belonging to band n.2. This value is obtained from the Fermi gas parabola shifted by g to the left (or to the right) (figure 93). Note that, similar to the case $k = g/2$ already analyzed (point 397), also for $k = 0$ bands n.2 and n.3 in the “empty lattice” model share a common point, that is, the energy shows a double degeneracy with respect to the band index n :

$$\epsilon_2(0) = \epsilon_3(0) \quad (734)$$

By going through the same steps of point 397 and following, you can verify that only two coefficients of the Fourier expansion of the eigenfunction corresponding to points $k \in [-\delta, \delta]$ have a value significantly different from 0, namely:

$$C_{k-g} \quad \text{and} \quad C_{k+g} \quad (735)$$

(that is: C_{k-jg} for $j = 1$ e $j = -1$)

The two “surviving” equations of the subsystem are thus:

$$\begin{aligned} j = -1 : \quad & \left(\frac{\hbar^2 (k+g)^2}{2m} - \epsilon \right) C_{k+g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k+g-ig} = 0 \\ j = 1 : \quad & \left(\frac{\hbar^2 (k-g)^2}{2m} - \epsilon \right) C_{k-g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-g-ig} = 0 \end{aligned}$$

The two sums can be approximated to the only two terms containing C_{k+g} and C_{k-g} , that is:

$$j = -1 \quad \left\{ \begin{array}{l} C_{k+g-ig} = C_{k+g} \\ C_{k+g-ig} = C_{k-g} \end{array} \right. \quad \begin{array}{l} \Longleftrightarrow \quad i = 0 \\ \Longleftrightarrow \quad i = 2 \end{array} \quad \Longrightarrow \quad \sum_{i=-\infty}^{\infty} U_{ig} C_{k+g-ig} \approx U_0 C_{k+g} + U_{2g} C_{k-g}$$

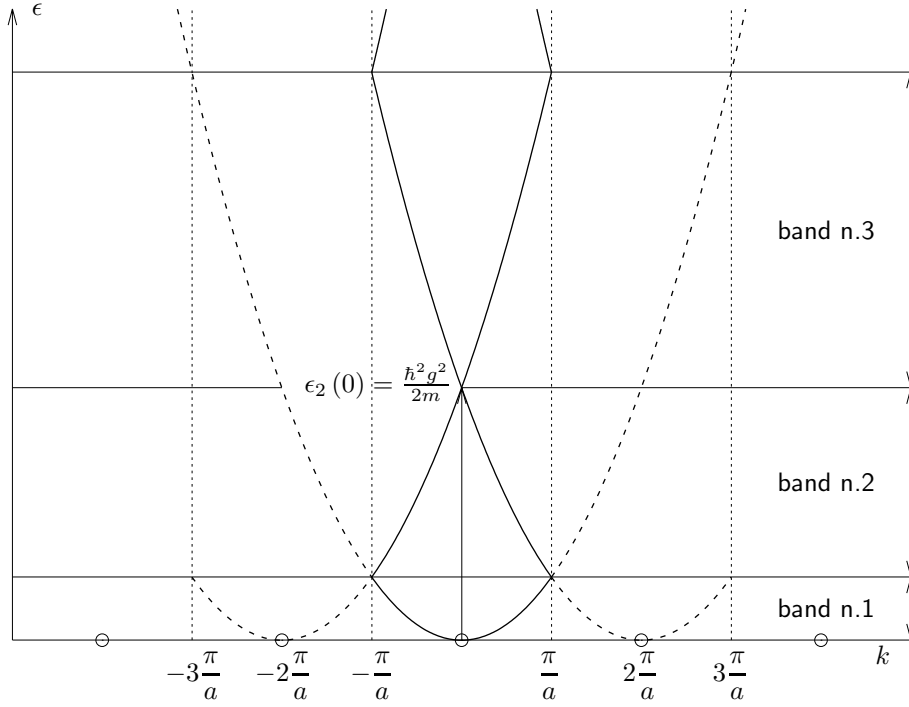


Figure 93: For the “nearly free electron” model the eigenvalue in band n.2 corresponding to $k = 0$ is, to a good approximation, $\frac{\hbar^2 g^2}{2m}$. This value is obtained from the Fermi gas parabola shifted by g to the left (or to the right).

$$j = 1 \quad \left\{ \begin{array}{l} C_{k-g-ig} = C_{k+g} \\ C_{k-g-ig} = C_{k-g} \end{array} \right. \begin{array}{l} \Longleftrightarrow \\ \Longleftrightarrow \end{array} \begin{array}{l} i = -2 \\ i = 0 \end{array} \implies \sum_{i=-\infty}^{\infty} U_{ig} C_{k-g-ig} \approx U_{-2g} C_{k+g} + U_0 C_{k-g}$$

With the steps and the additional approximations already seen the following system is obtained:

$$\left(\frac{\hbar^2 (k+g)^2}{2m} - \epsilon \right) C_{k+g} + U_{2g} C_{k-g} = 0 \quad (736)$$

$$U_{2g} C_{k+g} + \left(\frac{\hbar^2 (k-g)^2}{2m} - \epsilon \right) C_{k-g} = 0 \quad (737)$$

From here on the algebra is identical to that already seen in point 402. The final result is the opening of a band gap between bands n.2 and n.3, whose amplitude is equal to $2|U_{2g}|$, that is twice the absolute value of the second Fourier coefficient of the potential.

In figure 94 I have represented bands n.1–3 (only the lower part of band n.3 is shown) and the corresponding band gaps caused by the presence of the non null periodic potential in the crystal.

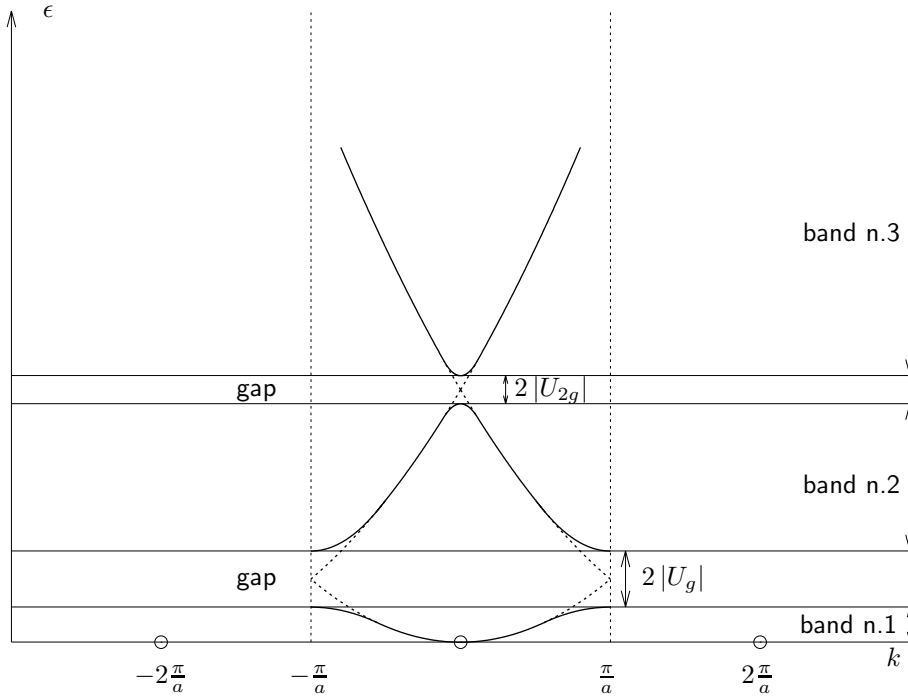


Figure 94: Band gap opening between bands n.1 and n.2 and n.2 and n.3. The dashed lines show the behavior of the energy in the “empty lattice” model (i.e. potential exactly null and contiguous bands). The scale of this figure is different from that of figure 93. Note that the lower part of this figure, that is the part referring to bands n.1 and n.2, is identical (apart from the scale) to figure 92.

6.1.5 Extrapolating to the general case

409. At this point it should be clear that the mathematical derivation of the formation of the band gap between bands n.1 and n.2 and n.2 and n.3 can be easily extended to the general case of any two consecutive bands.

It can be verified that the amplitude of the band gap between bands n. i and n. $(i + 1)$ is equal to $2|U_{ig}|$, U_{ig} being the i -th Fourier coefficient of the periodic potential (if you are interested, the procedure is detailed in section 6.1 of the extracurricular part). And since, in general, the absolute value of the coefficients in a Fourier expansion decreases at increasing i , we deduce that for this model the band gap decreases as the band index (i.e. the energy) increases.

If you think about it, in some ways, this is what would be expected for any *confined* quantum mechanical system: the spacing of the energetic levels tends to zero as the energy increases.

In comparison with an isolated atom, in the present case, the atomic energy levels (identified by individual, discrete energy values) are replaced by the energy bands (identified by energy intervals) and it is the spacing between the bands that becomes narrower and narrower as the energy increases.

410. Figure 95 shows the extended zone representation of the first bands of a crystal containing “nearly free” electrons. Compare this with figure 76.

In figure 96 the repeated zone representation for the same system as figure 95 is shown. This

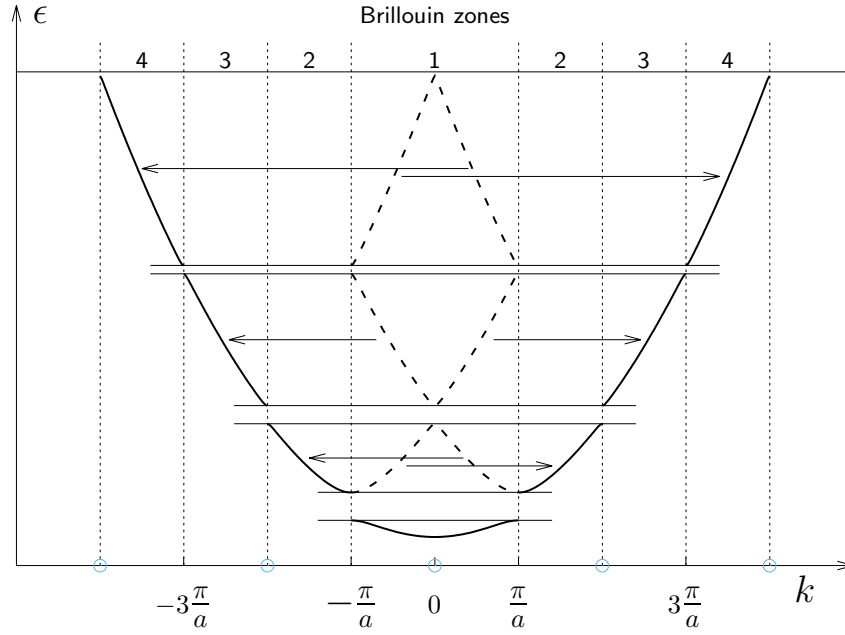


Figure 95: The extended zone representation of the first four bands for a monodimensional crystal containing “nearly free” electrons. I have highlighted the band gaps; moreover, the dash lines and the arrows show how this figure is obtained from the reduced zone representation of figure 94.

figure can be compared with figure 73.

6.2 A physical interpretation of the band gap

411. We can explain the result we obtained with the “nearly free electron” model for a monodimensional crystal also from a physical standpoint.

Let’s come back to the system of two equations (system 719) which is valid in a small left interval of $k = g/2$ and which leads to the opening of the band gap between bands n.1 and n.2.

$$\begin{aligned} \left(\frac{\hbar^2 (k - g)^2}{2m} - \epsilon \right) C_{k-g} + U_g C_k &= 0 \\ U_g C_{k-g} + \left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) C_k &= 0 \end{aligned} \quad (738)$$

When k is exactly equal to $g/2$, that is, when we are just on the (right) boundary of the first Brillouin zone, the system becomes:

$$(\lambda - \epsilon) C_{-\frac{g}{2}} + U_g C_{\frac{g}{2}} = 0 \quad (739)$$

$$U_g C_{-\frac{g}{2}} + (\lambda - \epsilon) C_{\frac{g}{2}} = 0 \quad (740)$$

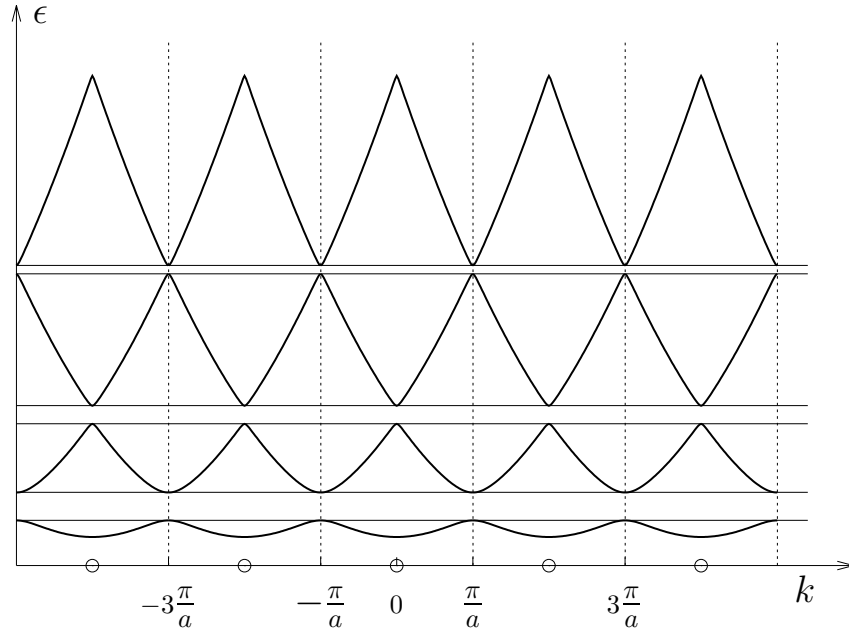


Figure 96: Repeated zone representation of the first four bands for a monodimensional crystal containing “nearly free” electrons; I have highlighted the band gaps with horizontal lines. This figure is obtained by periodic replication of the reduced zone representation, like the one in figure 94.

with:

$$\lambda = \frac{\hbar^2 \left(-\frac{g}{2}\right)^2}{2m} = \frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m}$$

In point 405 we saw that in these conditions the two solutions for the energy are (eq. 726):

$$\epsilon = \lambda \pm |U_g| \quad (741)$$

412. Plugging back this expression for ϵ into the first or second equation of the system we obtain:

$$(\lambda - \lambda \mp |U_g|) C_{-\frac{g}{2}} + U_g C_{\frac{g}{2}} = 0 \quad (742)$$

$$\mp |U_g| C_{-\frac{g}{2}} + U_g C_{\frac{g}{2}} = 0 \quad (743)$$

$$\frac{C_{\frac{g}{2}}}{C_{-\frac{g}{2}}} = -\frac{\mp |U_g|}{U_g} = \pm 1 \quad (744)$$

The meaning of this result is: the two coefficients $C_{\frac{g}{2}}$ and $C_{-\frac{g}{2}}$ have the same absolute value (their ratio is 1); their sign is also the same for one of the two possible ϵ values, but they are of opposite sign for the other one.

413. Recall that $C_{\frac{g}{2}}$ and $C_{-\frac{g}{2}}$ are the only two “important” coefficients in the Fourier expansion of the state function. This means that the two state functions corresponding to the two energy eigenvalues must have the form (review, for instance, eq. 616):

- when $C_{\frac{g}{2}} = C_{-\frac{g}{2}} = C$:

$$\begin{aligned}\Psi_+(r) &= C \exp\left(i\frac{g}{2}r\right) + C \exp\left(-i\frac{g}{2}r\right) = C \left(\exp\left(i\frac{g}{2}r\right) + \exp\left(-i\frac{g}{2}r\right)\right) \\ &\propto \exp\left(i\frac{g}{2}r\right) + \exp\left(-i\frac{g}{2}r\right) = 2 \cos\left(\frac{g}{2}r\right) = 2 \cos\left(\frac{\pi}{a}r\right)\end{aligned}\quad (745)$$

- when $C_{\frac{g}{2}} = -C_{-\frac{g}{2}} = C$:

$$\begin{aligned}\Psi_-(r) &= C \exp\left(i\frac{g}{2}r\right) - C \exp\left(-i\frac{g}{2}r\right) = C \left(\exp\left(i\frac{g}{2}r\right) - \exp\left(-i\frac{g}{2}r\right)\right) \\ &\propto \exp\left(i\frac{g}{2}r\right) - \exp\left(-i\frac{g}{2}r\right) = 2i \sin\left(\frac{g}{2}r\right) = 2i \sin\left(\frac{\pi}{a}r\right)\end{aligned}\quad (746)$$

(I have used the symbol $\propto$ to avoid writing the factor which multiplies the two expressions, determined by the normalization condition, which is totally unimportant in this context)

414. Now we observe that the two functions $\Psi_{\pm}(r)$ are *stationary* waves, that is their nodes (points where they nullify) on the r axis do not change with time. Remember that the complete solution of the Schrödinger equation is obtained by multiplying the spatial part by the exponential:

$$\exp(-i\omega t), \quad \omega = \frac{\epsilon}{\hbar} \quad (747)$$

(eq. 368)

If the spatial part is *not* of exponential form, as in the present case, space and time stay separated and the behavior is that of a stationary wave (point 131).

415. The probability density $\rho_{\pm}$, which is the probability of finding an electron in a given interval of the r axis at a given time, is proportional to the respective square modulus, that is:

$$\rho_+ \propto |\Psi_+(r)|^2 \propto \cos^2\left(\frac{\pi}{a}r\right) \quad (748)$$

$$\rho_- \propto |\Psi_-(r)|^2 \propto \sin^2\left(\frac{\pi}{a}r\right) \quad (749)$$

First off, notice that $\rho_{\pm}$ is *not* constant, differently from what happens for the probability density of a “free” electron or a “nearly free” electron having a wave vector far from the special points $\{0, g/2, -g/2\}$ (FE=“free electron”):

$$\rho_{FE} \propto |\Psi_{FE}(r)|^2 \propto |\exp(ikr)|^2 = 1 \quad (750)$$

Also notice that ρ_+ and ρ_- have wave length equal to a , that is they have the same spatial periodicity as the monodimensional crystal we are discussing:

$$\cos^2\left(\frac{\pi}{a}(r+a)\right) = \cos^2\left(\frac{\pi}{a}r + \pi\right) = \left(-\cos\left(\frac{\pi}{a}r\right)\right)^2 = \cos^2\left(\frac{\pi}{a}r\right)$$

$$\sin^2\left(\frac{\pi}{a}(r+a)\right) = \sin^2\left(\frac{\pi}{a}r + \pi\right) = \left(-\sin\left(\frac{\pi}{a}r\right)\right)^2 = \sin^2\left(\frac{\pi}{a}r\right)$$

Moreover, being proportional to $\cos^2$ and $\sin^2$, respectively, ρ_+ and ρ_- are out of phase by $a/2$ (half of the wave length):

$$\sin^2\left(\frac{\pi}{a}\left(r + \frac{a}{2}\right)\right) = \sin^2\left(\frac{\pi}{a}r + \frac{\pi}{2}\right) = \left(-\cos\left(\frac{\pi}{a}r\right)\right)^2 = \cos^2\left(\frac{\pi}{a}r\right) \quad (751)$$

and this means that one takes its maximum value when the other takes its minimum.

416. Look then at figure 97.^{vii} The figure shows the monodimensional crystal with a “reasonable” potential (that is: potential energy of the electrons about zero away from the nuclei, and rapidly decreasing ($\rightarrow -\infty$) close to the nuclei). Moreover, in the figure I have plotted the three probability densities ρ_+ , ρ_- and ρ_{FE} .

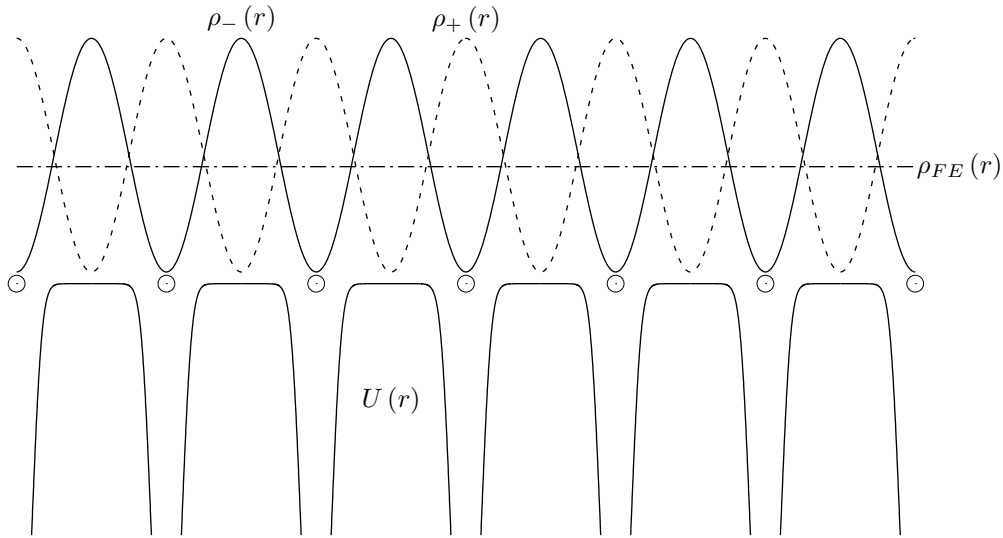


Figure 97: Behavior of the periodic potential $U(r)$, the probability densities $\rho_{\pm}$ and the free electron probability density ρ_{FE} for a monodimensional crystal; the circles indicate the positions of the nuclei; the relative position of the plots along the vertical axis is arbitrary.

ρ_{FE} is constant, meaning that the probability of finding a “free” electron (described by a traveling plane wave) is the same in any region within the macroscopic solid sample; the two probability densities $\rho_{\pm}$ are *not constant* and each tends to accumulate the electronic charge (i.e. to give higher probability values) in different regions of the r axis: ρ_+ tends to localize the electron with higher probability in regions *close* to the nuclei; on the other hand, ρ_- tends to localize the electron with higher probability in regions *away* from the nuclei (in the internuclear regions). But then the energy of an electron described by $\Psi_+(r)$ (hence spending more time near the nuclei) must be *lower* than the energy of an electron described by $\Psi_-(r)$ (which spends more time away from the nuclei).

We have discussed the case $k = g/2$, but you can easily verify that the same arguments apply for any value of k corresponding to the boundary of a Brillouin zone (plus $k = 0$):

^{vii}You find this figure in the book by Kittel³⁰ or in that by Ibach e Lüth.³¹

$$k = j \frac{g}{2} \quad j = 0, \pm 1, \pm 2, \dots \quad (752)$$

In conclusion, the band gap opening is physically explained with the fact that electrons having wave vectors corresponding to the boundaries of the Brillouin zones are described by state functions which behave as stationary waves and that, on average, localize them closer to or farther from the atomic nuclei; in turn, this makes the energy of the electrons, *which would be exactly the same in the absence of the nuclei* (Fermi gas) or in the presence of the nuclei, but *with a null potential* (“empty lattice” model), to be different instead.

6.3 Band gap and diffraction

417. In previous section we saw that when $k = g/2$ there are two possible solutions of Schrödinger’s equation, both having the form of stationary waves.

In this section we delve into this topic and see its ultimate relation with diffraction.

As you know very well, the electron has a wave character and as such it can undergo diffraction in a lattice, exactly like the X rays that we have discussed in section 2.7.1.

The condition which must be satisfied such that an electron can be diffracted by the lattice of ions which makes up a crystal is the same that we found in general (eq. 352):

$$\vec{k} \cdot \vec{n}_G = \frac{1}{2}G \quad (753)$$

Now: in one dimension, the angle between $\vec{k}$ and $\vec{n}_G$ can take only two values, namely 0 or π and thus the scalar product reduces to:

$$\vec{k} \cdot \vec{n}_G = \pm k \quad (754)$$

where $k \geq 0$ is the modulus of the electron’s wavevector $\vec{k}$.

In conclusion:

$$\pm k = \frac{1}{2}G \implies k = \pm \frac{1}{2}G = j \frac{g}{2} \quad j = 0, \pm 1, \pm 2 \dots \quad (755)$$

So: when the wave vector of the electron is far from the values $jg/2$ its interaction with the lattice is negligible (in the “nearly free electron” model, of course) and it behaves mostly as a free electron (point 391); however, when the wave vector of the electron is equal (or very close) to the value satisfying the Laue condition, it will undergo diffraction.

418. In 1D, diffraction is equivalent to a pure reflection; that is: when a wave (in our case the electron) impinges on to a nucleus, this latter behaves as a source reemitting the radiation which hit it *in all directions*: but in a monodimensional crystal “*all directions*” reduce to only two: either the same direction of the incoming wave, or the opposite direction. The reemission of the incoming wave in its same direction is not a diffraction: the wave simply travels undisturbed. Instead, the reemission in the opposite direction is a diffraction (actually, as I said above, a pure reflection).

Since the incoming and the diffracted electron are “the same electron”, the wave function describing its state must be the sum of the incoming and the outgoing (reflected) waves, for the superposition principle (point 176).

419. Just to better focus our mind, let’s consider an electron with a wave vector equal to the right boundary of the first Brillouin zone (thus satisfying the Laue condition $k = g/2 = \pi/a$, $j = 1$ in 755) moving to the right:

$$\Psi(r) \propto \exp\left(i\frac{g}{2}r\right) \quad (756)$$

$\Psi(r)$ has a wave length equal to $2a$ (recall that $g = 2\pi/a$ and thus: $g/2 = \pi/a = 2\pi/\lambda \implies \lambda = 2a$), that is: twice the cell constant of the monodimensional direct lattice. Since the diffracted waves are originated by the nuclei and these have a periodicity of a , the condition for a constructive interference (which requires the optical path of two diffracted waves to be equal to an integer number of wave lengths) is satisfied *separately* by the ions sitting on *even* lattice points and by those sitting on *odd* lattice points. This will result in *two* distinct diffracted waves, bearing a phase difference of a (refer to figure 98) and propagating to the left, that is, in the opposite direction of the incoming wave (because in the 1D case we are considering, the diffraction angle can be only π):

$$\Psi'(r) \propto \exp\left(-i\frac{g}{2}r\right) \quad (757)$$

$$\Psi''(r) \propto \exp\left(-i\frac{g}{2}(r+a)\right) \quad (758)$$

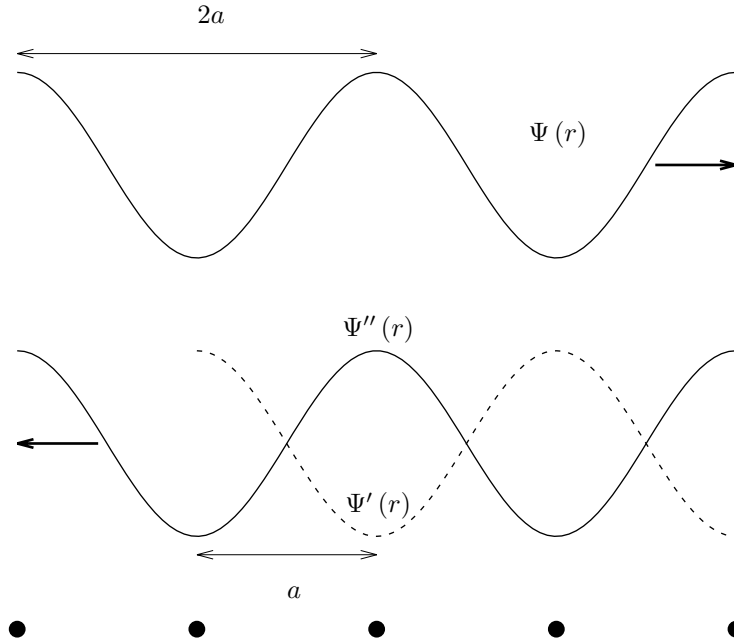


Figure 98: An electron with wave vector π/a travels to the right (upper plot); since the Laue condition is satisfied, the ions (filled dots) will generate electronic diffracted waves traveling to the left (lower plot); but, since the repetition period of the ions is half of the wave length of the diffracted waves, the condition for constructive interference (which requires the optical path of two diffracted waves to be equal to an integer number of wave lengths) is satisfied separately by the ions sitting on *even* and *odd* lattice points. In turn, both diffracted waves (bearing a phase difference of a) do interfere with the incoming wave producing two distinct stationary waves.

In turn, both the diffracted waves will interfere with the original incoming wave and, due to their phase difference, will produce *two different* states of the electron.

In fact:

$$\begin{aligned}
\Psi_+(r) &= \Psi(r) + \Psi'(r) \propto \exp\left(i\frac{g}{2}r\right) + \exp\left(-i\frac{g}{2}r\right) = 2\cos\left(\frac{g}{2}r\right) = 2\cos\left(\frac{\pi}{a}r\right) \quad (759) \\
\Psi_-(r) &= \Psi(r) + \Psi''(r) \propto \exp\left(i\frac{g}{2}r\right) + \exp\left(-i\frac{g}{2}(r+a)\right) \\
&= \exp\left(i\frac{g}{2}r\right) + \exp\left(-i\frac{g}{2}r\right) \exp\left(-i\frac{g}{2}a\right) \\
&= \exp\left(i\frac{g}{2}r\right) + \exp\left(-i\frac{g}{2}r\right) \exp(-i\pi) \quad (\text{nota: } \exp(-i\pi) = -1) \\
&= \exp\left(i\frac{g}{2}r\right) - \exp\left(-i\frac{g}{2}r\right) = 2i\sin\left(\frac{g}{2}r\right) \\
&= 2i\sin\left(\frac{\pi}{a}r\right) \quad (760)
\end{aligned}$$

And these are precisely the two stationary waves that we found in point 411 (eq. 745 and 746). So from here on, one applies the same steps and arrives at the same result.

420. At this point we can summarize our results for the “nearly free electron” model.

In the presence of a small but non null periodic potential (this is the difference with respect to the “empty lattice” model) the behavior of the electrons is described to a good approximation almost everywhere in $\vec{k}$ space by the eigenfunctions and eigenvalues of the free electrons (point 388 and following).

However, when the wave vector of the electron is equal or very close to the value satisfying the Laue condition, it will undergo diffraction by the lattice ions, and this, in turn, causes the degeneracy, which would be observed in the absence of a potential, to be removed: a forbidden energy interval (band gap) sets up, separating any two consecutive bands (point 397 and following).

6.4 Band gaps in two or three dimensions

421. We did analyze the formation mechanism of the band gap in only one dimension because this way all the related math is extremely simpler.

As you have by now realized, extending the obtained results to two or three dimensions does not require any new concept: it only becomes more complex from a purely mathematical standpoint. Also in more than one dimension, when the wave vector satisfies (exactly or almost exactly) the diffraction condition:

$$\vec{k} \cdot \vec{n}_G = \frac{1}{2}G$$

band gaps open and the bands become detached from one another.

We saw that in the most general 3D case the Laue condition is satisfied by all the wave vectors whose tip lays on a plane normal to a reciprocal $\vec{G}$ vector and sectioning it in two segments of equal length (figure 50). Such plane is precisely a face of a Brillouin zone (p. 105).

Therefore, also in the multidimensional cases the Brillouin zones in $\vec{k}$ space are the ultimate responsible for the formation of the band gaps.

The band structure when the system is 2D or 3D is obtained in the same way we discussed for the “empty lattice” model (points 370 and 372).

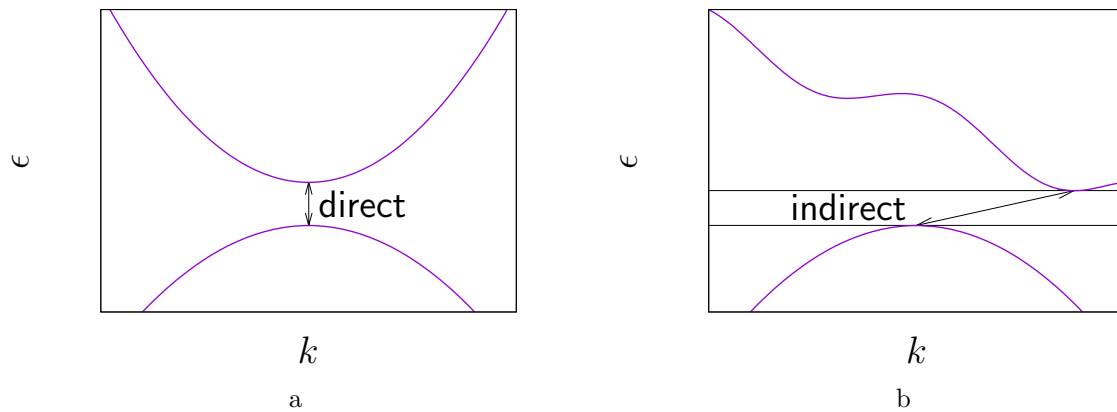


Figure 99: a: direct band gap separating two bands along a segment inside the first Brillouin zone; the maximum eigenvalue of the lower band and the minimum eigenvalue of the upper band share the same wave vector $\vec{k}$; b: indirect band gap separating two bands along a segment inside the first Brillouin zone; the maximum eigenvalue of the lower band and the minimum eigenvalue of the upper band correspond to two different wave vectors.

422. A possibility is to plot a number of bands for the $\vec{k}$ wave vectors corresponding to the points of a segment (or a series of segments) inside the first Brillouin zone. Of course, in the “nearly free electron” model, the bands will not be contiguous and band gaps will separate them. The band gaps separating two consecutive bands can be classified as *direct* or *indirect*.

When the eigenvalue of lowest energy of the “upper” band and that of highest energy of the “lower” band correspond to the same wave vector, the band gap is said to be direct (figure 99a). Instead, if the wave vectors corresponding to the two eigenvalues are different the band gap is said to be indirect (figure 99b).

As already seen for the “empty lattice” model, also in the case of the “nearly free electron” model band overlap can occur: of course, if two bands overlap, there cannot be any band gap between them.

6.4.1 The Fermi surface for the “nearly free electron” model

423. Also the Fermi surface becomes more complicated in the multidimensional case for the “nearly free electron” model. (Un?)fortunately there is no simple math allowing a comparison of the Fermi surface in the presence/absence of a band gap when the dimension is > 1 . The best we can do is a qualitative prediction of the modifications undergone by the Fermi surface when a small but non negligible periodic potential is present.

Let’s take back figure 86 which refers to a 2D system in the “empty lattice” model. As you can easily guess, if the Fermi energy is sufficiently small that the Fermi surface is wholly contained into the first Brillouin zone, like in figure 86a), then there will not be any difference between the “empty lattice” and the “nearly free electron” models. If, however, the Fermi surface intersects the boundaries of the first Brillouin zone, then discontinuities will appear in correspondence with the intersections, where, as we know, the conditions for diffraction are met (point 417).

424. We can figure out qualitatively the appearance of these discontinuities by recalling what we have found in point 406 and following, namely that the bands change their shape close to the Brillouin zone boundaries by “repelling” each other and intersecting the boundaries with an

orthogonal orientation.

Figure 86b shows the reduced zone representation of the Fermi surface for the “empty lattice” bidimensional system of section 5.6.1 in the case that the surface extends on the first two Brillouin zones. The same scenario in the “nearly free electron” model would appear as in figure 100 (where I have reproduced the corresponding figures for the “empty lattice” model, for convenience). Note how discontinuities have developed around the boundaries between the first and second Brillouin zones; note also how the profile of the Fermi surface enters orthogonally into the zone boundary. When we refold the branches of band n.2 into the first Brillouin zone (section 5.6.3.3) a plot very similar to 86b is obtained, save that the perimeter of the Fermi surface is now broken around the gaps generated by the periodic potential.

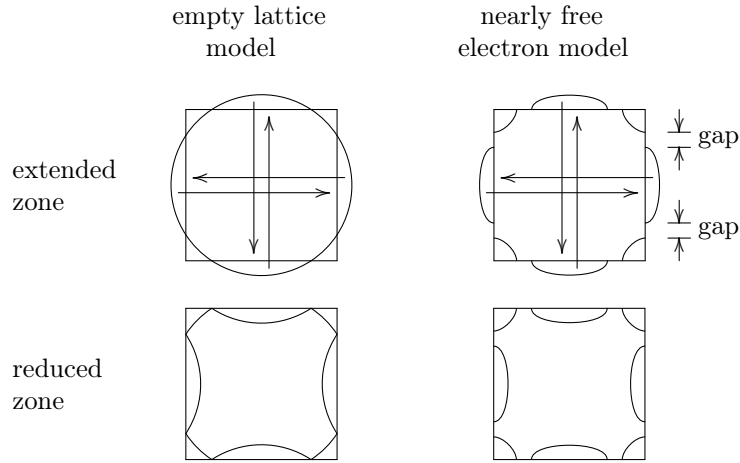


Figure 100: Comparison of the Fermi surfaces for the “empty lattice” and “nearly free electron” models for the bidimensional system of section 5.6.1 when the surface is composed by two branches originated by bands n.1 and n.2. The arrows indicate how the branches outside the first Brillouin zone can be refolded inside it in order to obtain the reduced zone from the extended zone representation; I have also marked two of the discontinuities which break the perimeter of the Fermi surface due to the presence of the non null periodic potential.

As a rule of thumb, the effect of a non null periodic potential is to broaden all the cusps which are present when it is exactly null. You can appreciate this in the repeated zone representation shown in figure 101.

Of course, as you can guess, if the non null periodic potential is not small then the “nearly free electron” model is no more appropriate: things get even more complicated and a purely computational approach becomes mandatory.

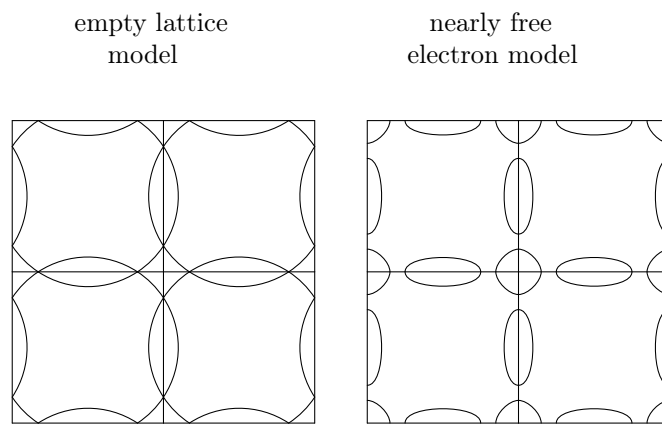


Figure 101: Comparison of the Fermi surface for the bidimensional system of section 5.6.1 in the “empty lattice” and “nearly free electron” models, in the repeated zone representation (I have replicated four cells). Besides the presence of gaps in the Fermi surface for the “nearly free electron” model, you can notice the broadening effect mentioned in the text.

7 The “tight binding” model

There used to be a chapter about the “tight binding” model here, but this year (2025) I was not able to fit it into the 48 hours of the course and I have moved it to the extracurricular part.

Extracurricular

1 Periodic functions, Fourier series and waves

1.1 More formal proof that: $\vec{k} \neq \vec{k}' \implies \int_V \exp(i(\vec{k} - \vec{k}') \cdot \vec{r}) d\vec{r} = 0$

425. Consider a D -dimensional direct lattice $\mathcal{R}$, with primitive vectors $\vec{a}_l$ and the associated reciprocal lattice $\mathcal{R}^*$ with primitive vectors $\vec{b}_j$.

We want to prove that:

$$\vec{k} \neq \vec{k}' \implies \int_V \exp(i(\vec{k} - \vec{k}') \cdot \vec{r}) d\vec{r} = 0 \quad (761)$$

where $\vec{k}, \vec{k}' \in \mathcal{R}^*$ and V is the primitive cell of $\mathcal{R}$.

426. The primitive vectors of $\mathcal{R}$, $\vec{a}_l$, are a basis, in an algebraic sense, of $\mathbb{R}^D$; we can then express the position vector $\vec{r}$ with its coordinates with respect to this (normalized) basis:

$$\vec{r} = \sum_{l=1}^D x_l \frac{\vec{a}_l}{a_l} \quad (762)$$

Note: $\vec{r}$ is a generic point in $\mathbb{R}^D$, not necessarily a vector of $\mathcal{R}$.

Also, realize that $\vec{a}_l/a_l$ is the *versor* in the $\vec{a}_l$ direction and hence x_l is the l -th coordinate of $\vec{r}$ in the (non-cartesian) reference system in which the axes are along the $\vec{a}_l$ vectors (hence, in general, not orthogonal to each other). I have tried to illustrate the meaning of the just introduced x_l coordinates for the case $D = 3$ in figure 102.

If we express $\vec{k}$ and $\vec{k}'$ in terms of the primitive vectors of $\mathcal{R}^*$:

$$\begin{aligned} \vec{k} &= \sum_{j=1}^D m_j \vec{b}_j \quad m_j \in \mathbb{Z} \\ \vec{k}' &= \sum_{j=1}^D m'_j \vec{b}_j \quad m'_j \in \mathbb{Z} \end{aligned}$$

we obtain:

$$\vec{k} - \vec{k}' = \sum_{j=1}^D m_j \vec{b}_j - \sum_{j=1}^D m'_j \vec{b}_j = \sum_{j=1}^D (m_j - m'_j) \vec{b}_j \quad (763)$$

Since $\mathcal{R}^*$ is the reciprocal lattice of $\mathcal{R}$ eq. 135 must hold:

$$\begin{aligned} (\vec{k} - \vec{k}') \cdot \vec{r} &= \left(\sum_{j=1}^D (m_j - m'_j) \vec{b}_j \right) \cdot \left(\sum_{l=1}^D x_l \frac{\vec{a}_l}{a_l} \right) = \sum_{j,l=1}^D (m_j - m'_j) \frac{x_l}{a_l} \vec{b}_j \cdot \vec{a}_l \\ &= 2\pi \sum_{j,l=1}^D (m_j - m'_j) \frac{x_l}{a_l} \delta_{jl} = 2\pi \sum_{j=1}^D (m_j - m'_j) \frac{x_j}{a_j} \end{aligned}$$

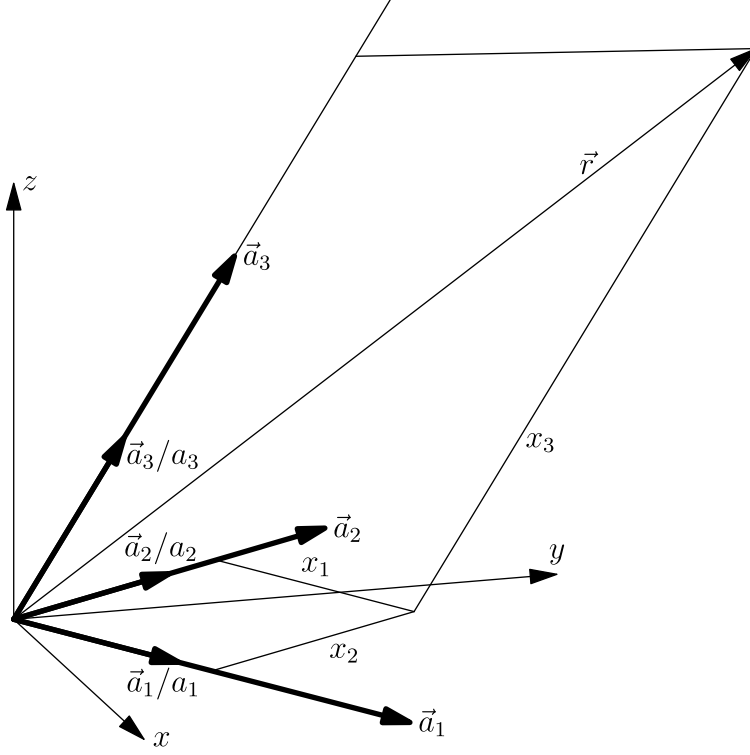


Figure 102: In a cartesian reference system xyz I have represented the three direct primitive vectors $\vec{a}_l$, the corresponding $\vec{a}_l/a_l$ versors and a generic position vector $\vec{r}$. x_1, x_2, x_3 are the lengths of the corresponding segments in the figure and also the coordinates of the point $\vec{r}$ with respect to the (normalized) basis made by $\vec{a}_1/a_1, \vec{a}_2/a_2, \vec{a}_3/a_3$; in other words, the point $\vec{r}$ is reached by the following linear combination:

$$\vec{r} = x_1 \frac{\vec{a}_1}{a_1} + x_2 \frac{\vec{a}_2}{a_2} + x_3 \frac{\vec{a}_3}{a_3}$$

Realize that the coordinates of the *same* point with respect to the versors of the *cartesian* axes (not shown in the figure) are *different* from x_1, x_2, x_3 .

By making use of what we have just obtained, the integral 761 becomes:

$$\int_V \exp \left(i2\pi \sum_{j=1}^D (m_j - m'_j) \frac{x_j}{a_j} \right) d\vec{r} \quad (764)$$

Now let's explicitly write down the D -ple (i.e. double or triple) integral and the differential of the $\vec{r}$ position vector in the coordinates with respect to the normalized basis made by the $\vec{a}_j$ primitive vectors:

$$\int_0^{a_1} \cdots \int_0^{a_D} \exp \left(i2\pi \sum_{j=1}^D (m_j - m'_j) \frac{x_j}{a_j} \right) \prod_{l=1}^D dx_l \quad (765)$$

Please note the following two things about the above step:

- don't be scared by the notation. The:

$$\prod_{l=1}^D dx_l$$

term is a general (but perhaps a bit heavy?) way to write:

$$\begin{array}{ll} dx_1 dx_2 & \text{if } D = 2 \\ dx_1 dx_2 dx_3 & \text{if } D = 3 \end{array}$$

Similarly, the:

$$\int_0^{a_1} \cdots \int_0^{a_D}$$

notation simply means:

$$\begin{array}{ll} \int_0^{a_1} \int_0^{a_2} & \text{if } D = 2 \\ \int_0^{a_1} \int_0^{a_2} \int_0^{a_3} & \text{if } D = 3 \end{array}$$

- since the integral over the primitive cell, which, in general, is a parallelepiped with *non-right* angles, is done with the coordinates referenced to the $\vec{a}_j$ normalized basis (that is: *not* in cartesian coordinates), each coordinate will vary between 0 and the length of the corresponding edge of the primitive cell (that is the modulus of the corresponding primitive vector); put into equivalent words: the above written integral evaluated with the coordinates referenced to the $\vec{a}_j$ normalized basis is logically equivalent to an integral in cartesian coordinates evaluated on a primitive cell with right angles (a so called “right prism” or “cuboid”)

427. The exponential (whose argument is a sum) can be rewritten as the product of the exponentials of each term of the sum:

$$\int_0^{a_1} \cdots \int_0^{a_D} \prod_{j=1}^D \exp \left(i2\pi (m_j - m'_j) \frac{x_j}{a_j} \right) \prod_{l=1}^D dx_l \quad (766)$$

428. Now realize that the argument of the multiple integral is a product of factors each depending on a *single coordinate* x_j ; it can then be written as the product of D single integrals, each evaluated on a single coordinate:

$$\prod_{j=1}^D \int_0^{a_j} \exp \left(i2\pi (m_j - m'_j) \frac{x_j}{a_j} \right) dx_j \quad (767)$$

At this point we have rewritten the integral 761 as a product of D single integrals, each on a single coordinate.

429. Since $\vec{k} \neq \vec{k}'$, we are assured that at least one of the $(m_j - m'_j)$ differences will be non null. Let n be the index for which:

$$(m_n - m'_n) \neq 0 \quad (768)$$

In the corresponding integral we perform the following change of variable:

$$u = i2\pi (m_n - m'_n) \frac{x_n}{a_n} \quad (769)$$

from which:

$$\begin{aligned} dx_n &= \frac{a_n}{i2\pi (m_n - m'_n)} du \quad (\text{it's here that we need: } (m_n - m'_n) \neq 0) \\ x_n = 0 &\implies u = 0 \\ x_n = a_n &\implies u = i2\pi (m_n - m'_n) \end{aligned}$$

Thus, the n -th integral in the product is null, since:

$$\begin{aligned} &\int_0^{a_n} \exp \left(i2\pi (m_n - m'_n) \frac{x_n}{a_n} \right) dx_n \\ &= \frac{a_n}{i2\pi (m_n - m'_n)} \int_0^{i2\pi (m_n - m'_n)} \exp(u) du \\ &= \frac{a_n}{i2\pi (m_n - m'_n)} \left[\exp(u) \right]_0^{i2\pi (m_n - m'_n)} \\ &= \frac{a_n}{i2\pi (m_n - m'_n)} \left(\overbrace{\exp(i2\pi (m_n - m'_n))}^{=1 \text{ eq. 22}} - \exp(0) \right) \\ &= \frac{a_n}{i2\pi (m_n - m'_n)} (1 - 1) \\ &= 0 \end{aligned}$$

430. But, of course, this implies that the whole product of D single integrals, that is the original integral 761, must be null:

$$\int_V \exp \left(i \left(\vec{k} - \vec{k}' \right) \cdot \vec{r} \right) d\vec{r} = \prod_{j=1}^D \overbrace{\int_0^{a_j} \exp \left(i2\pi (m_j - m'_j) \frac{x_j}{a_j} \right) dx_j}^{\text{the } n\text{-th integral of this product is null}} = 0$$

1.2 Analytic derivation of the expressions for the reciprocal primitive vectors in the 2D case

431. Let's introduce the following notation:

$$\vec{a}_1 = (a_{1x}, a_{1y})$$

$$\begin{aligned}
\vec{a}_2 &= (a_{2x}, a_{2y}) \\
\vec{b}_1 &= (b_{1x}, b_{1y}) \\
\vec{b}_2 &= (b_{2x}, b_{2y})
\end{aligned}$$

Our task is to find the components of the two vectors $\vec{b}_1$ and $\vec{b}_2$ as a function of those of $\vec{a}_1$ and $\vec{a}_2$.

The starting point is condition 135, which I report here in a more explicit form for the 2D case:

$$\begin{aligned}
\vec{b}_1 \cdot \vec{a}_2 &= 0 \\
\vec{b}_1 \cdot \vec{a}_1 &= 2\pi \\
\vec{b}_2 \cdot \vec{a}_1 &= 0 \\
\vec{b}_2 \cdot \vec{a}_2 &= 2\pi
\end{aligned}$$

As noted on p.73, if we perform the scalar products we get:

$$\begin{aligned}
b_{1x}a_{2x} + b_{1y}a_{2y} &= 0 \\
b_{1x}a_{1x} + b_{1y}a_{1y} &= 2\pi \\
b_{2x}a_{1x} + b_{2y}a_{1y} &= 0 \\
b_{2x}a_{2x} + b_{2y}a_{2y} &= 2\pi
\end{aligned}$$

Notice that the equations for $\vec{b}_1$ are decoupled from those for $\vec{b}_2$ and thus the initial four-dimensional linear system can be partitioned into two independent two-dimensional systems:

$$b_{1x}a_{2x} + b_{1y}a_{2y} = 0 \quad (770)$$

$$b_{1x}a_{1x} + b_{1y}a_{1y} = 2\pi \quad (771)$$

and

$$b_{2x}a_{1x} + b_{2y}a_{1y} = 0 \quad (772)$$

$$b_{2x}a_{2x} + b_{2y}a_{2y} = 2\pi \quad (773)$$

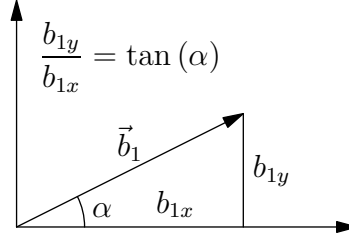
432. From the first equation for $\vec{b}_1$ we can obtain b_{1x} as a function of b_{1y} or the ratio of the two:

$$b_{1x} = -\frac{a_{2y}}{a_{2x}}b_{1y} \iff \frac{b_{1x}}{b_{1y}} = -\frac{a_{2y}}{a_{2x}} \quad (774)$$

The vector $\vec{b}_1$ can thus be written in the following way:

$$\vec{b}_1 = \left(-\frac{a_{2y}}{a_{2x}} b_{1y}, b_{1y} \right) = b_{1y} \left(-\frac{a_{2y}}{a_{2x}}, 1 \right) = \xi_1 \left(-\frac{a_{2y}}{a_{2x}}, 1 \right) \quad (775)$$

where I have set $b_{1y} = \xi_1$ to better evidence that the orthogonality condition between $\vec{b}_1$ and $\vec{a}_2$ defines $\vec{b}_1$ up to a yet unknown factor (ξ_1 , precisely). Realize that this is perfectly reasonable. Indeed, having obtained (only) the ratio between the components of $\vec{b}_1$ ((eq. 774 above) means knowing (only) its direction (but not its length):



Also note that if $a_{2x} = 0$ the just obtained expressions would become meaningless. But $a_{2x} = 0$ means that $\vec{a}_2$ is oriented along the y axis and thus, in this case, the orthogonality condition between $\vec{b}_1$ and $\vec{a}_2$ will be satisfied when $\vec{b}_1$ is oriented along the x axis; that is:

$$\vec{b}_1 = (\xi_1, 0) = \xi_1 (1, 0) \quad (776)$$

with $\xi_1 \in \mathbb{R}$ any real number (to be found).

In summary, considering only the orthogonality condition between $\vec{b}_1$ and $\vec{a}_2$ (eq. 770), we get to:

$$\vec{b}_1 = \begin{cases} \xi_1 \left(-\frac{a_{2y}}{a_{2x}}, 1 \right) & \text{if } a_{2x} \neq 0 \\ \xi_1 (1, 0) & \text{if } a_{2x} = 0 \end{cases} \quad (777)$$

with $\xi_1 \in \mathbb{R}$ still to be found.

Additionally notice that $a_{2x} = a_{2y} = 0$ is not possible, because $\vec{a}_2$, being a primitive vector of the direct lattice $\mathcal{R}$, cannot be null.

433. The ξ_1 constant is obtained from the second equation for $\vec{b}_1$ (eq. 771).

Based on 777, we must distinguish two cases.

If $a_{2x} \neq 0$, then plugging 777 into 771 we obtain:

$$\xi_1 \left(-\frac{a_{2y}}{a_{2x}} \right) a_{1x} + \xi_1 a_{1y} = \xi_1 \left(-\frac{a_{2y}}{a_{2x}} a_{1x} + a_{1y} \right) = 2\pi \iff \xi_1 = \frac{2\pi}{\left(-\frac{a_{2y}}{a_{2x}} a_{1x} + a_{1y} \right)} \quad (778)$$

and thus:

$$\vec{b}_1 = \frac{2\pi}{\underbrace{\left(-\frac{a_{2y}}{a_{2x}} a_{1x} + a_{1y} \right)}} \left(-\frac{a_{2y}}{a_{2x}}, 1 \right) \quad (779)$$

Note that the evidenced denominator cannot be null for, if so, we would have:

$$-\frac{a_{2y}}{a_{2x}}a_{1x} + a_{1y} = 0 \iff a_{1y} = \frac{a_{2y}}{a_{2x}}a_{1x} \iff \frac{a_{1y}}{a_{1x}} = \frac{a_{2y}}{a_{2x}} \quad (780)$$

that is: $\vec{a}_1$ and $\vec{a}_2$ would be parallel. But this cannot be since $\vec{a}_1$ and $\vec{a}_2$ are linearly independent, being the primitive vectors of the direct lattice.

If, on the other hand, $a_{2x} = 0$, plugging 777 into 771 gives:

$$\xi_1 a_{1x} = 2\pi \iff \xi_1 = \frac{2\pi}{a_{1x}} \quad (781)$$

Again, notice that, being in this case $a_{2x} = 0$, $a_{1x} = 0$ is not a possibility; if it would be so, then $\vec{a}_1$ and $\vec{a}_2$ would be parallel again (both along the y axis) and this cannot be, by what just stated above.

In conclusion, the final result for $\vec{b}_1$ is:

$$\vec{b}_1 = \begin{cases} \frac{2\pi}{\left(-\frac{a_{2y}}{a_{2x}}a_{1x} + a_{1y}\right)} \left(-\frac{a_{2y}}{a_{2x}}, 1\right) & \text{if } a_{2x} \neq 0 \\ \frac{2\pi}{a_{1x}} (1, 0) & \text{if } a_{2x} = 0 \end{cases} \quad (782)$$

434. Of course, by an identical procedure, for $\vec{b}_2$ we obtain:

$$\vec{b}_2 = \begin{cases} \frac{2\pi}{\left(-\frac{a_{1y}}{a_{1x}}a_{2x} + a_{2y}\right)} \left(-\frac{a_{1y}}{a_{1x}}, 1\right) & \text{if } a_{1x} \neq 0 \\ \frac{2\pi}{a_{2x}} (1, 0) & \text{if } a_{1x} = 0 \end{cases} \quad (783)$$

435. Here is an `octave` codelett which you can use to verify the formulas.

```
# octave start
## INPUT STARTS HERE
a1=[10.0,0.5];
a2=[0.1,2.0];
## INPUT ENDS HERE
a1x=a1(1);
a1y=a1(2);
a2x=a2(1);
a2y=a2(2);
## evaluate b1
if(abs(a2x)>1.e-9) # a2x!=0
fac=(-(a2y/a2x)*a1x+a1y);
fac=2*pi/fac;
b1=fac*[-a2y/a2x,1];
else # a2x==0
b1=(2*pi/a1x)*[1,0];
```

```

endif
## evaluate b2
if(abs(a1x)>1.e-9) # a1x!=0
fac=(-(a1y/a1x)*a2x+a2y);
fac=2*pi/fac;
b2=fac*[-a1y/a1x,1];
else # a1x==0
b2=(2*pi/a2x)*[1,0];
endif
## verify result
printf("%+15s %5.2f\n", "b1.a2:", dot(b1,a2));
printf("%+15s %5.2f\n", "b1.a1/(2pi):", dot(b1,a1)/(2*pi));
printf("%+15s %5.2f\n", "b2.a1:", dot(b2,a1));
printf("%+15s %5.2f\n", "b2.a2/(2pi):", dot(b2,a2)/(2*pi));
# octave end

```

1.3 Dimostrazione che il triplo prodotto e' invariante rispetto a permutazioni cicliche

436. Per verificare la proprieta' di permutazione ciclica del triplo prodotto tenete presente che, in generale, le coordinate cartesiane del prodotto vettoriale dei due vettori $\vec{a}_2$ e $\vec{a}_3$ si ottengono (mnemonicamente) sviluppando in minori 2×2 lungo la prima riga o la prima colonna i seguenti determinanti:

$$\begin{aligned}
\vec{a}_2 \times \vec{a}_3 &= \det \begin{pmatrix} \vec{i} & \vec{j} & \vec{k} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} = \det \begin{pmatrix} \vec{i} & a_{21} & a_{31} \\ \vec{j} & a_{22} & a_{32} \\ \vec{k} & a_{23} & a_{33} \end{pmatrix} \\
&= \vec{i}(a_{22}a_{33} - a_{23}a_{32}) - \vec{j}(a_{21}a_{33} - a_{23}a_{31}) + \vec{k}(a_{21}a_{32} - a_{22}a_{31})
\end{aligned}$$

dove a_{ij} e' la componente j -esima di $\vec{a}_i$ e $\vec{i}$, $\vec{j}$ e $\vec{k}$ sono i versori dei tre assi cartesiani. Poi, utilizzando anche la procedura mostrata sopra, realizzate che il prodotto triplo $\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3$ e' uguale ai seguenti determinanti (verificatelo con carta e penna e ricordate che i determinati di una matrice e della sua trasposta sono uguali):

$$\begin{aligned}
\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 &= \det \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} = \det \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix} \\
&= \det \begin{pmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{pmatrix} = \det(\vec{a}_1 \vec{a}_2 \vec{a}_3) \tag{784}
\end{aligned}$$

Do per scontato che tutti sappiate che scambiando due righe o due colonne di un determinante se ne cambia il segno, ma non il valore assoluto. Allora, la proprieta' 158 segue dal fatto che una

permutazione *ciclica* delle tre righe del determinante in 784 consiste sempre in *due* scambi (cioe' e' sempre una permutazione *pari*). Ad esempio:

$$\det \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \\ \vec{a}_3 \end{pmatrix} \begin{array}{c} \text{primo scambio} \\ \\ \text{cambio segno} \end{array} = - \det \begin{pmatrix} \vec{a}_3 \\ \vec{a}_2 \\ \vec{a}_1 \end{pmatrix} \begin{array}{c} \text{secondo scambio} \\ \\ \text{cambio segno} \end{array} = \det \begin{pmatrix} \vec{a}_2 \\ \vec{a}_3 \\ \vec{a}_1 \end{pmatrix}$$

(notate che quella centrale *non* e' una permutazione ciclica del determinante di partenza)
Ma questo significa proprio che il determinante (cioe' il triplo prodotto) rimane identico (anche nel segno) in seguito ad una permutazione ciclica.

1.4 Dimostrazione della proprieta' 202 in 3D

437. Partiamo dall'espressione del generico coefficiente di Fourier:

$$B_{\vec{k}} = \frac{1}{V} \int_V \exp \left(-i\vec{k} \cdot \vec{r} \right) f(\vec{r}) d\vec{r} \quad (785)$$

(V e' il volume della cella primitiva del reticolo diretto)

Per comodita' di notazione, poniamo:

$$\vec{r} = (x_1, x_2, x_3) \quad (786)$$

Ora, in modo analogo a quanto fatto in una sola dimensione, facciamo il cambio di variabile:

$$\vec{u} = -\vec{r} \quad (787)$$

Attenzione, pero': fare un cambio di variabile in un integrale multiplo (e quello sopra e' un integrale triplo) non e' la stessa cosa che farlo in un integrale su una sola variabile.¹³

In generale, dette (u_1, u_2, u_3) le componenti del vettore $\vec{u}$, il cambio di variabile e' definito dalle tre relazioni:

$$x_1 = X_1(u_1, u_2, u_3) \quad (788)$$

$$x_2 = X_2(u_1, u_2, u_3) \quad (789)$$

$$x_3 = X_3(u_1, u_2, u_3) \quad (790)$$

Allora l'integrale nelle variabili (x_1, x_2, x_3) e' legato a quello nelle variabili (u_1, u_2, u_3) dalla seguente relazione:

$$\int_V F(\vec{r}) d\vec{r} = \int_V F(x_1, x_2, x_3) dx_1 dx_2 dx_3 \quad (791)$$

$$= \int_{V'} F(X_1, X_2, X_3) |J| du_1 du_2 du_3 = \int_{V'} F(\vec{X}) |J| d\vec{u} \quad (792)$$

dove F e' la generica funzione da integrare espressa nelle variabili u_1, u_2, u_3 , V' e' la regione di spazio V espressa con le nuove coordinate (u_1, u_2, u_3) e $|J|$ e' il valore assoluto del determinante jacobiano delle vecchie coordinate rispetto alle nuove:

$$J = \det \begin{pmatrix} \frac{\partial X_1}{\partial u_1} & \frac{\partial X_1}{\partial u_2} & \frac{\partial X_1}{\partial u_3} \\ \frac{\partial X_2}{\partial u_1} & \frac{\partial X_2}{\partial u_2} & \frac{\partial X_2}{\partial u_3} \\ \frac{\partial X_3}{\partial u_1} & \frac{\partial X_3}{\partial u_2} & \frac{\partial X_3}{\partial u_3} \end{pmatrix} \quad (793)$$

Nel nostro caso, le relazioni che legano le vecchie variabili alle nuove sono :

$$x_1 = X_1(u_1, u_2, u_3) = -u_1 \quad (794)$$

$$x_2 = X_2(u_1, u_2, u_3) = -u_2 \quad (795)$$

$$x_3 = X_3(u_1, u_2, u_3) = -u_3 \quad (796)$$

e quindi il determinante jacobiano e' :

$$J = \det \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = -1 \implies |J| = 1 \quad (797)$$

In definitiva, operando il cambio di variabile otteniamo:

$$\begin{aligned} B_{\vec{k}} &= \frac{1}{V} \int_V \exp(-i\vec{k} \cdot \vec{r}) f(\vec{r}) d\vec{r} = \frac{1}{V} \int_{V'} \exp(-i\vec{k} \cdot (-\vec{u})) f(-\vec{u}) d\vec{u} \\ &\text{(qua sfruttiamo l'ipotesi che la } f \text{ sia pari)} \\ &= \frac{1}{V} \int_{V'} \exp(-i(-\vec{k}) \cdot \vec{u}) f(\vec{u}) d\vec{u} = B_{-\vec{k}} \end{aligned} \quad (798)$$

e questo prova che i coefficienti sono pari.

Inoltre, siccome la f e' reale per ipotesi, possiamo invocare la 798 appena dimostrata e la proprieta' 198 e quindi:

$$\left. \begin{aligned} B_{\vec{k}} &= B_{-\vec{k}} \\ B_{-\vec{k}} &= B_{\vec{k}}^* \end{aligned} \right\} \implies B_{\vec{k}} = B_{\vec{k}}^* \quad (799)$$

e questo prova che i coefficienti sono reali.

1.5 Dimostrazione della proprieta' 205 in 3D

438. Fate riferimento a quanto abbiamo gia' visto al punto 104.

L'espressione del generico coefficiente di Fourier e' :

$$B_{\vec{k}} = \frac{1}{V} \int_V \exp(-i\vec{k} \cdot \vec{r}) f(\vec{r}) d\vec{r} \quad (800)$$

(V e' il volume della cella primitiva del reticolo diretto)

Poniamo:

$$\vec{r} = (x_1, x_2, x_3) \quad (801)$$

Ora facciamo lo stesso cambio di variabile:

$$\vec{u} = -\vec{r} \quad (802)$$

Le relazioni che legano le variabili vecchie alle nuove sono esattamente le stesse:

$$x_1 = X_1(u_1, u_2, u_3) = -u_1 \quad (803)$$

$$x_2 = X_2(u_1, u_2, u_3) = -u_2 \quad (804)$$

$$x_3 = X_3(u_1, u_2, u_3) = -u_3 \quad (805)$$

e quindi anche il determinante jacobiano e' il medesimo (sezione 1.4):

$$J = \det \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = -1 \implies |J| = 1 \quad (806)$$

Operando il cambio di variabile otteniamo:

$$\begin{aligned} B_{\vec{k}} &= \frac{1}{V} \int_V \exp(-i\vec{k} \cdot \vec{r}) f(\vec{r}) d\vec{r} = \frac{1}{V} \int_{V'} \exp(-i\vec{k} \cdot (-\vec{u})) f(-\vec{u}) d\vec{u} \\ &\text{(qua sfruttiamo l'ipotesi che la } f \text{ sia dispari)} \\ &= -\frac{1}{V} \int_{V'} \exp(-i(-\vec{k}) \cdot \vec{u}) f(\vec{u}) d\vec{u} = -B_{-\vec{k}} \end{aligned} \quad (807)$$

e questo prova che i coefficienti sono dispari.

Inoltre, siccome la f e' reale per ipotesi, possiamo invocare la 807 appena dimostrata e la proprieta' 198 e quindi:

$$\left. \begin{aligned} B_{\vec{k}} &= -B_{-\vec{k}} \\ B_{-\vec{k}} &= B_{\vec{k}}^* \end{aligned} \right\} \implies B_{\vec{k}} = -B_{\vec{k}}^* \quad (808)$$

e questo prova che i coefficienti sono numeri immaginari puri.

1.6 Bravais lattice for (the spatial part of) a plane wave

In this section I want to show you that the spatial part of a plane wave, like any other periodic function and as we discussed in general, has a Bravais lattice associated with it.

Consider the traveling sinusoidal plane wave:

$$f(\vec{r}, t) = A \cos(k\vec{r} \cdot \vec{n} - \omega t) \quad (809)$$

Its spatial part is obtained by fixing the time coordinate and, for the sake of simplicity, let's take $t = 0$.

Let:

$$\vec{r} = (x, y, z) \quad (810)$$

$$\vec{n} = (n_x, n_y, n_z) \quad (811)$$

Then:

$$\begin{aligned} f(\vec{r}, 0) &= f(x, y, z, 0) = A \cos(k(x, y, z) \cdot (n_x, n_y, n_z)) \\ &= A \cos\left(\frac{2\pi}{\lambda} (n_x, n_y, n_z) \cdot (x, y, z)\right) \\ &= A \cos\left(2\pi \left(\frac{n_x}{\lambda}, \frac{n_y}{\lambda}, \frac{n_z}{\lambda}\right) \cdot (x, y, z)\right) \\ &= A \cos\left(2\pi \left(\frac{1}{\frac{\lambda}{n_x}}, \frac{1}{\frac{\lambda}{n_y}}, \frac{1}{\frac{\lambda}{n_z}}\right) \cdot (x, y, z)\right) \\ &= A \cos\left(2\pi \left(\frac{1}{\lambda_x}, \frac{1}{\lambda_y}, \frac{1}{\lambda_z}\right) \cdot \vec{r}\right) \end{aligned} \quad (812)$$

You can verify very easily that the function 812 is periodic on a Bravais lattice defined by the three primitive vectors:

$$\begin{aligned} \vec{a}_x &= \lambda_x (1, 0, 0) \\ \vec{a}_y &= \lambda_y (0, 1, 0) \\ \vec{a}_z &= \lambda_z (0, 0, 1) \end{aligned}$$

In fact, letting:

$$\vec{R} = m_x \vec{a}_x + m_y \vec{a}_y + m_z \vec{a}_z = (m_x \lambda_x, m_y \lambda_y, m_z \lambda_z)$$

be a generic vector of the Bravais lattice, the following holds:

$$\begin{aligned} f(\vec{r} + \vec{R}, 0) &= A \cos\left(2\pi \left(\frac{1}{\lambda_x}, \frac{1}{\lambda_y}, \frac{1}{\lambda_z}\right) \cdot (\vec{r} + \vec{R})\right) \\ &= A \cos\left(2\pi \left(\frac{1}{\lambda_x}, \frac{1}{\lambda_y}, \frac{1}{\lambda_z}\right) \cdot \vec{r} + 2\pi \left(\frac{1}{\lambda_x}, \frac{1}{\lambda_y}, \frac{1}{\lambda_z}\right) \cdot \vec{R}\right) \\ &= A \cos\left(2\pi \left(\frac{1}{\lambda_x}, \frac{1}{\lambda_y}, \frac{1}{\lambda_z}\right) \cdot \vec{r} + 2\pi \left(\frac{1}{\lambda_x}, \frac{1}{\lambda_y}, \frac{1}{\lambda_z}\right) \cdot (m_x \lambda_x, m_y \lambda_y, m_z \lambda_z)\right) \\ &= A \cos\left(2\pi \left(\frac{1}{\lambda_x}, \frac{1}{\lambda_y}, \frac{1}{\lambda_z}\right) \cdot \vec{r} + 2\pi \left(\overbrace{m_x + m_y + m_z}^{\in \mathbb{Z}}\right)\right) \\ &= A \cos\left(2\pi \left(\frac{1}{\lambda_x}, \frac{1}{\lambda_y}, \frac{1}{\lambda_z}\right) \cdot \vec{r}\right) = f(\vec{r}, 0) \quad \forall \vec{r}, \forall \vec{R} \end{aligned}$$

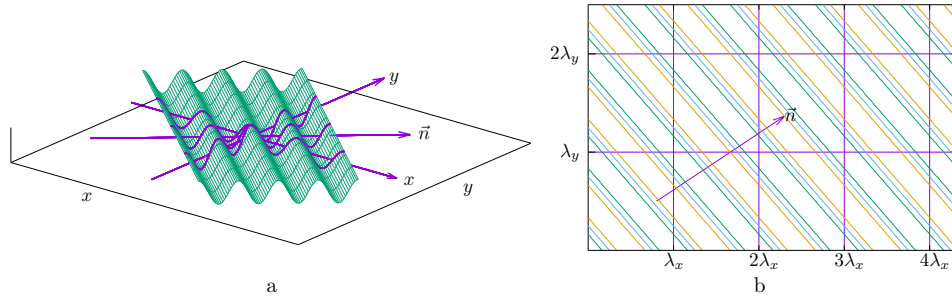


Figure 103: a: on the graph of a bidimensional plane wave (at fixed t) I have evidenced the sinusoidal tracks on vertical sections in the propagation direction $\vec{n}$ and in the directions of the cartesian axes x and y ; these sinusoids have wave lengths λ , λ_x and λ_y , respectively; b: the same graph of a: is represented with isocurves (actually: isolines, in this case) to evidence that (the spatial part of) the plane wave can be described as a bidimensional periodic function on a Bravais lattice whose primitive cell is a rectangle of sides λ_x and λ_y . Note how the “content” of each primitive cell is always the same (as it must be). I have also represented the direction of the vector $\vec{n}$, orthogonal to the isolines.

Note that $\lambda = 2\pi/k$ is the wave length in the propagation direction (that is, the direction of the vector $\vec{n}$) while λ_i , $i = x, y, z$ are wave lengths in the directions of the three cartesian axes and define corresponding wave numbers $k_i = 2\pi/\lambda_i$, $i = x, y, z$. All these wave lengths and wave numbers are, in general, different, as I anticipated at point 122.

To clarify further, in figure 103a I have evidenced these periodicities for a bidimensional plane wave (which is easier to represent). From the figure you should realize that by sectioning the graph of the plane wave with a plane orthogonal to the xy plane, you always obtain a sinusoid (except when the sectioning plane is also orthogonal to the propagation direction, of course). When the sectioning plane is parallel to the propagation direction, the resulting sinusoid has the minimum wave length (that is $\lambda = 2\pi/k$); when the sectioning plane is parallel to the x axis the wave length of the obtained sinusoid is λ_x and when it is parallel to the y axis the wave length is λ_y .

The (bidimensional) Bravais lattice defining the periodicity of the wave on the xy plane is evidenced in figure 103b, where the spatial graph is represented with isocurves, which, in this case, are parallel straight lines orthogonal to the propagation direction.

I do not want to confuse you: eq. 812 is nothing but a mathematical representation of the plane wave perfectly equivalent to 227: you can appreciate how the latter is much more elegant and useful.

1.7 An example of the use of complex exponential representation of plane waves

Here we see how we can take advantage of the complex exponential representation of plane waves to perform in a simple way algebraic manipulations which would be much more complicated if using only trigonometry.

The example is: turn the sum of two plane waves of same frequency and wavelength, but different amplitude and initial phase, into a single plane wave with the same frequency and wavelength

of the two original waves.

I found this derivation on the web.³²

We want to work out the following sum:

$$A_1 \cos(\vec{k} \cdot \vec{r} - \omega t + \phi_1) \pm A_2 \cos(\vec{k} \cdot \vec{r} - \omega t + \phi_2)$$

that is: the sum of two plane waves sharing a common wave vector ($\vec{k}$) and angular frequency (ω), but having different amplitudes (A_1 vs A_2) and initial phases (ϕ_1 vs ϕ_2).

To make notation lighter, let's set:

$$x = \vec{k} \cdot \vec{r} - \omega t \quad (813)$$

so that the original problem can be restated as:

$$A_1 \cos(x + \phi_1) \pm A_2 \cos(x + \phi_2)$$

As explained in section 1.4.6, we start by expressing the original problem in complex exponential notation, that is:

$$\Re \{A_1 \exp(i(x + \phi_1)) \pm A_2 \exp(i(x + \phi_2))\}$$

($\Re$ means “the real part of”)

Now we break the exponentials:

$$= \Re \{A_1 \exp(ix) \exp(i\phi_1) \pm A_2 \exp(ix) \exp(i\phi_2)\}$$

and factor out the $\exp(ix)$ factor:

$$= \Re \{\exp(ix) [A_1 \exp(i\phi_1) \pm A_2 \exp(i\phi_2)]\}$$

Use Euler identity for the two exponentials containing the initial phases ϕ_1 and ϕ_2 :

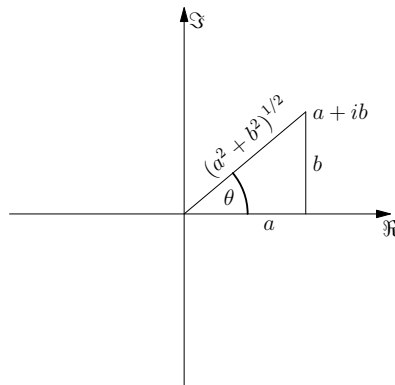
$$= \Re \{\exp(ix) [A_1 \cos \phi_1 + iA_1 \sin \phi_1 \pm A_2 \cos \phi_2 \pm iA_2 \sin \phi_2]\}$$

Group real and imaginary parts:

$$= \Re \{\exp(ix) [A_1 \cos \phi_1 \pm A_2 \cos \phi_2 + i(A_1 \sin \phi_1 \pm A_2 \sin \phi_2)]\}$$

and re-apply the Euler identity.

In this regard realize that any (non null) complex number in the form $a + ib$ can be always turned into a complex exponential, using Euler identity.



$$\begin{aligned}
a + ib &= \sqrt{a^2 + b^2} \cos \theta + i \sqrt{a^2 + b^2} \sin \theta \\
&= \sqrt{a^2 + b^2} (\cos \theta + i \sin \theta) = \sqrt{a^2 + b^2} \exp(i\theta)
\end{aligned} \tag{814}$$

with:

$$\theta = \tan^{-1} \left(\frac{b}{a} \right) \tag{815}$$

and the $\tan^{-1}$ function is understood to actually be the **atan2** function.³³ So we can continue with:

$$\begin{aligned}
&= \Re \left\{ \exp(ix) \left[\sqrt{(A_1 \cos \phi_1 \pm A_2 \cos \phi_2)^2 + (A_1 \sin \phi_1 \pm A_2 \sin \phi_2)^2} \times \right. \right. \\
&\quad \left. \left. \exp \left(i \left(\tan^{-1} \left(\frac{A_1 \sin \phi_1 \pm A_2 \sin \phi_2}{A_1 \cos \phi_1 \pm A_2 \cos \phi_2} \right) \right) \right) \right] \right\}
\end{aligned}$$

Now perform the multiplication of the two exponentials:

$$\begin{aligned}
&= \Re \left\{ \left[\sqrt{(A_1 \cos \phi_1 \pm A_2 \cos \phi_2)^2 + (A_1 \sin \phi_1 \pm A_2 \sin \phi_2)^2} \times \right. \right. \\
&\quad \left. \left. \exp \left(i \left(x + \tan^{-1} \left(\frac{A_1 \sin \phi_1 \pm A_2 \sin \phi_2}{A_1 \cos \phi_1 \pm A_2 \cos \phi_2} \right) \right) \right) \right] \right\}
\end{aligned}$$

We are done, because applying once again Euler identity and taking the real part we get the final result:

$$A_1 \cos(x + \phi_1) \pm A_2 \cos(x + \phi_2) =$$

$$\sqrt{(A_1 \cos \phi_1 \pm A_2 \cos \phi_2)^2 + (A_1 \sin \phi_1 \pm A_2 \sin \phi_2)^2} \cos \left(x + \tan^{-1} \left(\frac{A_1 \sin \phi_1 \pm A_2 \sin \phi_2}{A_1 \cos \phi_1 \pm A_2 \cos \phi_2} \right) \right)$$

In exactly the same way it is easy to derive the result for the sum of two sine plane waves:

$$A_1 \sin(\vec{k} \cdot \vec{r} - \omega t + \phi_1) \pm A_2 \sin(\vec{k} \cdot \vec{r} - \omega t + \phi_2)$$

or any “mixed” sum:

$$A_1 \cos(\vec{k} \cdot \vec{r} - \omega t + \phi_1) \pm A_2 \sin(\vec{k} \cdot \vec{r} - \omega t + \phi_2)$$

once we realize that:

$$A_2 \sin(\vec{k} \cdot \vec{r} - \omega t + \phi_2) = A_2 \cos\left(\vec{k} \cdot \vec{r} - \omega t + \phi_2 - \frac{\pi}{2}\right)$$

Challenge: if you can derive the same result without making resort to complex exponentials let me know.

And this is a minimal **gnuplot** script to verify that the final result is correct.

```

reset
# start of parameter definitions
A1=1.
A2=2.
Phi1=pi/3.
Phi2=0.9*pi
# end of parameter definitions

# this is the original sum of PWs
func1(x)=A1*cos(x+Phi1)+A2*cos(x+Phi2)

# evaluation of the obtained single PW
c1=A1*cos(Phi1)
c2=A2*cos(Phi2)
c3=(c1+c2)**2.

s1=A1*sin(Phi1)
s2=A2*sin(Phi2)
s3=(s1+s2)**2.

f=sqrt(c3+s3)

tan=atan2((s1+s2),(c1+c2))

# this is the single PW
func2(x)=f*cos(x+tan)

set terminal wxt

# the original sum of two PWs is plotted with a full line
# the equivalent single PW is plotted with points
plot func1(x),func2(x) with points pointtype 7

```

2 La struttura dei solidi cristallini

2.1 Dimostrazione che tutte le celle primitive dello stesso reticolo di Bravais hanno lo stesso volume

439. Per iniziare e' opportuno introdurre una notazione piu' concisa, ma piu' comoda da un punto di vista strettamente matematico.

Raggruppiamo i tre vettori primitivi $\vec{a}_1, \vec{a}_2, \vec{a}_3$ che generano un certo reticolo di Bravais $\mathcal{R}$ come colonne di una matrice $\mathbf{A}$:

$$\mathbf{A} = (\vec{a}_1 \ \vec{a}_2 \ \vec{a}_3) \quad (816)$$

Con questa notazione, il reticolo di Bravais $\mathcal{R}(\mathbf{A})$ generato dalla matrice $\mathbf{A}$ e' definito da:

$$\mathcal{R}(\mathbf{A}) = \{\mathbf{A} \cdot \vec{n}^T, \vec{n} \in \mathbb{Z}^3\} \quad (817)$$

con:

$$\vec{n}^T = (n_1 \ n_2 \ n_3)^T = \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} \quad (818)$$

Realizzate che la definizione 817 e' identica alla 139, solo scritta in matematiche un po' piu' stretto.

440. Al punto 89 abbiamo visto che il volume della cella primitiva individuata dai tre vettori $\vec{a}_1, \vec{a}_2, \vec{a}_3$ e' dato da:

$$|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| \quad (819)$$

Inoltre, come gia' detto nella sezione 1.3, e' facile verificare che:

$$\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = \det(\vec{a}_1 \ \vec{a}_2 \ \vec{a}_3) \quad (820)$$

per cui possiamo dire che il volume della cella primitiva determinata dalla matrice $\mathbf{A}$ e' dato da:

$$V_{\mathbf{A}} = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| = |\det(\vec{a}_1 \ \vec{a}_2 \ \vec{a}_3)| = |\det \mathbf{A}| \quad (821)$$

441. Quindi, per dimostrare che tutte le celle primitive hanno lo stesso volume, prese due terne qualsiasi $\vec{a}_1, \vec{a}_2, \vec{a}_3$ e $\vec{a}'_1, \vec{a}'_2, \vec{a}'_3$ di vettori primitivi che generano *lo stesso* reticolo di Bravais, basta dimostrare:

$$|\det \mathbf{A}| = |\det \mathbf{A}'| \quad (822)$$

dove $\mathbf{A}$ e $\mathbf{A}'$ sono le matrici costruite con le due terne di vettori primitivi come detto al punto 439. Arriveremo alla dimostrazione della 822 attraverso una sequenza di passi successivi.

442. Il primo e' l'introduzione della nozione di *matrice unimodulare*.

Definizione. Una matrice quadrata $\mathbf{U}$ si dice unimodulare se:

$$\det \mathbf{U} = \pm 1 \quad (823)$$

Ecco alcuni esempi di matrici unimodulari:

$$\begin{pmatrix} 7 & 2 \\ 3 & 1 \end{pmatrix} \quad \begin{pmatrix} 6 & 12 \\ \frac{1}{3} & \frac{1}{2} \end{pmatrix} \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & -1 \\ 1 & 1 & 0 \end{pmatrix} \quad \begin{pmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{pmatrix}$$

$$\begin{pmatrix} 8n^2 + 8n & 2n + 1 & 4n \\ 4n^2 + 4n & n + 1 & 2n + 1 \\ 4n^2 + 4n + 1 & n & 2n - 1 \end{pmatrix}, \quad n \in \mathbb{Z}$$

443. Per le matrici unimodulari vale la seguente proprieta'.

Proprieta'. Se $\mathbf{U}$ e' unimodulare e costituita da numeri interi (cioe' $\mathbf{U} \in \mathbb{Z}^{n \times n}$), allora anche $\mathbf{U}^{-1}$ e' unimodulare e $\mathbf{U}^{-1} \in \mathbb{Z}^{n \times n}$

Per provare che $\mathbf{U}^{-1}$ e' composta da numeri interi (intendo, come sempre, numeri relativi, $\in \mathbb{Z}$) dovete ricordare che, in generale, la matrice inversa di $\mathbf{U}$ e' data da:

$$\mathbf{U}^{-1} = \frac{\mathbf{U}^\dagger}{\det \mathbf{U}} \quad (824)$$

dove $\mathbf{U}^\dagger$ e' la *matrice aggiunta* di $\mathbf{U}$. La matrice aggiunta, a sua volta, e' definita come la trasposta della matrice dei *cofattori* di $\mathbf{U}$. Infine, i cofattori di una matrice sono i suoi minori con segno, cioe' il cofattore m_{ij} di $\mathbf{U}$ e' il determinate della matrice che si ottiene sopprimendo la riga i e la colonna j di $\mathbf{U}$, col segno $(-1)^{(i+j)}$.

Ora: dalla definizione di determinante:

$$\det \mathbf{U} = \sum_{\sigma} \operatorname{sgn}(\sigma) u_{1j_1} u_{2j_2} \dots u_{nj_n} \quad (825)$$

dove la somma e' fatta su tutte le permutazioni $\sigma = \{j_1 j_2 j_3 \dots j_n\}$ dell'insieme $\{1 2 3 \dots n\}$ e $\operatorname{sgn}(\sigma) = (-1)^{\text{parita' della permutazione}}$, e' banale realizzare che il determinante di una matrice di numeri interi e' sempre un numero intero ($\in \mathbb{Z}$) (perche' e' la somma di prodotti di numeri interi).

Ma allora e' provato che $\mathbf{U}^{-1}$ e' costituita da numeri interi perche' al numeratore della 824 c'e' una matrice, $\mathbf{U}^\dagger$, costituita da numeri interi (perche' i suoi elementi sono determinanti di matrici intere: i cofattori di $\mathbf{U} \in \mathbb{Z}^{n \times n}$) e al denominatore c'e' ± 1 ($\mathbf{U}$ e' unimodulare per ipotesi).

Infine, per provare che $\mathbf{U}^{-1}$ e' unimodulare basta osservare che:

$$\mathbf{U}^{-1} \mathbf{U} = \mathbf{I} \quad (826)$$

$$\det(\mathbf{U}^{-1} \mathbf{U}) = \det \mathbf{U}^{-1} \det \mathbf{U} = \det \mathbf{I} = 1 \quad (827)$$

$$\det \mathbf{U}^{-1} = \frac{1}{\det \mathbf{U}} = \pm 1$$

444. Ora siamo nella posizione di provare un utile teorema che riguarda l'equivalenza di due terne di vettori primitivi.

Teorema. Le due matrici:

$$\mathbf{A} = (\vec{a}_1 \vec{a}_2 \vec{a}_3) \quad (828)$$

$$\mathbf{A}' = (\vec{a}'_1 \vec{a}'_2 \vec{a}'_3) \quad (829)$$

le cui colonne sono costituite da vettori linearmente indipendenti generano lo stesso reticolo di Bravais se e solo se esiste una matrice unimodulare $\mathbf{U} \in \mathbb{Z}^{3 \times 3}$ tale che:

$$\mathbf{A} = \mathbf{A}' \mathbf{U} \quad (830)$$

In matematica:

$$\mathcal{R}(\mathbf{A}) = \mathcal{R}(\mathbf{A}') \iff \exists \mathbf{U} : \mathbf{A} = \mathbf{A}' \mathbf{U}, \mathbf{U} \in \mathbb{Z}^{3 \times 3}, \det \mathbf{U} = \pm 1 \quad (831)$$

Per provare l'implicazione verso destra ($\implies$) si procede nel modo seguente.

Siccome $\mathbf{A}$ e $\mathbf{A}'$ generano lo stesso reticolo per ipotesi, i vettori $\vec{a}_i$ che costituiscono le colonne di $\mathbf{A}$ possono essere espressi come combinazione lineare con coefficienti interi dei vettori primitivi che costituiscono le colonne di $\mathbf{A}'$:

$$\mathcal{R}(\mathbf{A}) = \mathcal{R}(\mathbf{A}') \implies \exists \vec{n}_i \in \mathbb{Z}^3 : \vec{a}_i = \mathbf{A}' \vec{n}_i^T, i = 1, 2, 3 \quad (832)$$

Ma questo significa che l'intera matrice $\mathbf{A}$ puo' essere scritta come:

$$\mathbf{A} = \mathbf{A}' (\vec{n}_1^T \vec{n}_2^T \vec{n}_3^T) = \mathbf{A}' \mathbf{U}, \text{ con } \mathbf{U} \in \mathbb{Z}^{3 \times 3} \quad (833)$$

e questo prova la prima parte della tesi, cioè $\mathbf{U} \in \mathbb{Z}^{3 \times 3}$ ($\mathbf{U}$ e' una matrice di numeri interi).

Resta da provare che $\mathbf{U}$ e' unimodulare.

In modo speculare a quanto appena visto ed esattamente per lo stesso motivo, possiamo dire che i vettori $\vec{a}'_i$ che costituiscono le colonne di $\mathbf{A}'$ possono essere espressi come combinazione lineare con coefficienti interi dei vettori primitivi che costituiscono le colonne di $\mathbf{A}$:

$$\mathcal{R}(\mathbf{A}) = \mathcal{R}(\mathbf{A}') \implies \exists \vec{m}_i \in \mathbb{Z}^3 : \vec{a}'_i = \mathbf{A} \vec{m}_i^T, \quad i = 1, 2, 3 \quad (834)$$

ovvero:

$$\mathbf{A}' = \mathbf{A} \begin{pmatrix} \vec{m}_1^T & \vec{m}_2^T & \vec{m}_3^T \end{pmatrix} = \mathbf{A} \mathbf{V}, \quad \text{con } \mathbf{V} \in \mathbb{Z}^{3 \times 3} \quad (835)$$

Combinando le 833 e 835 si ha:

$$\mathbf{A} = \mathbf{A}' \mathbf{U} = \mathbf{A} \mathbf{V} \mathbf{U} \quad (836)$$

Siccome le colonne di $\mathbf{A}$ sono linearmente indipendenti, abbiamo la garanzia dell'esistenza di $\mathbf{A}^{-1}$. Quindi:

$$\mathbf{A} = \mathbf{A} \mathbf{V} \mathbf{U} \iff \mathbf{A}^{-1} \mathbf{A} = \mathbf{V} \mathbf{U} \iff \mathbf{I} = \mathbf{V} \mathbf{U} \quad (837)$$

da cui vediamo che:

$$\mathbf{V} = \mathbf{U}^{-1} \quad (838)$$

ovvero:

$$\det \mathbf{U} = \frac{1}{\det \mathbf{U}^{-1}} = \frac{1}{\det \mathbf{V}} \quad (839)$$

Sia $\mathbf{U}$ che $\mathbf{V}$ sono matrici intere e quindi, in base a quanto detto al punto 443, il loro determinante deve essere intero. Ma allora dalla 839 segue che deve essere:

$$\det \mathbf{U} = \det \mathbf{V} = \pm 1 \quad (840)$$

ovvero $\mathbf{U}$ e' unimodulare.

La prova dell'implicazione verso sinistra ($\Leftarrow$) si ottiene nel modo seguente. Supponiamo che sia:

$$\mathbf{A} = \mathbf{A}' \mathbf{U} \quad (841)$$

Detto $\vec{v}$ un generico vettore del reticolo $\mathcal{R}(\mathbf{A})$ generato da $\mathbf{A}$, per definizione di reticolo di Bravais (equazione 817) deve esistere un opportuno vettore intero $\vec{n} \in \mathbb{Z}^3$ tale che:

$$\vec{v} = \mathbf{A} \vec{n}^T \quad (842)$$

Ma per ipotesi si ha anche:

$$\vec{v} = \mathbf{A} \vec{n}^T = \mathbf{A}' \mathbf{U} \vec{n}^T = \mathbf{A}' \vec{m}^T, \quad \vec{m} \in \mathbb{Z}^3 \quad (843)$$

perche' $\vec{n} \in \mathbb{Z}^3$ e $\mathbf{U} \in \mathbb{Z}^{3 \times 3}$. Quindi tutti i vettori di $\mathcal{R}(\mathbf{A})$ sono anche vettori di $\mathcal{R}(\mathbf{A}')$, ovvero:

$$\mathcal{R}(\mathbf{A}) \subseteq \mathcal{R}(\mathbf{A}') \quad (844)$$

D'altro canto:

$$\mathbf{A} = \mathbf{A}'\mathbf{U} \implies \mathbf{A}' = \mathbf{A}\mathbf{U}^{-1} \quad (845)$$

con:

$$\mathbf{U}^{-1} \in \mathbb{Z}^{3 \times 3} \quad (846)$$

per la proprieta' vista al punto 443.

E allora, preso un generico vettore di $\mathcal{R}(\mathbf{A}')$, si puo' ripetere il ragionamento appena fatto sopra per giungere a:

$$\mathcal{R}(\mathbf{A}') \subseteq \mathcal{R}(\mathbf{A}) \quad (847)$$

e quindi:

$$\mathcal{R}(\mathbf{A}) \subseteq \mathcal{R}(\mathbf{A}'), \mathcal{R}(\mathbf{A}') \subseteq \mathcal{R}(\mathbf{A}) \implies \mathcal{R}(\mathbf{A}) = \mathcal{R}(\mathbf{A}') \quad (848)$$

445. E arriviamo infine alla dimostrazione di cio' che e' lo scopo di questa sezione, e cioe' che tutte le celle primitive dello stesso reticolo di Bravais hanno lo stesso volume.

Dato un certo reticolo di Bravais, consideriamo due qualsiasi celle primitive rappresentate dalle matrici $\mathbf{A}$ e $\mathbf{A}'$. Per il teorema visto al punto 444, le due matrici sono legate da:

$$\mathbf{A} = \mathbf{A}'\mathbf{U}, \quad \mathbf{U} \in \mathbb{Z}^{3 \times 3}, \quad \det \mathbf{U} = \pm 1 \quad (849)$$

E allora:

$$|\det \mathbf{A}| = |\det(\mathbf{A}'\mathbf{U})| = |\det \mathbf{A}'| |\det \mathbf{U}| = |\det \mathbf{A}'| \quad (850)$$

ovvero le due celle primitive hanno lo stesso volume (eq. 822); e siccome le due celle erano qualsiasi, questo deve valere per tutte le celle primitive del reticolo dato.

2.2 Reason why eq. 316 cannot hold

446. The reason why eq. 316 cannot be true is that, given the plane wave:

$$\exp(i\vec{k}' \cdot \vec{r}) \quad (851)$$

there cannot exist any wave front with isovalue $v : |v| = 1$ (that is: such that $\exp(i\vec{k}' \cdot \vec{r}) = \pm 1$) in between two *consecutive* wave fronts with the same isovalue.

The simplest way to realize this is to consider the graphical representation of the wave on a plane containing the propagation direction (that is the direction of $\vec{k}'$) as a function of the projection $r_{\parallel}$ of $\vec{r}$ along $\vec{k}'$ (please: review section 1.4.4.2):

$$\cos(k'r_{\parallel}) = \Re\left(\exp(i\vec{k}' \cdot \vec{r})\right) = \Re(\exp(ik'r_{\parallel})) \quad (852)$$

This is shown in figure 104, from which it should be clear that, when the isovalue of two consecutive wave fronts is 1, no other wave fronts with the same isovalue can be found in between.

Of course, the same holds for consecutive wave fronts with isovalue -1 .

447. Note that the above remark does hold only for wave fronts with isovalue $|v| = 1$; it does *not* hold for wave fronts with isovalue $|v| < 1$, as shown in figure 105.

448. This same fact can be viewed also in a more formal way.

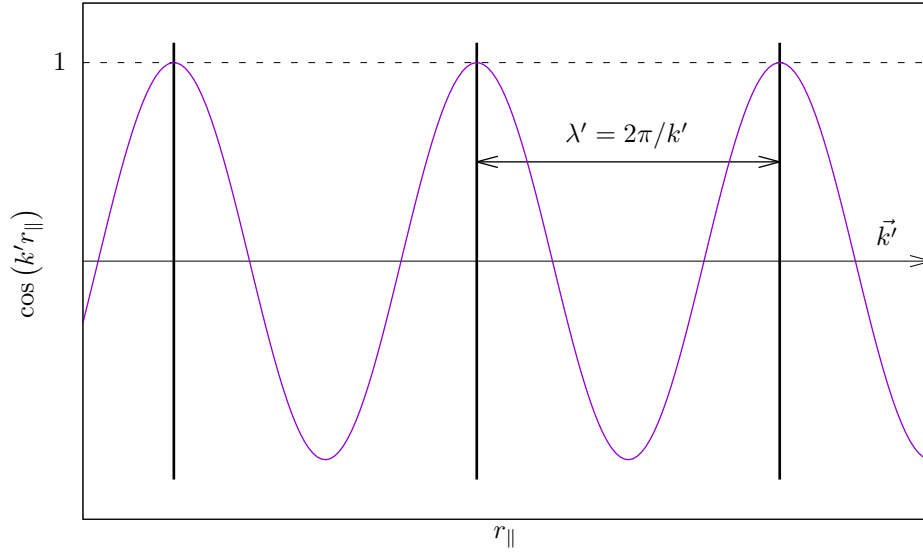


Figure 104: The function $\exp(i\vec{k}' \cdot \vec{r})$ is the complex exponential representation of the plane wave (actually, only the spatial part):

$$\cos(\vec{k}' \cdot \vec{r})$$

This figure shows its graph on a plane containing the propagation direction (that is the direction of $\vec{k}'$) as a function of the projection $r_{\parallel}$ of $\vec{r}$ along $\vec{k}'$, as explained in section 1.4.4.2. The three vertical lines are the projections on the same plane of three consecutive wave fronts (equispaced at a distance equal to the wave length $\lambda' = 2\pi/k'$) on which the wave takes the unit value. From the graph it is unequivocally evident that for no $r_{\parallel}$ value within the interval between two consecutive wave fronts can the wave take again a unit value.

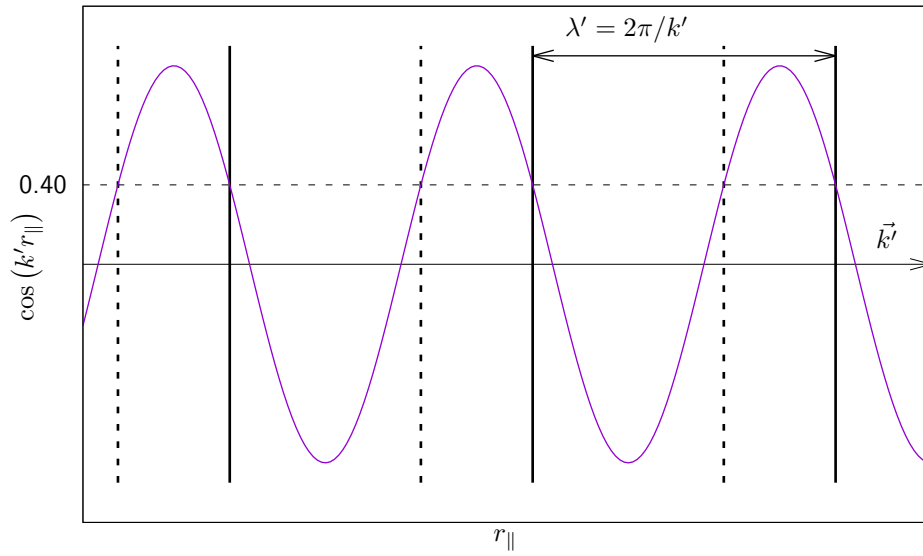


Figure 105: This is the same as figure 104 (see the caption of that figure for general explanation), but now the isovalue of the wave fronts (vertical solid lines) is 0.40. Call $\mathcal{S}$ the set of these wave fronts. In this case (and, in general, when the isovalue of the wave fronts is $v : |v| < 1$) there is *always* a wave front ($\notin \mathcal{S}$) on which the wave takes the same isovalue in between any two consecutive wave fronts of $\mathcal{S}$: see the dashed vertical lines. The value taken by the wave on these “extra” wave fronts is the same, but the phase of the wave is different from that corresponding to the wave fronts of $\mathcal{S}$.

The function $\exp\left(i\vec{k}' \cdot \vec{r}\right)$ is the complex exponential representation of the plane wave (actually, only the spatial part):

$$\cos\left(\vec{k}' \cdot \vec{r}\right) \quad (853)$$

The phase of the wave is:

$$\Phi = \vec{k}' \cdot \vec{r} \quad (854)$$

Call $\mathcal{S}_v$ the set of wave wave fronts Π_j

- a. on which the wave takes a given value v :

$$\cos\left(\vec{k}' \cdot \vec{r}\right) = v \quad (855)$$

- b. whose phases differ by an integer multiple of 2π :

$$\Phi_i - \Phi_k = 2\pi n, \quad n \in \mathbb{Z}, \quad \forall \vec{r} \in \Pi_i \quad \forall \vec{r} \in \Pi_k \quad (856)$$

$$\mathcal{S}_v = \left\{ \Pi_j : \cos\left(\vec{k}' \cdot \vec{r}\right) = v \quad \forall \vec{r} \in \Pi_j, \quad \Phi_i - \Phi_k = 2\pi n, \quad n \in \mathbb{Z}, \quad \forall \vec{r} \in \Pi_i \quad \forall \vec{r} \in \Pi_k \right\} \quad (857)$$

There are two possible cases.

1. $|v| = 1$, that is $v = \pm 1$

In this case, the equation:

$$\cos\left(\vec{k}' \cdot \vec{r}\right) = v \quad (858)$$

has a single (infinite) set of solutions:

$$\Phi = \arccos(v) + 2\pi n, \quad n \in \mathbb{Z} \quad (859)$$

Which means that there is a single $\mathcal{S}_v$ set of wave fronts satisfying the two above conditions and thus there cannot be any wave front with isovalue v in between any two consecutive wave fronts of $\mathcal{S}_v$.

This is the case shown in figure 104.

2. $|v| < 1$, that is $-1 < v < 1$

In this case, the equation:

$$\cos\left(\vec{k}' \cdot \vec{r}\right) = v \quad (860)$$

has *two* distinct sets of (infinite) solutions:

$$\begin{aligned} \Phi^\alpha &= \arccos(v) + 2\pi n, \quad n \in \mathbb{Z} \\ \Phi^\beta &= -\arccos(v) + 2\pi n, \quad n \in \mathbb{Z} \end{aligned}$$

with:

$$|(\Phi^\alpha \bmod 2\pi) - (\Phi^\beta \bmod 2\pi)| < 2\pi \quad (861)$$

(($\Phi^\alpha \bmod 2\pi$) means “ $\Phi^\alpha \bmod 2\pi$ ”, that is, in our case, $\arccos(v)$)

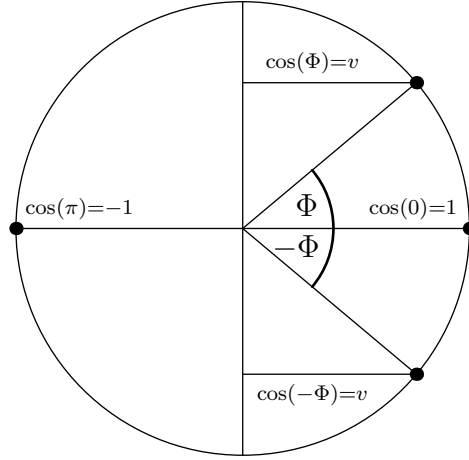
and thus there will be *two* distinct $\mathcal{S}_v$ sets:

$$\begin{aligned} \mathcal{S}_v^\alpha &= \left\{ \Pi_j^\alpha : \cos(\vec{k}' \cdot \vec{r}) = v \ \forall \vec{r} \in \Pi_j^\alpha, \ \Phi_i^\alpha - \Phi_k^\alpha = 2\pi n, \ n \in \mathbb{Z}, \ \forall \vec{r} \in \Pi_i^\alpha \ \forall \vec{r} \in \Pi_k^\alpha \right\} \\ \mathcal{S}_v^\beta &= \left\{ \Pi_j^\beta : \cos(\vec{k}' \cdot \vec{r}) = v \ \forall \vec{r} \in \Pi_j^\beta, \ \Phi_i^\beta - \Phi_k^\beta = 2\pi n, \ n \in \mathbb{Z}, \ \forall \vec{r} \in \Pi_i^\beta \ \forall \vec{r} \in \Pi_k^\beta \right\} \end{aligned}$$

Each wave front of $\mathcal{S}_v^\alpha$ is in between two consecutive wave fronts of $\mathcal{S}_v^\beta$, and viceversa; or, equivalently, the two sequences of wave fronts are shifted with respect to each other by an amount $< 2\pi$.

This is the case shown in figure 105.

449. Basically, all this boils down to realize that on the trigonometric circle there is a *single* point where the cos function takes the value 1, a *single* point where it takes the value -1 , but always *two* points where it takes a value $v : |v| < 1$:



3 Il modello del gas di Fermi

3.1 Perche' il potenziale chimico del gas di Fermi non puo' essere nullo a $T = 0$ K?

Per quanto visto al punto 236:

$$\mu = F_{N+1} - F_N \quad (862)$$

e, a $T = 0$ K:

$$F = U - TS = U \quad (863)$$

L'energia interna del gas di Fermi U non e' altro che la somma delle energie degli stati monoelettronici occupati:

$$U_N = \epsilon_1 + \epsilon_2 + \cdots + \epsilon_N = \sum_1^N \epsilon_i$$

$$U_{N+1} = \epsilon_1 + \epsilon_2 + \cdots + \epsilon_N + \epsilon_{N+1} = \sum_1^{N+1} \epsilon_i$$

Quindi:

$$\mu = F_{N+1} - F_N = U_{N+1} - U_N = \sum_1^{N+1} \epsilon_i - \sum_1^N \epsilon_i = \epsilon_{N+1} \quad (864)$$

dove, chiaramente, ϵ_{N+1} non e' altro che l'energia di Fermi per il sistema di $N + 1$ elettroni; siccome il numero di elettroni e' considerato enorme e l'energia del livello piu' basso e' nulla, ϵ_{N+1} sara' senz'altro > 0 (assumendo che il livello piu' basso non abbia un grado di degenerazione dell'ordine del numero di Avogadro!).

3.2 Densita' degli stati dal gradiente della relazione di dispersione

450. Un'altra espressione (equivalente) per la densita' degli stati, quando, come spesso succede, non si dispone di un'espressione analitica per $N(\epsilon)$, puo' essere ottenuta nel modo seguente. Dalla definizione 473 abbiamo:

$$g(\epsilon) d\epsilon = \frac{1}{V} dN(\epsilon) \quad (865)$$

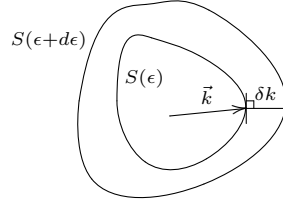
$dN(\epsilon)$ e' il numero di stati permessi nel range di energia compreso fra ϵ e $\epsilon + d\epsilon$.

Come ora vedremo, e' possibile ricavare un'espressione piuttosto generale per $dN(\epsilon)$: uguagliando tale espressione a $g(\epsilon) d\epsilon$ sara' poi possibile ottenere la corrispondente espressione per $g(\epsilon)$.

451. Abbiamo visto che per un gas di elettroni di Fermi in un campione cubico ci sono delle superfici sferiche nello spazio $\vec{k}$ tali che tutti i punti su di esse individuano stati elettronici alla stessa energia (degeneri).

In generale, per un campione qualunque (non cubico) e, come vedremo, anche per il caso in cui gli elettroni non siano (completamente) liberi (cioe' risentano di un potenziale dovuto alla presenza dei nuclei), ci sono ancora delle superfici isoenergetiche nello spazio $\vec{k}$, ma questa volta non sono delle semplici sfere, bensì delle superfici qualunque.

452. Consideriamo allora due di queste superfici isoenergetiche nello spazio $\vec{k}$ a energie ϵ ed $\epsilon + d\epsilon$ (nella figura di seguito e' mostrata la loro proiezione sul piano):



In modo simile a quanto abbiamo fatto per ricavare la forma analitica di $N(\epsilon)$ per il gas di elettroni di Fermi in un campione cubico, detto δV il volume di spazio $\vec{k}$ compreso fra le due superfici isoenergetiche, dovra' essere:

$$dN(\epsilon) = \frac{\delta V}{\left[\text{volume di una cella primitiva contenente un sin-} \right.} \quad (866)$$

$$\left. \text{golo punto } \vec{k} \right]$$

Come abbiamo visto in generale (eq. 294) e anche al punto 217, il volume della cella primitiva dello spazio $\vec{k}$ e' $8\pi^3/V$; quindi l'espressione per $dN(\epsilon)$ puo' essere riscritta come:

$$dN(\epsilon) = \frac{\delta V}{\frac{8\pi^3}{V}} = \frac{V}{8\pi^3} \delta V \quad (867)$$

Vediamo ora come possiamo esprimere δV , il volume compreso fra le due superfici isoenergetiche. Detto $d\vec{k}$ un elemento infinitesimo di volume dello spazio $\vec{k}$, dovra' chiaramente essere:

$$\delta V = \int_{\delta V} d\vec{k} \quad (868)$$

Ora: prendiamo il volume infinitesimo $d\vec{k}$ usato per l'integrazione come un "cilindretto" infinitesimo avente per base un elemento infinitesimo dS della superficie interna $S(\epsilon)$ e per altezza la distanza δk , misurata perpendicolarmente rispetto alla superficie $S(\epsilon)$, fra le due superfici isoenergetiche (guardate la figura):

$$d\vec{k} = \delta k dS \quad (869)$$

δk e' normale in ogni punto alla superficie $S(\epsilon)$ e dipende da $\vec{k}$, cioe' dal particolare punto di $S(\epsilon)$ in cui ci troviamo (perche' le due superfici sono di forma qualunque).

Quindi, a questo punto, l'integrale calcolato sul volume δV puo' essere sostituito da un integrale calcolato sulla superficie $S(\epsilon)$ in cui il differenziale per l'integrazione e' l'elemento infinitesimo di superficie dS :

$$\delta V = \int_{\delta V} d\vec{k} = \int_{S(\epsilon)} \delta k_{\vec{k}} dS \quad (870)$$

(con $\delta k_{\vec{k}}$ ho sottolineato che δk dipende da $\vec{k}$)

Ora esprimiamo $\delta k_{\vec{k}}$ in funzione di $d\epsilon$ nel modo seguente.

Sappiamo che, in termini del tutto generali, l'energia degli stati di un sistema solido e' funzione della posizione nello spazio $\vec{k}$, cioe':

$$\epsilon = \epsilon(\vec{k}) = \epsilon(k_x, k_y, k_z) \quad (871)$$

ϵ e' una funzione di tre variabili.

Consideriamo il gradiente di tale funzione: $\vec{\nabla}\epsilon(\vec{k})$.

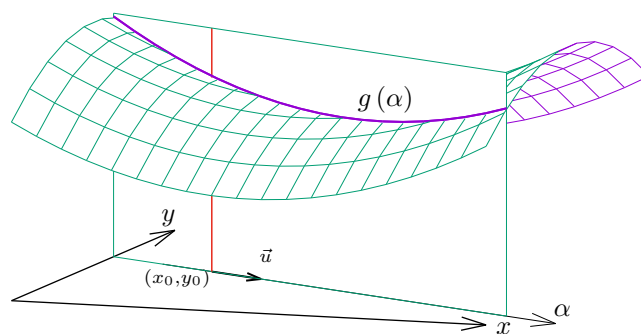


Figure 106: La derivata direzionale di una funzione di due variabili $f(x, y)$ nel punto x_0, y_0 e nella direzione individuata dal vettore $\vec{u}$ e' la derivata della funzione *della sola variabile* che rappresenta la distanza lungo l'asse passante per il punto x_0, y_0 e avente la direzione di $\vec{u}$ e il cui grafico e' la traccia ottenuta sezionando il grafico della $f(x, y)$ con un piano ortogonale al piano xy e contenente il vettore $\vec{u}$.

3.2.1 Breve richiamo sul gradiente di una funzione

453. Per una funzione scalare di tre coordinate $f(\vec{r}) = f(x, y, z)$ il gradiente e' il vettore le cui componenti cartesiane sono le derivate parziali della funzione rispetto alle tre coordinate:

$$\vec{\nabla} f = \hat{x} \frac{\partial f}{\partial x} + \hat{y} \frac{\partial f}{\partial y} + \hat{z} \frac{\partial f}{\partial z} \quad (872)$$

dove $\hat{x}$, $\hat{y}$ e $\hat{z}$ sono i versori (vettori di modulo unitario) nella direzione dei tre assi cartesiani.

454. Il prodotto scalare del gradiente della funzione $f(x, y, z)$ e di un vettore $\vec{u}$ in una direzione arbitraria fornisce la *derivata direzionale* della funzione, cioe' la variazione della funzione *per unita' di spostamento nella direzione di $\vec{u}$* :

$$D_{f, \vec{u}} = \vec{\nabla} f \cdot \vec{u} \quad (873)$$

455. Il significato "concreto" della derivata direzionale e' mostrato nella figura 106 per una funzione di due sole variabili $f(x, y)$ (per la quale e' possibile disegnare il grafico). In pratica: sezionate il grafico della f con un piano ortogonale al piano xy e contenente il vettore $\vec{u}$, quest'ultimo uscente dal punto x_0, y_0 in cui si vuole calcolare la derivata direzionale. La traccia che il grafico della f lascia su tale piano e' il grafico di una funzione $g(\alpha)$ della sola variabile α che rappresenta la distanza misurata (rispetto a un'origine che puo' essere fissata arbitrariamente) lungo la direzione di $\vec{u}$; la derivata direzionale della $f(x, y)$ nel punto x_0, y_0 coincide con la derivata della $g(\alpha)$ fatta rispetto ad α e calcolata per il valore di α che corrisponde al punto x_0, y_0 . Se vi interessa, ho inserito una spiegazione un po' piu' formale di questo aspetto nella sezione 3.3 della parte fuori programma.

456. In pratica, la derivata direzionale rispetto a un vettore $\vec{u}$ e' la generalizzazione ad una direzione qualsiasi di cio' che rappresentano le tre derivate parziali rispetto a x, y, z .

457. Alcune proprieta' del gradiente di cui faremo uso sono:

1. Il gradiente della funzione $f(x, y, z)$ si annulla nei punti di massimo o minimo e nei punti di sella. Questo segue banalmente dal fatto che in un punto di massimo o minimo o in un punto di sella le derivate parziali della f sono tutte nulle.

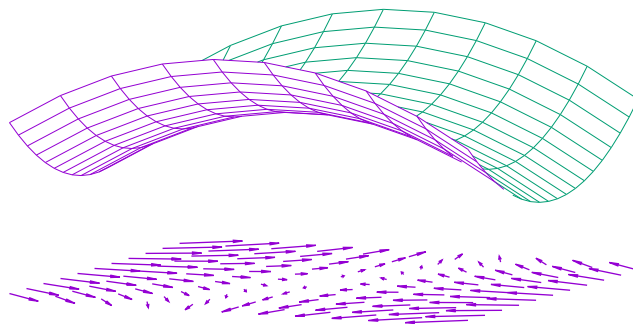


Figure 107: Il gradiente della funzione $f(x, y) = x^2 - y^2$ in un intorno del punto di sella.

2. In un certo punto dello spazio (x, y, z) , il gradiente della funzione $f(x, y, z)$ e' orientato *nella direzione di massimo incremento* della funzione e il suo modulo, $|\vec{\nabla} f|$, e' uguale *alla variazione della funzione per unita' di spostamento* (nel punto (x, y, z) e nella direzione del gradiente), cioe' la derivata direzionale della funzione nella direzione di $\vec{\nabla} f$. Cio' si puo' vedere in modo semplice. La derivata direzionale nella direzione di un arbitrario versore $\vec{u}$ e':

$$D_{f, \vec{u}} = \vec{\nabla} f \cdot \vec{u} = |\vec{\nabla} f| \cos \theta \quad (\text{il modulo di } \vec{u} \text{ e' unitario}) \quad (874)$$

La derivata direzionale (che e' la variazione della funzione per unita' di spostamento nella direzione di $\vec{u}$) assume il suo valore massimo positivo quando $\theta = 0$, cioe' quando $\vec{u}$ e' *nella stessa direzione del gradiente*; ma questo equivale a dire che il gradiente e' nella direzione del massimo incremento della funzione f . Inoltre, in queste condizioni, si ha:

$$D_{f, \vec{u}} = D_{f, \vec{\nabla} f} = |\vec{\nabla} f| \quad (875)$$

cioe' il modulo del gradiente e' uguale *alla variazione della funzione per unita' di spostamento* (nel punto (x, y, z) e nella direzione del gradiente)

Ho cercato di illustrare questa proprieta' del gradiente nella figura 107 dove e' mostrato il gradiente della funzione di due variabili $f(x, y) = x^2 - y^2$ in un intorno del punto di sella della funzione, localizzato a $(x, y) = (0, 0)$. Il gradiente della funzione:

$$\vec{\nabla} f = \hat{x}(2x) - \hat{y}(2y) = (2x, -2y) \quad (876)$$

e' calcolato su un griglia regolare di punti centrata sul punto di sella ed e' rappresentato dai vettori mostrati.

Dalla figura dovrebbe essere evidente che, in un certo punto del piano xy il gradiente e' sempre orientato nella direzione in cui si ha il massimo incremento della funzione. Inoltre il gradiente e' nullo nel punto di sella.

3. Il gradiente della funzione $f(x, y, z)$ e' normale in ogni punto ad una sua qualsiasi isosuperficie. Anche questa proprieta' e' giustificata facilmente.

Consideriamo un punto arbitrario P della isosuperficie e un versore $\vec{v}$ ad essa parallelo in P (cioe' tangente alla isosuperficie nel punto P). Per la derivata direzionale della funzione nel punto P rispetto al versore $\vec{v}$ deve valere:

$$D_{f,\vec{v}} = \vec{\nabla} f \cdot \vec{v} \quad (877)$$

Ma siccome $\vec{v}$ e' parallelo alla isosuperficie e il valore della funzione e' ovviamente costante su tutti i punti di essa, dovra' essere:

$$D_{f,\vec{v}} = 0 = \vec{\nabla} f \cdot \vec{v} \quad (878)$$

ovvero, $\vec{\nabla} f$ deve essere normale a $\vec{v}$, cioe' normale alla isosuperficie. E siccome P era stato scelto arbitrariamente, questo deve valere per qualsiasi punto della isosuperficie.

Chiusa parentesi.

458. Tornando alle due superfici isoenergetiche e al gradiente della funzione $\epsilon(\vec{k})$, alla luce di quanto ricordato sopra in generale riguardo al gradiente di una funzione, possiamo dire che:

- $\Rightarrow \vec{\nabla} \epsilon(\vec{k})$ e' normale a $S(\epsilon)$ in ogni suo punto (proprietà 3, p. 306) e quindi e' orientato nella stessa direzione di $\delta k_{\vec{k}}$
- $\Rightarrow$ la variazione $d\epsilon$ della funzione $\epsilon(\vec{k})$ nel passare dalla isosuperficie $S(\epsilon)$ a quella $S(\epsilon + d\epsilon)$ nella direzione del gradiente (che coincide col cammino lungo δk nella figura precedente) deve essere data da:

$$d\epsilon = \left| \vec{\nabla} \epsilon(\vec{k}) \right| \delta k_{\vec{k}} \quad (879)$$

cioe':

$$\underbrace{\left[\text{variaz. di } \epsilon(\vec{k}) \right]}_{d\epsilon} = \underbrace{\left[\text{variaz. di } \epsilon(\vec{k}) \text{ per unita' di spostamento nella direzione di } \delta k_{\vec{k}} \right]}_{\substack{\text{[spostamento]} \\ \delta k_{\vec{k}}}} \times \overbrace{\left| \vec{\nabla} \epsilon(\vec{k}) \right|}^{\text{(prop. 2, p. 306)}}$$

459. Notate che $d\epsilon$, essendo la variazione della funzione $\epsilon(\vec{k})$ nel passaggio da $S(\epsilon)$ a $S(\epsilon + d\epsilon)$, e' indipendente da $\vec{k}$, cioe' dal particolare punto considerato sulla isosuperficie $S(\epsilon)$ (quando si passa da un qualsiasi punto di $S(\epsilon)$ a un qualsiasi punto di $S(\epsilon + d\epsilon)$ la variazione subita dalla funzione $\epsilon(\vec{k})$ e' sempre la stessa, $d\epsilon$, per definizione di isosuperficie!). Al contrario, sia $\left| \vec{\nabla} \epsilon(\vec{k}) \right|$ che $\delta k_{\vec{k}}$ dipendono dal punto di $S(\epsilon)$ considerato, cioe' da $\vec{k}$: infatti, essendo le due isosuperfici di forma qualunque, $\left| \vec{\nabla} \epsilon(\vec{k}) \right|$ e $\delta k_{\vec{k}}$ devono variare in ogni punto di $S(\epsilon)$ proprio per fare in modo che il loro prodotto ($d\epsilon$) resti costante.

460. A questo punto possiamo ricavare $\delta k_{\vec{k}}$ dalla 879 e sostituire nell'integrale 870, facendo uso del fatto appena rimarcato sopra che $d\epsilon$ non dipende dal punto considerato sulla isosuperficie $S(\epsilon)$:

$$\delta V = \int_{S(\epsilon)} \frac{d\epsilon}{|\vec{\nabla}\epsilon(\vec{k})|} dS = d\epsilon \int_{S(\epsilon)} \frac{1}{|\vec{\nabla}\epsilon(\vec{k})|} dS \quad (880)$$

461. Infine, sostituendo δV nella 867 e riarrangiando otteniamo il risultato finale:

$$dN(\epsilon) = \frac{V}{8\pi^3} d\epsilon \int_{S(\epsilon)} \frac{1}{|\vec{\nabla}\epsilon(\vec{k})|} dS \quad (881)$$

$$g(\epsilon) = \frac{1}{V} \frac{dN(\epsilon)}{d\epsilon} = \frac{1}{8\pi^3} \int_{S(\epsilon)} \frac{1}{|\vec{\nabla}\epsilon(\vec{k})|} dS \quad (882)$$

462. Osservazioni.

- Anche in questo caso, come avevamo preannunciato a p. 158, vedete che $dN(\epsilon)/d\epsilon$ e' direttamente proporzionale al volume V del solido (eq. 881) e quindi ha senso definire la densita' degli stati normalizzandola rispetto al volume (eq. 882)
- Notate che la dipendenza di $g(\epsilon)$ da ϵ nell'eq. 882 sta nell'isovalore ϵ della superficie su cui viene calcolato l'integrale: cioe', la "ricetta" per calcolare la densita' degli stati g al valore di energia ϵ e': "(i) trova la isosuperficie il cui valore di energia costante e' ϵ ; (ii) calcola l'integrale dell'eq. 882 su tale superficie; (iii) il valore del secondo membro della 882 e' $g(\epsilon)$ ".
- Come gia' detto, quella ottenuta e' la densita' di punti $\vec{k}$ permessi; ad ogni punto $\vec{k}$ corrispondono 2 stati monoelettronici che differiscono per lo spin; quindi la densita' degli stati monoelettronici e' l'espressione scritta sopra, ma con un 4 al posto dell'8 (ad esempio l'eq. 8.63 del libro di Mermin e Ashcroft³⁴).
- Il risultato ottenuto mette in relazione la densita' degli stati con il gradiente (ovvero la rapidita' di variazione) della loro energia: la densita' degli stati e' alta nelle regioni dello spazio $\vec{k}$ dove l'energia degli stati permessi varia lentamente con $\vec{k}$, e viceversa.
- E' possibile che l'energia degli stati permessi attraversi punti di massimo o minimo nello spazio $\vec{k}$: in corrispondenza di tali punti il gradiente di $\epsilon(\vec{k})$ diventa nullo (proprietà 1, p. 305) e il valore dell'argomento dell'integrale nella 882 diventa infinito (si puo' comunque dimostrare che la presenza di un numero finito di questi punti singolari non pregiudica l'esistenza, in senso matematico, dell'integrale). Questo effetto e' osservabile come la comparsa di cuspidi (con una tangente verticale) nella densita' degli stati. Tali cuspidi possono essere osservate sperimentalmente e vengono dette *singularita' di Van Hove*.

3.2.2 Applicazione al gas di Fermi

463. L'eq. 882 puo' essere considerata la generalizzazione della 487 al caso in cui le superfici isoenergetiche non sono delle semplici sfere; va osservato che entrambe le espressioni si basano tuttavia sul calcolo approssimato del numero di stati $\vec{k}$ permessi come rapporto fra il volume di una regione dello spazio reciproco e il volume per singolo punto $\vec{k}$ (eq. 478 e 867, rispettivamente). Come vedremo, la natura discontinua della funzione $N(\epsilon)$ viene considerata in modo "naturale" nella terza definizione della densita' degli stati, che e' quella piu' rigorosa.

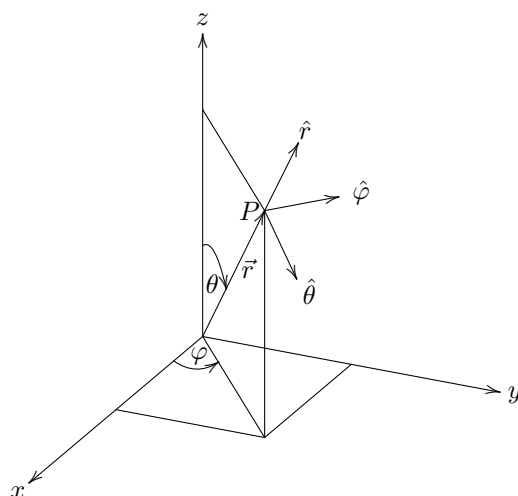


Figure 108: Coordinate sferiche.

Prima di discutere questa terza definizione, tuttavia, e' istruttivo verificare che l'equazione 882 si riduce alla 487 per un gas di Fermi confinato in un campione di forma cubica. In pratica, si tratta di risolvere l'integrale di superficie per questo particolare sistema. Sappiamo gia' che in questo caso le superfici isoenergetiche sono delle sfere concentric centrate nell'origine dello spazio $\vec{k}$:

$$\epsilon(\vec{k}) = \frac{\hbar^2}{2m} k^2$$

Data la simmetria delle superfici isoenergetiche, conviene usare coordinate sferiche.

3.2.3 Richiamo sulle coordinate sferiche

464. Le coordinate sferiche di un punto P nello spazio sono definite come (r, θ, φ) , dove (guardate la figura 108):

- r e' il modulo del vettore posizione $\vec{r}$ del punto P . Quindi: $0 \leq r \leq +\infty$
- θ e' l'angolo fra il vettore $\vec{r}$ e l'asse z positivo; per definizione: $0 \leq \theta \leq 180$. Questo angolo viene anche detto "angolo di zenith" o "angolo polare".
- φ e' l'angolo fra la proiezione del vettore $\vec{r}$ sul piano xy e l'asse x positivo, misurato in senso antiorario. Per definizione: $0 \leq \varphi \leq 360$. Questo angolo viene anche detto "angolo di azimuth" o "angolo equatoriale".

465. Le relazioni per la trasformazione fra coordinate cartesiane e sferiche sono (rendetene conto guardando la figura):

$$x = r \sin \theta \cos \varphi \quad (883)$$

$$y = r \sin \theta \sin \varphi \quad (884)$$

$$z = r \cos \theta \quad (885)$$

$$r = \sqrt{x^2 + y^2 + z^2} \quad (886)$$

$$\theta = \begin{cases} \arctan \frac{\sqrt{x^2+y^2}}{z} & \text{se } z > 0 \\ 180 - \arctan \frac{\sqrt{x^2+y^2}}{|z|} & \text{se } z < 0 \end{cases} \quad (887)$$

$$\varphi = \begin{cases} \arctan \frac{y}{x} & \text{se } x > 0, y > 0 \\ 360 - \arctan \frac{|y|}{x} & \text{se } x > 0, y < 0 \\ 180 - \arctan \frac{y}{|x|} & \text{se } x < 0, y > 0 \\ 180 + \arctan \frac{y}{x} & \text{se } x < 0, y < 0 \end{cases} \quad (888)$$

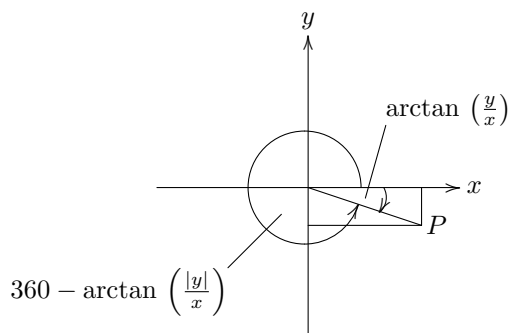
Notate come nelle espressioni per θ e φ si debbano distinguere diversi casi a seconda del segno di x e/o y e/o z ; cio' e' dovuto al fatto che, per definizioneⁱ, $0 \leq \theta \leq 180$ e $0 \leq \varphi \leq 360$.

Ad esempio, guardando la proiezione sul piano xy (figura in basso), se un punto P ha $x > 0$ e $y < 0$, allora per esso si avrebbe:

$$\varphi = \arctan \left(\frac{y}{x} \right) < 0 \quad (889)$$

cioe' $\varphi \notin [0, 360]$. Per avere il valore dell'angolo misurato in senso antiorario rispetto all'asse x positivo e interno all'intervallo $[0, 360]$, bisogna esprimerlo come:

$$\varphi = 360 - \left| \arctan \left(\frac{y}{x} \right) \right| = 360 - \arctan \left(\frac{|y|}{x} \right)$$



466. I versori di un sistema di coordinate sferiche sono $\hat{r}$, $\hat{\theta}$ e $\hat{\varphi}$ (guardate la figura 108). Come i versori cartesiani, essi sono una terna di vettori ortonormali (cioe' che hanno modulo unitario e sono mutuamente ortogonali) che costituiscono la base (nel senso dell'algebra lineare) rispetto a cui qualsiasi altro elemento (vettore) di $\mathbb{R}^3$ puo' essere espresso. La definizione dei tre versori e':

- $\hat{r}$ e' nella direzione di $\vec{r}$, orientato nel verso di un allontanamento dall'origine
- $\hat{\theta}$ e' normale a $\hat{r}$, giace nel piano definito da $\vec{r}$ e dall'asse z ed e' orientato nella direzione in cui θ aumenta (θ e' misurato rispetto all'asse z positivo)

ⁱIn realta' esistono molte convenzioni e definizioni diverse per le coordinate sferiche, e in particolare per la misura e l'intervallo di variazione degli angoli θ e φ

$\hat{\varphi}$ e' normale a $\hat{r}$ e $\hat{\theta}$ ed e' orientato nella direzione in cui φ (che e' misurato in senso antiorario rispetto all'asse x positivo) aumenta

Notate che, diversamente da quanto accade per un sistema cartesiano, $\hat{r}$, $\hat{\theta}$ e $\hat{\varphi}$ sono funzioni di $\vec{r}$, θ e φ : la loro orientazione (ma non il loro modulo) cambia con $\vec{r}$, θ e φ . Cio' e' ragionevole: i tre versori devono essere sempre ortogonali; quindi, se il punto dello spazio considerato cambia, anche il suo vettore posizione $\vec{r}$ cambia e cio', a sua volta, fa cambiare l'orientazione di $\hat{r}$; ma allora $\hat{\theta}$ e $\hat{\varphi}$ devono cambiare orientazione anch'essi per mantenere l'ortogonalita' reciproca. L'espressione del gradiente di una funzione delle tre coordinate sferiche $f(r, \theta, \varphi)$ e' ^{23,ii}:

$$\vec{\nabla} f = \hat{r} \frac{\partial f}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial f}{\partial \theta} + \hat{\varphi} \frac{1}{r \sin \theta} \frac{\partial f}{\partial \varphi} \quad (890)$$

Chiusa parentesi.

467. Tornando alla relazione di dispersione:

$$\epsilon(\vec{k}) = \frac{\hbar^2}{2m} k^2$$

dovreste rendervi conto facilmente che essa esprime ϵ proprio in coordinate sferiche, dove abbiamo usato il modulo del vettore $\vec{k}$, k , per indicare il modulo del vettore posizione del punto dello spazio $\vec{k}$ (in pratica, il simbolo k che compare nella relazione di dispersione cosi' come l'abbiamo usata finora non e' altro che il simbolo r che abbiamo usato nel richiamo sulle coordinate sferiche). Tanto per chiarire ulteriormente, la relazione di dispersione in coordinate cartesiane dovrebbe essere scritta come:

$$\epsilon(\vec{k}) = \epsilon(k_x, k_y, k_z) = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \quad (891)$$

con k_x , k_y e k_z le componenti del vettore $\vec{k}$ lungo i tre assi cartesiani.

468. Data la simmetria sferica, in coordinate sferiche l'energia dipende solo dal modulo (al quadrato) del vettore $\vec{k}$, ma *non* dagli angoli θ e/o φ :

$$\epsilon(\vec{k}) = \epsilon(k, \theta, \varphi) = \frac{\hbar^2}{2m} k^2 \quad (892)$$

E allora il suo gradiente e':

$$\vec{\nabla} \epsilon(\vec{k}) = \hat{r} \frac{\partial \epsilon}{\partial k} + \hat{\theta} \frac{1}{r} \overbrace{\frac{\partial \epsilon}{\partial \theta}}^{=0} + \hat{\varphi} \frac{1}{r \sin \theta} \overbrace{\frac{\partial \epsilon}{\partial \varphi}}^{=0} \quad (893)$$

$$= \hat{r} \frac{\partial \epsilon}{\partial k} \quad (894)$$

e per il modulo del gradiente si ha:

$$|\vec{\nabla} \epsilon(\vec{k})| = \left| \frac{\partial \epsilon}{\partial k} \right| = 2 \left(\frac{\hbar^2}{2m} \right) k \quad (895)$$

ⁱⁱNon riporto la derivazione perche' e' troppo lunga; nella maggior parte dei libri si fa altrettanto, ma nel libro di McQuarrie²³ l'autore scrive: "[la conversione del gradiente in coordinate sferiche] is a long, tedious, standard problem that arises in every quantum-chemistry course and should be done once (and only once!) by any serious student"

(k , essendo il modulo di $\vec{k}$, e' sempre > 0)
Sostituendo nella 882 si ha:

$$g(\epsilon) = \frac{1}{8\pi^3} \int_{S(\epsilon)} \frac{1}{2 \left(\frac{\hbar^2}{2m} \right) k} dS \quad (896)$$

Sempre per il fatto che le isosuperfici sono sferiche, k e' uguale in tutti i punti di $S(\epsilon)$ e quindi tutto il denominatore si puo' portare fuori dal segno di integrale:

$$g(\epsilon) = \frac{1}{8\pi^3} \frac{1}{2 \left(\frac{\hbar^2}{2m} \right) k} \int_{S(\epsilon)} dS \quad (897)$$

A questo punto l'integrale e' diventato semplicemente l'area della superficie di una sfera di raggio k :

$$g(\epsilon) = \frac{1}{8\pi^3} \frac{1}{2 \left(\frac{\hbar^2}{2m} \right) k} 4\pi k^2 = \frac{1}{4\pi^2} \frac{2m}{\hbar^2} k = \frac{1}{4\pi^2} \frac{2m}{\hbar^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{1}{2}} \epsilon^{\frac{1}{2}} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} \quad (898)$$

che e' proprio l'eq. 487.

3.3 Approfondimento sul significato della derivata direzionale

469. Il fatto che la derivata direzionale coincida con la derivata della "traccia" di una funzione lasciata sul piano, parallelo all'asse su cui vengono riportati i valori della funzione, che ne seziona il grafico e che contiene il vettore $\vec{u}$ si puo' vedere anche analiticamente. Limitiamoci per semplicita' a una funzione di due sole variabili $f(x, y)$ (ma tutto funziona perfettamente anche per una funzione di qualsiasi numero di variabili, solo che in questo caso non possiamo rappresentare la cosa graficamente). Fate riferimento alla figura 109. Considerate il piano Π parallelo all'asse z e contenente il versore $\vec{u}$ uscente dal punto $\vec{p}_0 = (x_0, y_0)$ (il punto $\vec{p}_0$ e il versore $\vec{u} = (u_x, u_y)$ giacciono sul piano xy). La traccia del grafico della $f(x, y)$ su Π si ottiene calcolando la $f(x, y)$ sui punti della retta R_α giacente sul piano xy e individuata dal punto $\vec{p}_0$ e dal versore $\vec{u}$. Realizzate che i punti $\vec{p}$ di tale retta sono individuati dalla seguente relazione vettoriale:

$$\vec{p} = \vec{p}_0 + \alpha \vec{u} \quad (899)$$

dove α e' uno scalare che vale 0 in $\vec{p}_0$, e' positivo per uno spostamento lungo R_α nel verso di $\vec{u}$ ed e' negativo per uno spostamento lungo R_α nel verso opposto. In pratica α e' la distanza da $\vec{p}_0$ misurata lungo R_α , cioe', in altre parole, α e' una variabile (scalare) rappresentata sulla retta (orientata) R_α .

Per calcolare la $f(x, y)$ sui punti di R_α ci serve conoscere come x e y sono legate ad α . Questo e' molto semplice: basta proiettare i punti di R_α sui due assi cartesiani; cio' e' ottenuto facendo il prodotto scalare del generico punto $\vec{p} \in R_\alpha$ coi due versori $\hat{x} = (1, 0)$ e $\hat{y} = (0, 1)$ degli assi cartesiani (guardate la figura 109):

$$x(\alpha) = \vec{p} \cdot \hat{x} = (\vec{p}_0 + \alpha \vec{u}) \cdot \hat{x} = x_0 + \alpha u_x \quad (900)$$

$$y(\alpha) = \vec{p} \cdot \hat{y} = (\vec{p}_0 + \alpha \vec{u}) \cdot \hat{y} = y_0 + \alpha u_y \quad (901)$$

Siccome sui punti di R_α sia x che y sono funzioni di α , la $f(x, y)$ calcolata sulla retta R_α si riduce ad una funzione $g(\alpha)$ di una sola variabile:

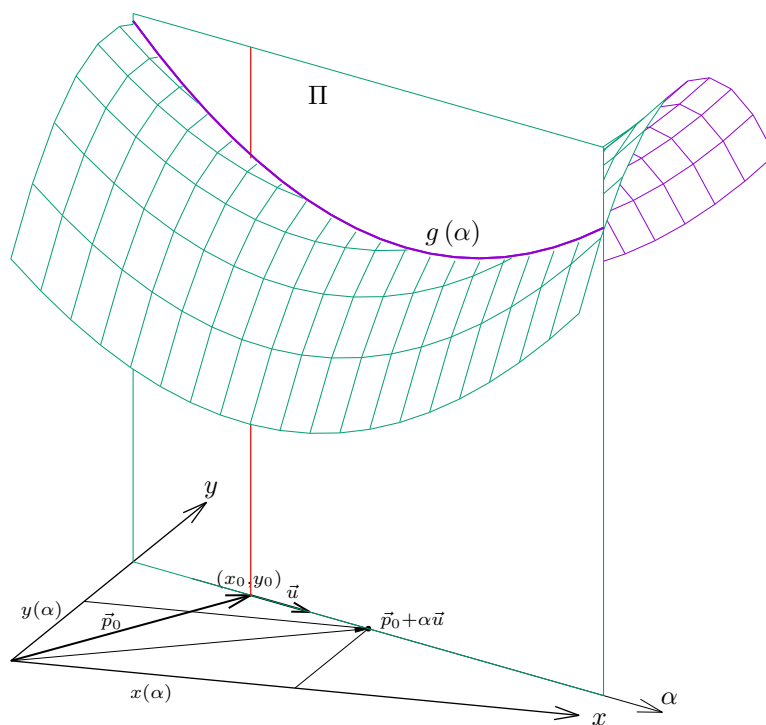


Figure 109: La derivata direzionale di una funzione di due variabili $f(x, y)$ nel punto x_0, y_0 e nella direzione individuata dal vettore $\vec{u}$ e' la derivata della funzione *della sola variabile* che rappresenta la distanza lungo l'asse passante per il punto x_0, y_0 e avente la direzione di $\vec{u}$ e il cui grafico e' la traccia ottenuta sezionando il grafico della $f(x, y)$ con un piano ortogonale al piano xy e contenente il vettore $\vec{u}$.

$$f(x, y) = f(x(\alpha), y(\alpha)) = g(\alpha) \quad \forall x, y \in R_\alpha \quad (902)$$

che e' la traccia del grafico della $f(x, y)$ su Π (guardate la figura 109).

Come detto, possiamo verificare che la derivata direzionale della $f(x, y)$ nella direzione di $\vec{u}$ e' proprio la derivata $dg(\alpha)/d\alpha$:

$$D_{f, \vec{u}} = \frac{dg}{d\alpha} \quad (903)$$

Il differenziale della $f(x, y)$ e' dato da:

$$df = \left(\frac{\partial f}{\partial x} \right) dx + \left(\frac{\partial f}{\partial y} \right) dy \quad (904)$$

A questo punto la 903 e' ottenuta considerando i soli punti della retta R_α (sui quali abbiamo visto che vale: $f(x, y) = g(\alpha)$), dividendo ambo i membri della 904 per $d\alpha$ e facendo uso delle 900 e 901 (che valgono per tutti i punti della retta R_α):

$$\frac{df}{d\alpha} = \frac{dg}{d\alpha} = \left(\frac{\partial f}{\partial x} \right) \frac{dx}{d\alpha} + \left(\frac{\partial f}{\partial y} \right) \frac{dy}{d\alpha} \quad (905)$$

$$= \left(\frac{\partial f}{\partial x} \right) u_x + \left(\frac{\partial f}{\partial y} \right) u_y = \vec{\nabla} f \cdot \vec{u} = D_{f, \vec{u}} \quad (906)$$

3.4 Una derivazione alternativa dell'integrale 515

470. Una derivazione alternativa, meno formale, ma forse piu' intuitiva, dell'integrale 515 e' la seguente.

Dovremmo sommare il valore di $Q(\epsilon(\vec{k})) f(\epsilon(\vec{k}))$ su tutti i punti $\vec{k}$ permessi. Per alleggerire la notazione poniamo:

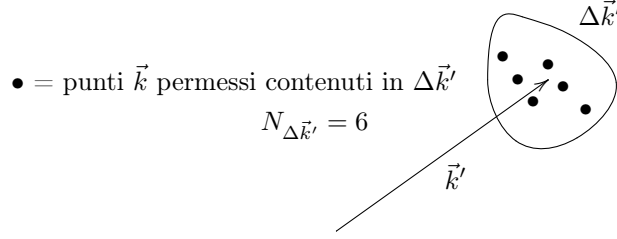
$$Q(\epsilon(\vec{k})) f(\epsilon(\vec{k})) = F(\epsilon(\vec{k}))$$

Si tratta quindi di valutare la somma:

$$\sum_{\vec{k}} Q(\epsilon(\vec{k})) f(\epsilon(\vec{k})) = \sum_{\vec{k}} F(\epsilon(\vec{k})) \quad (907)$$

su tutti i punti $\vec{k}$ permessi, cioe' su tutti i punti del reticolo reciproco.

Per semplificare la somma, potremmo pensare di ripartire l'intero spazio reciproco (in cui il reticolo reciproco e' "immerso") in elementi di volume $\Delta\vec{k}'$, ciascuno centrato sul vettore $\vec{k}'$ (un vettore *qualsiasi* dello spazio reciproco, non necessariamente un vettore permesso). Ciascun elemento di volume $\Delta\vec{k}'$ puo' contenere $N_{\Delta\vec{k}'}$ punti $\vec{k}$ permessi; $N_{\Delta\vec{k}'}$ e' ≥ 0 , essendo uguale a 0 se $\Delta\vec{k}'$ non contiene punti $\vec{k}$ permessi.



Ad ogni elemento di volume $\Delta\vec{k}'$ corrisponde un determinato range di possibili energie $[\epsilon(\vec{k}'), \epsilon(\vec{k}') + \Delta\epsilon_{\Delta\vec{k}'}]$, dove $\epsilon(\vec{k}')$ e $\epsilon(\vec{k}') + \Delta\epsilon_{\Delta\vec{k}'}$ sono, rispettivamente, il minimo e il massimo valore di energia corrispondenti a un punto (non necessariamente permesso) interno all'elemento di volume $\Delta\vec{k}'$; quindi $\Delta\epsilon_{\Delta\vec{k}'}$ dipende da $\Delta\vec{k}'$, cioè da dove l'elemento di volume è localizzato nello spazio reciproco.

Ora, supponendo che $F(\epsilon(\vec{k}'))$ sia *approssimativamente costante* nell'intervallo di energia $[\epsilon(\vec{k}'), \epsilon(\vec{k}') + \Delta\epsilon_{\Delta\vec{k}'}]$ possiamo dire:

$$\left[\begin{array}{l} \text{somma dei valori di } F(\epsilon(\vec{k}')) \text{ su tutti i punti } \vec{k} \text{ per-} \\ \text{ssi nell'elemento di volume } \Delta\vec{k}' \text{ centrato a } \vec{k}' \end{array} \right] \approx F(\epsilon(\vec{k}')) N_{\Delta\vec{k}'}$$

dove $F(\epsilon(\vec{k}'))$ è il valore (assunto costante) della F .

Assumendo che anche la densità degli stati $g(\epsilon(\vec{k}'))$ sia *approssimativamente costante* nell'intervallo di energia $[\epsilon(\vec{k}'), \epsilon(\vec{k}') + \Delta\epsilon_{\Delta\vec{k}'}]$, possiamo scrivere:

$$N_{\Delta\vec{k}'} \approx V g(\epsilon(\vec{k}')) \Delta\epsilon_{\Delta\vec{k}'} \quad (908)$$

(il fattore V è dovuto al fatto che $g(\epsilon(\vec{k}'))$ dà il numero di stati $\vec{k}$ permessi per unità di energia e *per unità di volume del solido*)

Arriviamo quindi a:

$$\left[\begin{array}{l} \text{somma} \\ \text{ori di } F(\epsilon(\vec{k}')) \text{ su tutti i punti } \vec{k} \text{ per-} \\ \text{ssi nell'elemento di volume } \Delta\vec{k}' \text{ centrato a } \vec{k}' \end{array} \right] \approx F(\epsilon(\vec{k}')) V g(\epsilon(\vec{k}')) \Delta\epsilon_{\Delta\vec{k}'}$$

Questa è la somma (approssimata) dei valori di $F(\epsilon(\vec{k}'))$ sui punti $\vec{k}$ permessi interni a un singolo elemento di volume $\Delta\vec{k}'$ (se $\Delta\vec{k}'$ non contiene punti $\vec{k}$ permessi, cioè significa che non ci sono stati permessi nell'intervallo di energia $[\epsilon(\vec{k}'), \epsilon(\vec{k}') + \Delta\epsilon_{\Delta\vec{k}'}]$ e quindi $g(\epsilon(\vec{k}')) = 0$, come deve essere).

Alla luce di quanto sopra, la somma 907 su tutti i punti $\vec{k}$ permessi può essere sostituita con una somma equivalente su tutti gli elementi di volume $\Delta\vec{k}'$:

$$\sum_{\vec{k}} F(\epsilon(\vec{k})) \approx \sum_{\Delta\vec{k}'} F(\epsilon(\vec{k}')) V g(\epsilon(\vec{k}')) \Delta\epsilon_{\Delta\vec{k}'} \quad (909)$$

In pratica, abbiamo raggruppato i punti $\vec{k}$ permessi in gruppi $\Delta\vec{k}'$ (ciascun gruppo e' formato dai punti permessi interni all'elemento di volume $\Delta\vec{k}'$) e assunto che:

- il valore di $F\left(\epsilon(\vec{k}')$ sia costante in ciascun gruppo di punti, cioe' in ciascun elemento di volume $\Delta\vec{k}'$
- il numero di punti $\vec{k}$ permessi in ciascun gruppo sia ottenuto dalla densita' degli stati moltiplicata per l'intervallo (finito) di energia corrispondente all'elemento di volume dello spazio reciproco $\Delta\vec{k}'$

Queste due assunzioni sono solo approssimativamente vere se $\Delta\vec{k}'$ e' finito, ma diventano esatte se $\Delta\vec{k}' \rightarrow 0$. Ma in questo caso, la somma al secondo membro della 909 diventa un integrale:

$$\lim_{\Delta\vec{k}' \rightarrow 0} \sum_{\Delta\vec{k}'} F\left(\epsilon(\vec{k}')$$

che e' lo stesso integrale della 515.

4 La struttura elettronica dei solidi cristallini

4.1 More formal workout of the final step for obtaining the central equation

471. In order to show that eq. 611 implies that all the factors which multiply the plane waves:

$$\left\{ \left(\frac{\hbar^2}{2m} k^2 - \epsilon \right) C_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} \right\} \quad (911)$$

must be null, we follow a procedure very similar to the one we followed in section 1.3.3.3 when we derived the expression of the Fourier coefficients for a function of multiple variables.

472. Pick a particular vector $\vec{k}' \in \mathcal{R}_M^*$, multiply both sides of 611 by $\exp(-i\vec{k}' \cdot \vec{r})$ and integrate over the volume V of the primitive cell of the macroscopic direct lattice $\mathcal{R}_M$ (V is simply the volume of the macroscopic sample):

$$\int_V \sum_{\vec{k}} \exp(i\vec{k} \cdot \vec{r}) \exp(-i\vec{k}' \cdot \vec{r}) \left\{ \left(\frac{\hbar^2}{2m} k^2 - \epsilon \right) C_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} \right\} d\vec{r} = 0 \quad (912)$$

Swap the integral and the sum over $\vec{k}$ and note that the term in braces does not depend on $\vec{r}$:

$$\sum_{\vec{k}} \left\{ \left(\frac{\hbar^2}{2m} k^2 - \epsilon \right) C_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} \right\} \int_V \exp(i(\vec{k} - \vec{k}') \cdot \vec{r}) d\vec{r} = 0 \quad (913)$$

When $\vec{k} = \vec{k}'$ in the sum, the integral is trivially equal to V ; we take advantage of this fact and factor out of the sum the term corresponding to $\vec{k} = \vec{k}'$:

$$V \left\{ \left(\frac{\hbar^2}{2m} k'^2 - \epsilon \right) C_{\vec{k}'} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}'-\vec{G}} \right\}$$

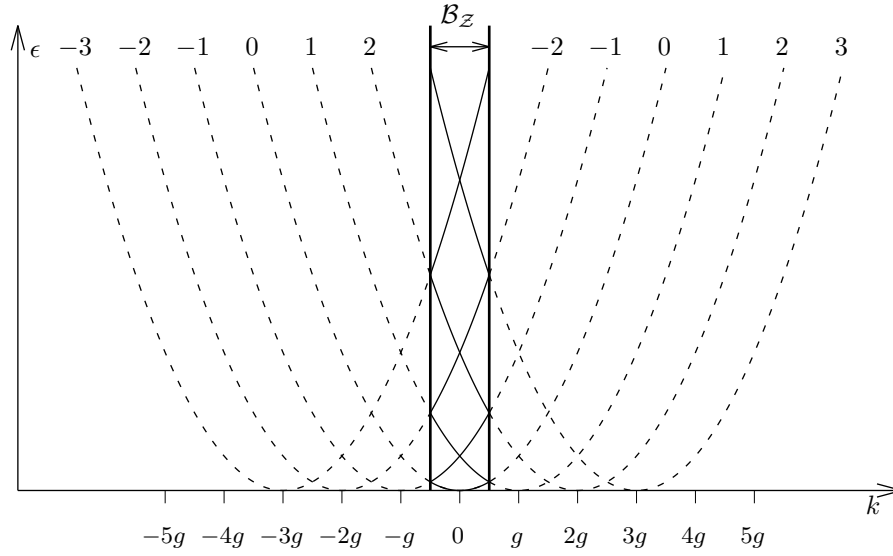


Figure 110: Replica della figura 70, da cui si deduce la relazione fra l'indice di banda n e l'indice j che individua un particolare vettore $G = jg$ di $\mathcal{R}_\mu^*$ (e un corrispondente tratto di parabola interno alle prima zona di Brillouin).

$$+ \sum_{\vec{k} \neq \vec{k}'} \left\{ \left(\frac{\hbar^2}{2m} k^2 - \epsilon \right) C_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} \right\} \int_V \exp \left(i \left(\vec{k} - \vec{k}' \right) \cdot \vec{r} \right) d\vec{r} = 0 \quad (914)$$

In section 1.3.3.3 we already proved that all the integrals in 914 must be null, since $\vec{k} \neq \vec{k}'$ and this means that the whole sum over $\vec{k} \neq \vec{k}'$ is null.

Therefore eq. 914 reduces to:

$$\left\{ \left(\frac{\hbar^2}{2m} k'^2 - \epsilon \right) C_{\vec{k}'} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}'-\vec{G}} \right\} = 0 \quad (915)$$

and since k' was arbitrary, the just written equality must hold $\forall \vec{k}$:

$$\left(\frac{\hbar^2}{2m} k^2 - \epsilon \right) C_{\vec{k}} + \sum_{\vec{G}} U_{\vec{G}} C_{\vec{k}-\vec{G}} = 0 \quad \forall \vec{k} \in \mathcal{R}_M^* \quad (916)$$

5 Il modello “empty lattice”

5.1 Una relazione analitica fra indice di banda e vettori reciproci per il modello “empty lattice”

473. Come detto a p. 353 la corrispondenza fra l'indice di banda n e l'indice j che etichetta un certo tratto di parabola della relazione di dispersione interno alla prima zona di Brillouin *dipende* anche dal segno del “vettore” d'onda k .

Basandovi sulla figura 70, che riporto qua per convenienza come figura 110, potete realizzare quanto avevamo gia' osservato a suo tempo:

$$k \leq 0 : \quad \begin{array}{cccccccc} n : & 1 & 2 & 3 & 4 & 5 & 6 & 7 & \dots \\ j : & 0 & -1 & 1 & -2 & 2 & -3 & 3 & \dots \end{array} \quad (917)$$

$$k \geq 0 : \quad \begin{array}{cccccccc} n : & 1 & 2 & 3 & 4 & 5 & 6 & 7 & \dots \\ j : & 0 & 1 & -1 & 2 & -2 & 3 & -3 & \dots \end{array} \quad (918)$$

Per i valori "speciali" $k = 0$ e $k = \pm g/2$ due tratti di parabola hanno un punto in comune (guardate la figura 110): cio' significa che i due corrispondenti autovalori coincidono; in altri termini i due corrispondenti stati sono degeneri. Per quanto riguarda la relazione fra n e j in questi casi non cambia nulla: semplicemente coppie di autovalori hanno lo stesso valore. In particolare:

$$\begin{aligned} k = \pm g/2 : & \quad \epsilon_{k1} = \epsilon_{k2}, \epsilon_{k3} = \epsilon_{k4}, \epsilon_{k5} = \epsilon_{k6}, \dots \\ k = 0 : & \quad \epsilon_{k2} = \epsilon_{k3}, \epsilon_{k4} = \epsilon_{k5}, \epsilon_{k6} = \epsilon_{k7}, \dots \end{aligned}$$

Quindi le mappe fra n e j mostrate sopra rimangono valide anche per i casi speciali: quella per $k < 0$ e' valida anche per $k = -g/2$; quella per $k > 0$ e' valida anche per $k = g/2$. Quando $k = 0$, entrambe le mappe sono applicabili poiche' i valori di n corrispondenti a valori *opposti* di j indicizzano autovalori identici.

Ci proponiamo di trovare una relazione analitica che, dati valori qualsiasi di k (interno alla prima zona di Brillouin) e j , fornisca il corrispondente indice di banda n :

$$n = n(k, j)$$

Se guardate la mappa 918 per $k \geq 0$ vi rendete conto che:

$$\begin{aligned} j > 0 & \implies n = 2|j| \\ j < 0 & \implies n = 2|j| + 1 \end{aligned}$$

Quindi una possibile relazione generale fra n e j (per $k \geq 0$) potrebbe avere la forma:

$$n(j) = 2|j| + f(j)$$

con:

$$f(j) = \begin{cases} 0 & \text{quando } j > 0 \\ 1 & \text{quando } j < 0 \end{cases}$$

Non dovrete avere difficolta' a realizzare che la funzione:

$$f(j) = \frac{\frac{j}{|j|} - 1}{-2}$$

gode della proprieta' richiesta ($j/|j|$ vale 1 quando $j > 0$ e -1 quando $j < 0$).
Quindi:

$$n(j) = 2|j| + \frac{\frac{j}{|j|} - 1}{-2} \quad (919)$$

fornisce la relazione fra n e j quando $k \geq 0$.

Se ora analizzate la mappa 917 che vale quando $k \leq 0$ vi rendete conto che essa e' molto simile alla 918: l'unica differenza e' l'inversione del segno dei valori di j che danno origine a corrispondenti valori di n . Cioe', per la mappa 917, vale:

$$\begin{aligned} j < 0 &\implies n = 2|j| \\ j > 0 &\implies n = 2|j| + 1 \end{aligned}$$

Quindi in questo caso una possibile relazione generale fra n e j dovrebbe avere la forma:

$$n(j) = 2|j| + h(j)$$

con, questa volta:

$$h(j) = \begin{cases} 0 & \text{quando } j < 0 \\ 1 & \text{quando } j > 0 \end{cases}$$

E' facile rendersi conto che una possibile funzione $h(j)$ che soddisfi la condizione richiesta si ottiene direttamente dalla $f(j)$ definita piu' sopra semplicemente moltiplicando per -1 il termine $j/|j|$:

$$h(j) = \frac{(-1) \frac{j}{|j|} - 1}{-2}$$

Quindi, per $k \leq 0$ si ha:

$$n(j) = 2|j| + \frac{(-1) \frac{j}{|j|} - 1}{-2} \quad (920)$$

Ora confrontate le equazioni 919 e 920: l'unica differenza e' il fattore (-1) , presente quando $k \leq 0$; questo ci offre la possibilita' di fondere le due equazioni in un'unica forma che tiene conto del segno di k nel modo seguente:

$$n(j) = 2|j| + \frac{\frac{k}{|k|} \frac{j}{|j|} - 1}{-2} \quad (921)$$

Questa e' una possibile forma (non e' detto che sia l'unica ne' la piu' elegante) per la relazione che fornisce il valore dell'indice di banda corrispondente a un punto k interno alla prima zona di Brillouin e a un dato vettore $G = jg$ del reticolo reciproco microsocopico.

C'e' ancora un'osservazione da fare. Come vi sarete resi conto, la 921 non e' definita per $k = 0$ e/o $j = 0$. Questi casi vanno dunque trattati separatamente.

Quando $j = 0$, per qualsiasi valore di k si ha sempre $n = 1$ (guardate la figura 110).

Inoltre, come già' accennato all'inizio di questa sezione, quando $k = 0$ qualsiasi delle due relazioni valide per $k \leq 0$ o $k \geq 0$ può essere adoperata, per il fatto che in questo caso gli autovalori sono a due a due identici.

In definitiva, le espressioni finali sono:

$$n(k, j) = \begin{cases} 1 & \text{quando } j = 0 \\ 2|j| + \frac{(-1) \frac{j}{|j|} - 1}{-2} = 2|j| + \frac{\frac{j}{|j|} - 1}{-2} & \text{quando } k = 0, j \neq 0 \\ 2|j| + \frac{\frac{k}{|k|} \frac{j}{|j|} - 1}{-2} & \text{quando } k \neq 0, j \neq 0 \end{cases}$$

Potete verificare che le cose funzionano con questo frammento di codice `octave`:

```
# octave start
## Given a k point inside the 1st BZ and a vector G=jg, compute the
## corresponding band index for the MPL model
k=-1.; # change this: + or - sign: absolute value doesn't matter; 0 is
      # also supported
l=1; # counter
for j=[0,1,-1,2,-2,3,-3,4,-4] # take some j values
if(j==0)M(l,1)=1;M(l,2)=0;++l;continue;endif; # j=0 is special
if(k==0) # k=0 is also special
M(l,2)=j;
M(l,1)=2*abs(j)+((j)/abs(j)-1)/(-2);
# this would be equivalent:
# M(l,1)=2*abs(j)+((-j*)/abs(j)-1)/(-2);
++l;
continue;
endif; # k=0 is special
M(l,2)=j;
M(l,1)=2*abs(j)+((j*(k/abs(k)))/abs(j)-1)/(-2);
++l;
endfor
M=sortrows(M,1);
S="(k>0)";
if(k<0)S="(k<0)";endif;
if(k==0)S="(k=0)";endif;
printf("%5s: %4s %4s\n",S,"n","j");
printf("      ----- \n");
for i=1:rows(M)
printf("      %4d %4d\n",M(i,1),M(i,2));
endfor
# octave end
```

5.2 Doppia degenerazione nel modello “empty lattice”

474. Riprendiamo la relazione di dispersione per il modello “empty lattice” (eq. 645):

$$\epsilon(k) = \frac{\hbar^2}{2m} (k - jg)^2 \quad j \in \mathbb{Z}$$

Per trovare possibili coppie di valori di j che danno lo stesso valore di energia cerchiamo soluzioni per:

$$\frac{\hbar^2}{2m} (k - j_1 g)^2 = \frac{\hbar^2}{2m} (k - j_2 g)^2 \quad (922)$$

$$(k - j_1 g)^2 = (k - j_2 g)^2 \quad (923)$$

In generale, per valori qualsiasi di k e $j_1, j_2 \in \mathbb{Z}$, la 923 ha soltanto la soluzione banale: $j_1 = j_2$ (che significa un autovalore *non* degenerare).

Tuttavia, come potete vedere dalla figura 70, la 923 ammette soluzioni non banali (cioe' $j_1 \neq j_2$) quando $k = 0, \pm g/2$.

475. Analizziamo i tre casi separatamente, anche se il procedimento logico e' lo stesso.

k = 0

La 923 diventa:

$$(-j_1 g)^2 = (-j_2 g)^2 \quad (924)$$

equivalente a:

$$|j_1 g| = |j_2 g| \iff \begin{cases} j_1 &= j_2 \\ j_1 &= -j_2 \end{cases} \quad (925)$$

Se prendiamo entrambi gli argomenti del valore assoluto con lo stesso segno, otteniamo di nuovo la soluzione banale: $j_1 = j_2$.

Se pero' prendiamo gli argomenti con segno opposto ci sono infinite soluzioni non banali:

$$\begin{array}{cccccccc} j_1 = & 1 & 2 & 3 & 4 & 5 & 6 & 7 & \dots \\ j_2 = & -1 & -2 & -3 & -4 & -5 & -6 & -7 & \dots \end{array}$$

Notate che le coppie j_1, j_2 esauriscono tutti i possibili valori di j (tranne $j = 0$; ma $j_1 = 0$ darebbe $j_2 = 0$, che e' di nuovo una soluzione non degenerare).

Inoltre, valori di $j_1 < 0$ darebbero corrispondenti valori di $j_2 > 0$, che non costituirebbero soluzioni differenti da quelle mostrate sopra.

Potete verificare il risultato guardando la figura 70.

$$\mathbf{k} = \mathbf{g}/2$$

La 923 diventa:

$$\left(\frac{g}{2} - j_1 g\right)^2 = \left(\frac{g}{2} - j_2 g\right)^2 \quad (926)$$

equivalente a:

$$\left|\frac{g}{2} - j_1 g\right| = \left|\frac{g}{2} - j_2 g\right| \iff \begin{cases} \frac{1}{2} - j_1 = \frac{1}{2} - j_2 \\ \frac{1}{2} - j_1 = -\frac{1}{2} + j_2 \end{cases} \quad (927)$$

Anche ora, se prendiamo l'equazione in cui gli argomenti del valore assoluto hanno segno opposto, otteniamo infinite soluzioni non banali che esauriscono tutti i possibili valori di j :

$$j_2 = 1 - j_1 \quad (928)$$

$$\begin{array}{cccccccc} j_1 = & 1 & 2 & 3 & 4 & 5 & 6 & 7 & \dots \\ j_2 = & 0 & -1 & -2 & -3 & -4 & -5 & -6 & \dots \end{array}$$

Verificate il risultato con la figura 70.

$$\mathbf{k} = -\mathbf{g}/2$$

La 923 diventa:

$$\left(-\frac{g}{2} - j_1 g\right)^2 = \left(-\frac{g}{2} - j_2 g\right)^2 \quad (929)$$

equivalente a:

$$\left|-\frac{g}{2} - j_1 g\right| = \left|-\frac{g}{2} - j_2 g\right| \iff \begin{cases} -\frac{1}{2} - j_1 = -\frac{1}{2} - j_2 \\ -\frac{1}{2} - j_1 = \frac{1}{2} + j_2 \end{cases} \quad (930)$$

Prendendo l'equazione in cui gli argomenti del valore assoluto hanno segno opposto, otteniamo infinite soluzioni non banali:

$$j_2 = -1 - j_1 \quad (931)$$

$$\begin{array}{cccccccc} j_1 = & 0 & 1 & 2 & 3 & 4 & 5 & 6 & \dots \\ j_2 = & -1 & -2 & -3 & -4 & -5 & -6 & -7 & \dots \end{array}$$

Verificate il risultato con la figura 70.

5.3 La banda n.2 del modello “empty lattice” ha simmetria pari

476. Riporto per comodita’ l’espressione analitica della banda n.2 per il modello “empty lattice” (eq. 648):

$$\epsilon_2(k) = \begin{cases} \frac{\hbar^2}{2m} \left(k + \frac{2\pi}{a}\right)^2 & k \in \left[-\frac{\pi}{a}, 0\right] \\ \frac{\hbar^2}{2m} \left(k - \frac{2\pi}{a}\right)^2 & k \in \left[0, \frac{\pi}{a}\right] \end{cases}$$

Si puo’ vedere che questa funzione e’ pari (cioe’ simmetrica rispetto all’asse delle ordinate) nel modo seguente.

La banda n.2 puo’ essere definita *sull’intero intervallo* $[-\pi/a, \pi/a]$ (tranne che nel punto $k = 0$) nel modo seguente:

$$\epsilon_2(k) = \frac{\hbar^2}{2m} \left(k - \frac{k}{|k|} \frac{2\pi}{a}\right)^2 \quad k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right] - \{0\}$$

(il termine $k/|k|$ e’ un modo per esprimere matematicamente il segno di k : $k/|k| = \mp 1$ quando $k \lessgtr 0$)

$\epsilon_2(k)$ e’ pari se:

$$\epsilon_2(-k) = \epsilon_2(k) \quad \forall k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right] - \{0\}$$

(per discutere la parita’ di $\epsilon_2(k)$, possiamo ovviamente ignorarne il valore $\epsilon_2(0)$, perche’ questo si trova proprio *sull’*asse delle ordinate)

E allora:

$$\begin{aligned} \epsilon_2(-k) &= \frac{\hbar^2}{2m} \left(-k - \frac{-k}{|k|} \frac{2\pi}{a}\right)^2 = \frac{\hbar^2}{2m} \left(-k + \frac{k}{|k|} \frac{2\pi}{a}\right)^2 \\ &= \frac{\hbar^2}{2m} \left(k - \frac{k}{|k|} \frac{2\pi}{a}\right)^2 = \epsilon_2(k) \end{aligned}$$

dove, nella penultima uguaglianza, abbiamo sfruttato il fatto che il segno di cio’ che viene elevato al quadrato puo’ essere invertito senza problemi.

6 Il modello “nearly free electrons” e il band gap

6.1 Un’espressione generale per il sistema di due equazioni nel modello degli elettroni quasi liberi

477. E’ possibile scrivere una forma generale del sistema di due equazioni da cui si ottiene il band gap fra le bande n e $n+1$ nel modello monodimensionale di un cristallo contenente elettroni quasi liberi.

Ricapitoliamo ed estendiamo quanto visto dal punto 397 in poi.

Per il seguito, fate riferimento alla figura 111.

Band gap bande 1-2 (punto 397)

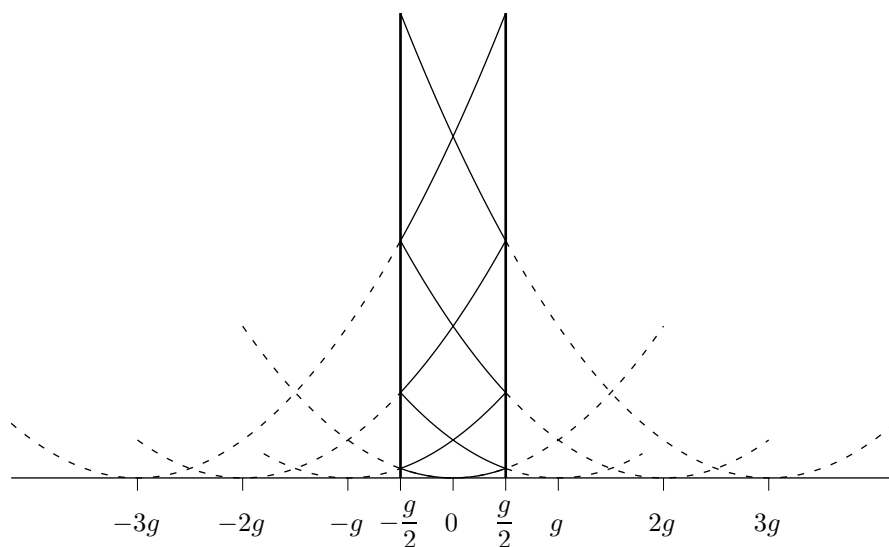


Figure 111: Le prime sette bande nel modello “empty lattice” monodimensionale. Sono evidenziate le parabole del gas di Fermi da cui si originano i rami delle varie bande.

- ⇒ Il band gap si apre in un intorno del punto: $k = g/2$ (e del punto: $k = -g/2$)
- ⇒ L'energia dell'autovalore è:

$$\epsilon = \frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} + \alpha \quad (|\alpha| \rightarrow 0)$$

- ⇒ La generica equazione del sottosistema può essere scritta come:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} + \alpha - \frac{\hbar^2 \left(\frac{g}{2} - jg\right)^2}{2m}}$$

- ⇒ I valori di j per cui il denominatore diventa infinitesimo sono:

$$j = 0, 1$$

- ⇒ Gli unici due coefficienti C_{k-jg} apprezzabilmente diversi da zero sono:

$$C_k, C_{k-g}$$

- ⇒ Il sottosistema corrispondente al punto k si riduce a:

$$j = 0 : \quad \left(\frac{\hbar^2 k^2}{2m} - \epsilon \right) C_k + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} = 0$$

$$j = 1 : \quad \left(\frac{\hbar^2 (k - g)^2}{2m} - \epsilon \right) C_{k-g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-g-ig} = 0$$

⇒ Le due sommatorie possono essere approssimate così:

$$\begin{aligned} j = 0 : \quad & \begin{cases} C_{k-ig} = C_k & \Longleftrightarrow & i = 0 \\ C_{k-ig} = C_{k-g} & \Longleftrightarrow & i = 1 \end{cases} \Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} \approx U_0 C_k + U_g C_{k-g} \\ j = 1 : \quad & \begin{cases} C_{k-g-ig} = C_k & \Longleftrightarrow & i = -1 \\ C_{k-g-ig} = C_{k-g} & \Longleftrightarrow & i = 0 \end{cases} \Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} \approx U_{-g} C_k + U_0 C_{k-g} \end{aligned}$$

⇒ L'energia dei due autostati per $k = g/2$ e':

$$\epsilon = \frac{\hbar^2 \left(\frac{g}{2}\right)^2}{2m} \pm |U_g|$$

⇒ Il band gap e':

$$2|U_g|$$

Band gap bande 2-3 (punto 408)

⇒ Il band gap si apre in un intorno del punto: $k = 0$

⇒ L'energia dell'autovalore e':

$$\epsilon = \frac{\hbar^2 g^2}{2m} + \alpha \quad (|\alpha| \rightarrow 0)$$

⇒ La generica equazione del sottosistema può essere scritta come:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\frac{\hbar^2 g^2}{2m} + \alpha - \frac{\hbar^2 (-jg)^2}{2m}}$$

⇒ I valori di j per cui il denominatore diventa infinitesimo sono:

$$j = 1, -1$$

⇒ Gli unici due coefficienti C_{k-jg} apprezzabilmente diversi da zero sono:

$$C_{k+g}, C_{k-g}$$

⇒ Il sottosistema corrispondente al punto k si riduce a:

$$\begin{aligned} j = 1 : \quad & \left(\frac{\hbar^2 (k - g)^2}{2m} - \epsilon \right) C_{k-g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-g-ig} = 0 \\ j = -1 : \quad & \left(\frac{\hbar^2 (k + g)^2}{2m} - \epsilon \right) C_{k+g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k+g-ig} = 0 \end{aligned}$$

⇒ Le due sommatorie possono essere approssimate così:

$$j = 1 : \quad \begin{cases} C_{k-g-ig} = C_{k-g} & \Longleftrightarrow & i = 0 \\ C_{k-g-ig} = C_{k+g} & \Longleftrightarrow & i = -2 \end{cases} \Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} \approx U_0 C_{k-g} + U_{-2g} C_{k+g}$$

$$j = -1 : \quad \begin{cases} C_{k+g-ig} = C_{k-g} & \Longleftrightarrow & i = 2 \\ C_{k+g-ig} = C_{k+g} & \Longleftrightarrow & i = 0 \end{cases} \Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} \approx U_{2g} C_{k-g} + U_0 C_{k+g}$$

⇒ L'energia dei due autostati per $k = 0$ e':

$$\epsilon = \frac{\hbar^2 g^2}{2m} \pm |U_{2g}|$$

⇒ Il band gap e':

$$2|U_{2g}|$$

Band gap bande 3-4 (verificate da soli)

⇒ Il band gap si apre in un intorno del punto: $k = g/2$ (e del punto: $k = -g/2$)

⇒ L'energia dell'autovalore e':

$$\epsilon = \frac{\hbar^2 \left(\frac{3}{2}g\right)^2}{2m} + \alpha \quad (|\alpha| \rightarrow 0)$$

⇒ La generica equazione del sottosistema può essere scritta come:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\frac{\hbar^2 \left(\frac{3}{2}g\right)^2}{2m} + \alpha - \frac{\hbar^2 \left(\frac{g}{2} - jg\right)^2}{2m}}$$

⇒ I valori di j per cui il denominatore diventa infinitesimo sono:

$$j = -1, 2$$

⇒ Gli unici due coefficienti C_{k-jg} apprezzabilmente diversi da zero sono:

$$C_{k+g}, C_{k-2g}$$

⇒ Il sottosistema corrispondente al punto k si riduce a:

$$j = -1 : \quad \left(\frac{\hbar^2 (k+g)^2}{2m} - \epsilon \right) C_{k+g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k+g-ig} = 0$$

$$j = 2 : \quad \left(\frac{\hbar^2 (k-2g)^2}{2m} - \epsilon \right) C_{k-2g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-2g-ig} = 0$$

⇒ Le due sommatorie possono essere approssimate così:

$$j = -1 : \quad \begin{cases} C_{k+g-ig} = C_{k+g} & \Longleftrightarrow & i = 0 \\ C_{k+g-ig} = C_{k-2g} & \Longleftrightarrow & i = 3 \end{cases} \Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} \approx U_0 C_{k+g} + U_{3g} C_{k-2g}$$

$$j = 2 : \quad \begin{cases} C_{k-2g-ig} = C_{k+g} & \Longleftrightarrow & i = -3 \\ C_{k-2g-ig} = C_{k-2g} & \Longleftrightarrow & i = 0 \end{cases} \Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} \approx U_{-3g} C_{k+g} + U_0 C_{k-2g}$$

⇒ L'energia dei due autostati per $k = g/2$ è:

$$\epsilon = \frac{\hbar^2 \left(\frac{3}{2}g\right)^2}{2m} \pm |U_{3g}|$$

⇒ Il band gap è:

$$2|U_{3g}|$$

Band gap bande 4-5 (verificate da soli)

⇒ Il band gap si apre in un intorno del punto: $k = 0$

⇒ L'energia dell'autovalore è:

$$\epsilon = \frac{\hbar^2 (2g)^2}{2m} + \alpha \quad (|\alpha| \rightarrow 0)$$

⇒ La generica equazione del sottosistema può essere scritta come:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\frac{\hbar^2 (2g)^2}{2m} + \alpha - \frac{\hbar^2 (-jg)^2}{2m}}$$

⇒ I valori di j per cui il denominatore diventa infinitesimo sono:

$$j = -2, 2$$

⇒ Gli unici due coefficienti C_{k-jg} apprezzabilmente diversi da zero sono:

$$C_{k+2g}, C_{k-2g}$$

⇒ Il sottosistema corrispondente al punto k si riduce a:

$$j = -2 : \quad \left(\frac{\hbar^2 (k+2g)^2}{2m} - \epsilon \right) C_{k+2g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k+2g-ig} = 0$$

$$j = 2 : \quad \left(\frac{\hbar^2 (k-2g)^2}{2m} - \epsilon \right) C_{k-2g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-2g-ig} = 0$$

⇒ Le due sommatorie possono essere approssimate così:

$$\begin{aligned}
 j = -2 : \quad & \begin{cases} C_{k+2g-ig} = C_{k+2g} & \Longleftrightarrow & i = 0 \\ C_{k+2g-ig} = C_{k-2g} & \Longleftrightarrow & i = 4 \end{cases} \Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} \approx U_0 C_{k+2g} + U_{4g} C_{k-2g} \\
 j = 2 : \quad & \begin{cases} C_{k-2g-ig} = C_{k+2g} & \Longleftrightarrow & i = -4 \\ C_{k-2g-ig} = C_{k-2g} & \Longleftrightarrow & i = 0 \end{cases} \Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-ig} \approx U_{-4g} C_{k+2g} + U_0 C_{k-2g}
 \end{aligned}$$

⇒ L'energia dei due autostati per $k = 0$ è:

$$\epsilon = \frac{\hbar^2 (2g)^2}{2m} \pm |U_{4g}|$$

⇒ Il band gap è:

$$2|U_{4g}|$$

Il pattern generale che emerge dai casi analizzati più sopra può essere espresso nel modo seguente.

Si devono distinguere due casi, a seconda che n sia dispari (band gap fra le bande $1/2$, $3/4$, $5/6$ etc) o pari (band gap fra le bande $2/3$, $4/5$, $6/7$ etc). A tale scopo conviene definire il seguente numero intero:

$$s = \frac{1 - (-1)^n}{2} \quad (932)$$

E banale realizzare che:

$$s = \begin{cases} 0 & \Longleftrightarrow & n \text{ pari} \\ 1 & \Longleftrightarrow & n \text{ dispari} \end{cases} \quad (933)$$

Allora:

⇒ Il band gap si apre in un intorno del punto: $k = sg/2$ (e del punto: $k = -g/2$ quando n è dispari)

⇒ L'energia dell'autovalore è:

$$\epsilon = \frac{\hbar^2 \left(n \frac{g}{2}\right)^2}{2m} + \alpha \quad (|\alpha| \rightarrow 0)$$

⇒ La generica equazione del sottosistema può essere scritta come:

$$C_{k-jg} = \frac{\sum_{i=-\infty}^{\infty} U_{ig} C_{k-jg-ig}}{\frac{\hbar^2 \left(n \frac{g}{2}\right)^2}{2m} + \alpha - \frac{\hbar^2 \left(s \frac{g}{2} - jg\right)^2}{2m}}$$

⇒ I valori di j per cui il denominatore diventa infinitesimo si trovano imponendo:

$$s \frac{g}{2} - jg = \pm n \frac{g}{2} \Longleftrightarrow j = \frac{s}{2} \mp \frac{n}{2} = \frac{s \mp n}{2} \quad (934)$$

cioe':

$$j = \frac{s+n}{2}, \frac{s-n}{2}$$

⇒ Gli unici due coefficienti C_{k-jg} apprezzabilmente diversi da zero sono:

$$C_{k-\frac{s+n}{2}g}, C_{k-\frac{s-n}{2}g}$$

⇒ Il sottosistema corrispondente al punto k si riduce a:

$$j = \frac{s+n}{2} : \left(\frac{\hbar^2 \left(k - \frac{s+n}{2}g \right)^2}{2m} - \epsilon \right) C_{k-\frac{s+n}{2}g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-\frac{s+n}{2}g-ig} = 0$$

$$j = \frac{s-n}{2} : \left(\frac{\hbar^2 \left(k - \frac{s-n}{2}g \right)^2}{2m} - \epsilon \right) C_{k-\frac{s-n}{2}g} + \sum_{i=-\infty}^{\infty} U_{ig} C_{k-\frac{s-n}{2}g-ig} = 0$$

⇒ Le due sommatorie possono essere approssimate così:

$$j = \frac{s+n}{2} : \begin{cases} C_{k-\frac{s+n}{2}g-ig} = C_{k-\frac{s+n}{2}g} & \Longleftrightarrow i = 0 \\ C_{k-\frac{s+n}{2}g-ig} = C_{k-\frac{s-n}{2}g} & \Longleftrightarrow i = -n \end{cases}$$

$$\Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-\frac{s+n}{2}g-ig} \approx U_0 C_{k-\frac{s+n}{2}g} + U_{-ng} C_{k-\frac{s-n}{2}g}$$

$$j = \frac{s-n}{2} : \begin{cases} C_{k-\frac{s-n}{2}g-ig} = C_{k-\frac{s+n}{2}g} & \Longleftrightarrow i = n \\ C_{k-\frac{s-n}{2}g-ig} = C_{k-\frac{s-n}{2}g} & \Longleftrightarrow i = 0 \end{cases}$$

$$\Rightarrow \sum_{i=-\infty}^{\infty} U_{ig} C_{k-\frac{s-n}{2}g-ig} \approx U_{-ng} C_{k-\frac{s+n}{2}g} + U_0 C_{k-\frac{s-n}{2}g}$$

⇒ L'energia dei due autostati per $k = sg/2$ e':

$$\epsilon = \frac{\hbar^2 \left(n \frac{g}{2} \right)^2}{2m} \pm |U_{ng}|$$

⇒ Il band gap e':

$$2|U_{ng}|$$

7 Il modello “tight binding”

478. In previous sections we have studied two of the simplest models for the (non numerical) analysis of the electronic structure of crystalline solids: the “empty lattice” model and the “nearly free electron” model. In both cases the key point is to assume that the valence electrons of the atoms in a solid either do not feel at all (“empty lattice”) or feel very little (“nearly free electron”) the potential due to the ions sitting at the lattice sites of the crystalline structure.

As suggested by its name, the “tight binding” model tackles the problem starting from the opposite standpoint, namely by considering the valence electrons of a solid strongly bound to the constituent atoms.

As you will realize, another big difference between the “tight binding” model and the two previous models is the mathematical approach. The two previous models are based on the central equation and the Fourier expansion mathematical tool (section 4.4): therefore, they use periodic functions which, by their nature, are non localized functions (I mean: a periodic function extends uninterruptedly over the whole $\mathbb{R}^D$, $D \in \{1, 2, 3\}$, *by definition*). In the “tight binding” model, as we will see, the electronic state function is expressed through non periodic functions tightly localized around the nuclei: at a first sight this might create some perplexity, since our ultimate purpose is to describe an electron free to move *in all the volume* occupied by the macroscopic solid; you will see, however, that this goal will be nonetheless achieved and the final result will be in a perfect agreement with that we obtained using plane waves.

Arriving at the same result from seemingly so different assumptions is reassuring about the validity and correctness of both approaches.

Finally, never forget that both the previous two and the “tight binding” model which we will analyze in this section are anyway at least simplistic and the study of the electronic structure in “real” systems is currently performed completely numerically, using extremely sophisticated computational technologies.

However, as you should have realized along this course, simple (simplistic?) models have the very nice feature that they allow an analytic approach, which, this is my hope, very much helps to understand the *physics* of these systems.

7.1 An “exaggerated” crystal

479. In order to understand the conceptual basis of the “tight binding” model, that is, the reason why it is actually a “logical” approach to the problem of the description of the electronic structure of a crystalline solid, imagine to uniformly expand a sodium crystal (body centered cubic lattice) so to make the internuclear distance become of the order of 1 cm. It is clear that under such conditions each atom, with its 11 electrons, completely ignores the presence of the others.

480. For a *single* isolated sodium atom, letting $V_{at}(\vec{r})$ be the potential acting on an electron of a given type j (j identifies the type of atomic orbital: $1s$, $2s$, $2p$, $3s$) and $\varphi_j(\vec{r})$ and E_j the corresponding eigenfunction and eigenvalue, respectively, the monoelectronic Schrödinger equation is:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{at}(\vec{r})\right)\varphi_j(\vec{r}) = E_j\varphi_j(\vec{r}) \quad (935)$$

7.1.1 The hamiltonian of the exaggerated crystal

481. We now ask ourselves: what will be the form of the hamiltonian describing the behavior of a (single) electron in the sodium crystal with an internuclear distance of 1 cm? As we have

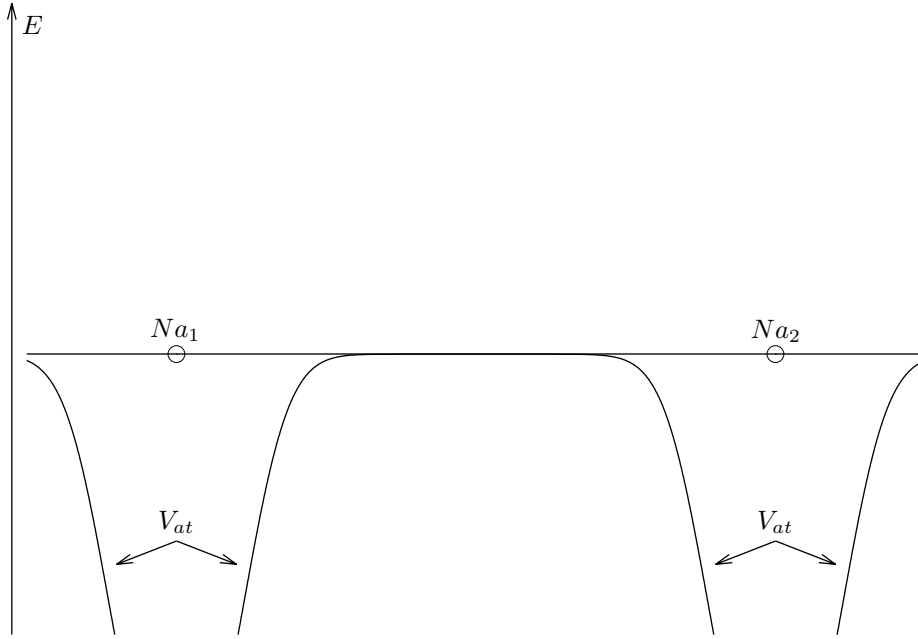


Figure 112: Two nearest neighbors sodium atoms in a monodimensional crystal in which the interatomic distance is ridiculously large (say 1 cm). An electron located half way between Na_1 and Na_2 feels a null potential; an electron located close to Na_2 will only feel the potential due to the latter (and such potential will be identical to the potential generated by atom Na_2 completely isolated). The potential due to Na_1 (as well as the potential of any other atom in the crystal) has become totally negligible in the vicinity of Na_2 . A perfectly specular argument applies when the electron is located close to Na_1 .

remarked, such internuclear distance means that the sodium atoms in the “crystal” are for all intents and purposes completely isolated from each other.

When a single electron moving in the solid sample is far from any nucleus (for instance, half way between two sodium atoms, thus at a distance of about 0.5 cm from the closest nucleus) it is clearly subject to a null potential and has only kinetic energy; on the other hand, when the electron gets close to a nucleus (at a distance of the order of the atomic radius of sodium), it will feel a potential V_{at} , centered on the sodium atom to which it is close, which will be identical to that of a *perfectly isolated single sodium atom*: indeed, close to a given sodium atom, the potential energy contribution due to any other atom in the sample will have effectively decayed to zero. The situation is depicted in figure 112 for a monodimensional case.

If you followed this argument, it should not be difficult to understand that the monoelectronic hamiltonian which describes the state of an electron in this crystal (in which, do not forget it, the interatomic distance is huge) can be written as:

$$-\frac{\hbar^2}{2m}\nabla^2 + \sum_n V_{at}(\vec{r} - \vec{r}_n) \quad (936)$$

The first term is the kinetic energy.

The second term is the potential energy. This latter is obtained by translating the potential of

the isolated atom, $V_{at}(\vec{r} - \vec{r}_n)$, on all the lattice sites $\vec{r}_n$ of the solid sample and adding the so obtained images (please note: the sum contains a number of terms which is equal to the number of primitive cells present in the solid sample: such number is huge, of the order of Avogadro's number, but *finite*).

In order to be independent on any border effect we apply also in this case the periodic boundary conditions of Born and von Karman. As we know, such conditions periodically replicate the solid sample on what we called “macroscopic Bravais lattice” (review point 302 and following): as usual, we will use symbols $\mathcal{R}_M$ and $\mathcal{R}_\mu$ to designate this macroscopic Bravais lattice and the Bravais lattice which defines the crystalline structure, respectively.¹

Finally, as we did in all previous cases, we will assume that the macroscopic solid sample is commensurate to the primitive cell of the crystal structure and hence it is a $N_1 \times N_2 \times N_3$ supercell of the primitive cell of $\mathcal{R}_\mu$. The macroscopic sample contains, therefore, $N = N_1 N_2 N_3$ microscopic primitive cells.

482. It should be clear that the hamiltonian 936 is the translation in mathematical language of what I have said in words above and depicted in figure 112: when $\vec{r}$ is a point in space far from any nucleus, the sum is almost null, because all the $V_{at}(\vec{r} - \vec{r}_n)$ terms are, for all intents and purposes, null, and the hamiltonian operator reduces to the only kinetic energy term; on the other hand, when $\vec{r}$ is a point close to a nucleus on a lattice site $\vec{r}_i$ (at a distance of the order of the atomic radius of sodium), then the sum will be effectively equal to $V_{at}(\vec{r} - \vec{r}_i)$ because, again, all other terms, $(V_{at}(\vec{r} - \vec{r}_n)$ with $n \neq i$), have decayed to zero: so, for these values of $\vec{r}$ the hamiltonian becomes the one for an isolated sodium atom located on the lattice site $\vec{r}_i$ (in this regard you should recall that the Laplace operator, ∇^2 , is invariant with respect to any translation, eq. 558, and thus: $\nabla_{\vec{r}}^2 = \nabla_{\vec{r} - \vec{r}_i}^2$).

483. Given the hamiltonian 936, our target is to find the eigenfunctions $\Psi(\vec{r})$ and the eigenvalues ϵ of the following time-independent and monoelectronic Schrödinger's equation:

$$H\Psi(\vec{r}) = \epsilon\Psi(\vec{r})$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \sum_n V_{at}(\vec{r} - \vec{r}_n) \right) \Psi(\vec{r}) = \epsilon\Psi(\vec{r})$$

7.1.2 The hamiltonian operator is periodic on the microscopic Bravais lattice

484. For the follow-up it is important to note that, as it must be, the potential of the hamiltonian 936 is periodic on the whole (infinite) Bravais lattice of the sodium crystal ($\mathcal{R}_\mu$) *by construction*, since the *same* function V_{at} is replicated on the lattice sites of the solid sample (these are in a finite number), but then the whole macroscopic crystal is replicated *ad infinitum* by the conditions of Born and von Karman.

Since the Laplace ∇^2 operator is translationally invariant (eq. 558), the final result is that the whole hamiltonian is periodic on $\mathcal{R}_\mu$ (besides being periodic, trivially, on $\mathcal{R}_M$).

That is:

$$H(\vec{r} + \vec{R}) = H(\vec{r}) \quad \forall \vec{R} \in \mathcal{R}_\mu \quad (937)$$

I have clarified this point in figure 113.

¹Calling “microscopic” the Bravais lattice which defines a crystal where the internuclear distance is 1 cm seems inappropriate! I hope, however, that it is absolutely clear to you “who is who”.

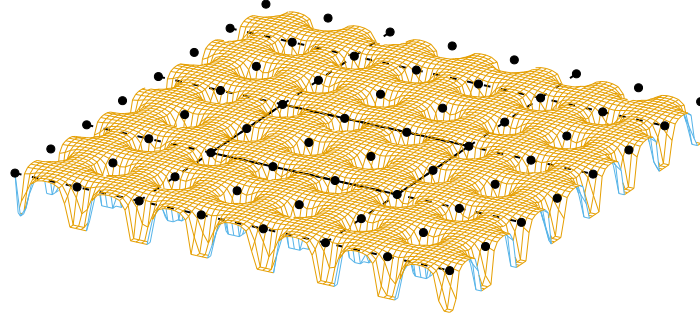


Figure 113: In this figure I want to show, for a simpler to render bidimensional case, the periodicity of the hamiltonian 936 on $\mathcal{R}_\mu$, as a consequence of the periodic boundary conditions. The solid sample is the primitive cell of the macroscopic Bravais lattice $\mathcal{R}_M$ (the rectangle delimited by bold lines in the center). The potential $V_{at}(\vec{r})$ is replicated, always identical to itself, on each atomic site (in this case the sample contains only six atoms). The periodic boundary conditions repeat *ad infinitum* the solid sample (the replicas are shown with dashed lines): since $V_{at}(\vec{r})$ is replicated on every atomic site of the sample, the repetition of this latter due to the periodic boundary conditions leads to $V_{at}(\vec{r})$ being periodic on the whole microscopic Bravais lattice $\mathcal{R}_\mu$ (and not only on $\mathcal{R}_M$). Since ∇^2 is itself periodic (with respect to *any* translation, not only with respect to the translations of $\mathcal{R}_M$ or $\mathcal{R}_\mu$), we conclude that the whole hamiltonian operator is periodic on $\mathcal{R}_\mu$ (and not only on $\mathcal{R}_M$).

7.1.3 Eigenfunctions and eigenvalues of the “exaggerated” crystal

485. What are the eigenfunctions and eigenvalues of the hamiltonian 936?

It is easily seen that the eigenfunction $\varphi_j(\vec{r} - \vec{r}_i)$ of the *isolated* atom corresponding to the eigenvalue E_j and centered on lattice site $\vec{r}_i$ is also an eigenfunction of the hamiltonian 936 with the same eigenvalue.

Let's start with:

$$\begin{aligned} & \left(-\frac{\hbar^2}{2m} \nabla^2 + \sum_n V_{at}(\vec{r} - \vec{r}_n) \right) \varphi_j(\vec{r} - \vec{r}_i) \\ &= -\frac{\hbar^2}{2m} \nabla^2 \varphi_j(\vec{r} - \vec{r}_i) + \sum_n V_{at}(\vec{r} - \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_i) \end{aligned}$$

Since $\varphi_j(\vec{r} - \vec{r}_i)$ is centered on site $\vec{r}_i$ and the distance between lattice sites (that is: the inter-atomic distance) is so large, only the product:

$$V_{at}(\vec{r} - \vec{r}_i) \varphi_j(\vec{r} - \vec{r}_i) \quad (938)$$

in the sum will be different from zero; all other terms are negligibly small because, when $n \neq i$, then $V_{at}(\vec{r} - \vec{r}_n) = 0$ when $\varphi_j(\vec{r} - \vec{r}_i) \neq 0$ and viceversa.

Therefore we can continue with:

$$= -\frac{\hbar^2}{2m} \nabla^2 \varphi_j(\vec{r} - \vec{r}_i) + V_{at}(\vec{r} - \vec{r}_i) \varphi_j(\vec{r} - \vec{r}_i)$$

$$= \left(-\frac{\hbar^2}{2m} \nabla^2 + V_{at}(\vec{r} - \vec{r}_i) \right) \varphi_j(\vec{r} - \vec{r}_i) \quad (939)$$

$$= E_j \varphi_j(\vec{r} - \vec{r}_i) \quad (940)$$

where the last equality follows from the fact that $\varphi_j(\vec{r} - \vec{r}_i)$ is an eigenfunction of the isolated atom with eigenvalue E_j (eq. 935) (again: recall that the ∇^2 Laplace operator is invariant to any translation, eq. 558, and thus $\nabla^2(r) = \nabla^2(r - \vec{r}_i)$).

So far so good. But: $\varphi_j(\vec{r} - \vec{r}_i)$ is not an acceptable solution of eq. 937. Why? As remarked in point 484 the potential in 936 is periodic on $\mathcal{R}_\mu$ and thus the solutions of Schrödinger's equation must be of the form required by Bloch's theorem; it is immediate to realize that $\varphi_j(\vec{r} - \vec{r}_i)$ does not satisfy Bloch's theorem (try to apply condition 528).

If you think about it, intuitively, it is perfectly reasonable that $\varphi_j(\vec{r} - \vec{r}_i)$ is not acceptable: it is a *localized* function, centered on a particular lattice site ($\vec{r}_i$) and as such it cannot appropriately describe an electron free to move *in all* the volume occupied by the solid sample.

7.1.4 Bloch eigenfunctions

486. It is possible to construct functions which are both eigenfunctions of the hamiltonian 936 and do satisfy Bloch's requirement. I will give only the result, without proof, but it is fairly acceptable intuitively.

Since $\forall i \varphi_j(\vec{r} - \vec{r}_i)$ is a solution of the hamiltonian and, trivially, the latter is linear, then also a linear combination of all the $\varphi_j(\vec{r} - \vec{r}_i)$ ($\forall i$) is still a solution:

$$\sum_n a_n \varphi_j(\vec{r} - \vec{r}_n) \quad (941)$$

Taking the a_n coefficients as:

$$a_n = \exp(i\vec{k} \cdot \vec{r}_n) \quad (942)$$

where $\vec{k}$ is an allowed wave vector in the first Brillouin zone and $\vec{r}_n$ is a lattice site of the crystal, ensures that the above sum satisfies Bloch's theorem.

487. Let's verify that:

$$\Psi_{\vec{k}}(\vec{r}) = \sum_n \exp(i\vec{k} \cdot \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_n) \quad (943)$$

indeed satisfies Bloch's theorem.

For a generic vector $\vec{R}$ of the direct lattice $\mathcal{R}_\mu$ (not necessarily within the solid sample) we have:

$$\begin{aligned} \Psi_{\vec{k}}(\vec{r} + \vec{R}) &= \sum_n \exp(i\vec{k} \cdot \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_n + \vec{R}) \\ &\text{add and subtract } \vec{R} \text{ in the exponential} \\ &= \sum_n \exp(i\vec{k} \cdot (\vec{r}_n - \vec{R} + \vec{R})) \varphi_j(\vec{r} - \vec{r}_n + \vec{R}) \\ &= \sum_n \exp(i\vec{k} \cdot (\vec{r}_n - \vec{R})) \exp(i\vec{k} \cdot \vec{R}) \varphi_j(\vec{r} - (\vec{r}_n - \vec{R})) \\ &= \exp(i\vec{k} \cdot \vec{R}) \sum_n \exp(i\vec{k} \cdot (\vec{r}_n - \vec{R})) \varphi_j(\vec{r} - (\vec{r}_n - \vec{R})) \end{aligned} \quad (944)$$

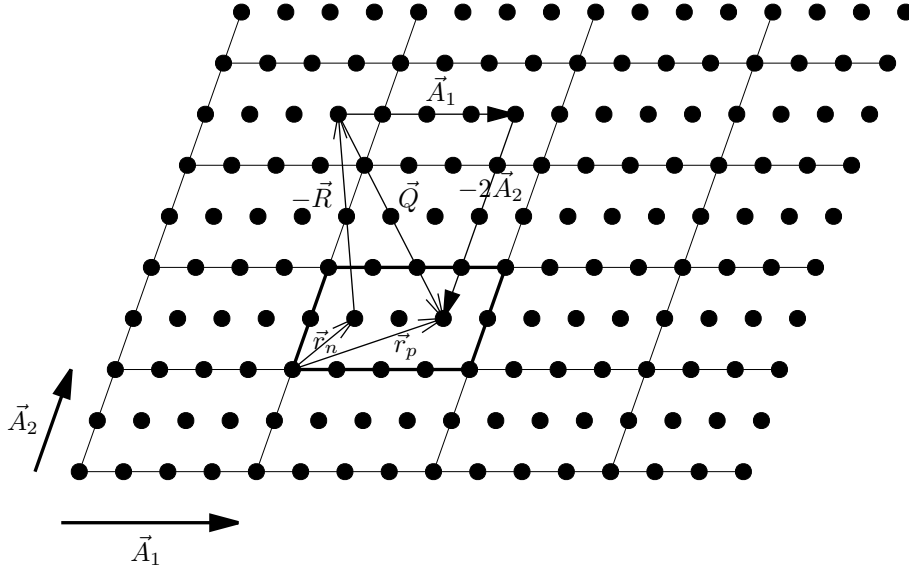


Figure 114: The vector $\vec{r}_n - \vec{R}$ “overflows” the volume of the macroscopic sample (marked with a bold line). However, the vector $\vec{Q} = \vec{A}_1 - 2\vec{A}_2 \in \mathcal{R}_M$ takes it back inside V , that is:

$$\vec{r}_n - \vec{R} + \vec{Q} = \vec{r}_p \in V$$

7.1.5 The Bloch sum can be taken back into the volume of the solid sample

488. In eq. 944 there seems to be a problem. The function $\Psi_{\vec{k}}$ is expressed by a sum (eq. 943) which, by definition, runs over the lattice sites *inside the solid sample*; on the other hand, $\vec{R}$ is *any* vector of $\mathcal{R}_\mu$ and, therefore, $\vec{r}_n - \vec{R}$ in 944 might locate a lattice site *outside* the volume of the sample.

We can overcome this apparent difficulty based on the following three remarks.

489. Remark n.1.

As we know, $\mathcal{R}_\mu$ and $\mathcal{R}_M$ are commensurate (section 2.3.1 and, in particular, property f.). This means that *all* the points of $\mathcal{R}_\mu$ can be reached starting from those within a single primitive cell of $\mathcal{R}_M$, by adding to each of them all the lattice vectors of $\mathcal{R}_M$, or, in perfectly equivalent terms, that for each lattice point of $\mathcal{R}_\mu$ it exists, and is unique, a vector $\vec{Q} \in \mathcal{R}_M$ connecting that point with its image inside the primitive cell of $\mathcal{R}_M$ (that is: the macroscopic solid sample). Then, keeping in mind that, trivially, $\vec{r}_n - \vec{R}$ is a vector of $\mathcal{R}_\mu$, we have:

$$\forall \vec{r}_n \in V \quad \forall \vec{R} \in \mathcal{R}_\mu \quad \exists! \vec{Q} \in \mathcal{R}_M : \vec{r}_n - \vec{R} + \vec{Q} = \vec{r}_p \in V$$

I have illustrated this idea in figure 114.

490. Remark n.2.

Since $\vec{k}$ is a vector of $\mathcal{R}_M^*$ (reciprocal lattice of $\mathcal{R}_M$) the exponentials in sum 944 do not change if we add any vector $\vec{T} \in \mathcal{R}_M$ to the vector $\vec{r}_n - \vec{R}$:

$$\exp \left(i\vec{k} \cdot \left(\vec{r}_n - \vec{R} + \vec{T} \right) \right) = \exp \left(i\vec{k} \cdot \left(\vec{r}_n - \vec{R} \right) \right) \overbrace{\exp \left(i\vec{k} \cdot \vec{T} \right)}^{=1, \text{ eq.197}}$$

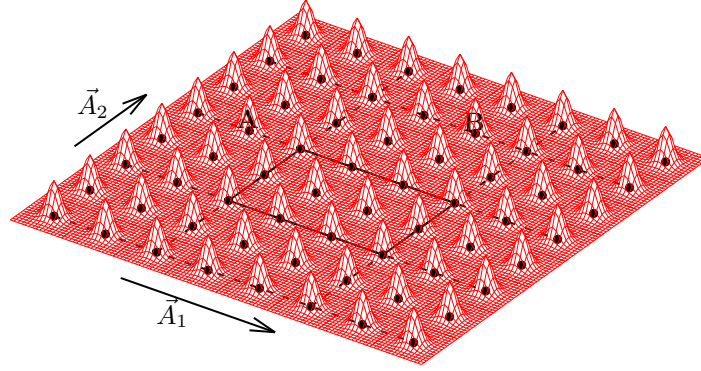


Figure 115: Thanks to the periodic boundary conditions the function φ_j (represented as a gaussian, for simplicity) is replicated on all the infinite points of $\mathcal{R}_\mu$, and thus is periodic on $\mathcal{R}_\mu$; but periodicity on $\mathcal{R}_\mu$ trivially implies periodicity also on $\mathcal{R}_M$, because $\mathcal{R}_M$ is commensurate to $\mathcal{R}_\mu$ (recall that the primitive cell of $\mathcal{R}_M$, i.e. the solid sample, is a $N_1 \times N_2 \times N_3$ supercell of the primitive cell of $\mathcal{R}_\mu$, p. 332). The two replicas marked with A and B are separated by the vector $\vec{T} = \vec{A}_1 + \vec{A}_2 \in \mathcal{R}_M$. Letting $\vec{s} \in \mathcal{R}_\mu$ the lattice point on which function A is centered, it must be:

$$\begin{aligned} \varphi_j(\vec{r} - \vec{s}) &= \varphi_j(\vec{r} - (\vec{s} + \vec{T})) \\ &= \exp\left(i\vec{k} \cdot (\vec{r}_n - \vec{R})\right) \quad \forall \vec{T} \in \mathcal{R}_M \end{aligned}$$

491. Remark n.3.

An atom is located at each lattice point $\vec{r}_n$ inside the sample volume and thus there is a function $\varphi_j(\vec{r} - \vec{r}_n)$ centered on each point $\vec{r}_n$ (of course, all other $\varphi_i(\vec{r} - \vec{r}_n)$ atomic functions are also centered on each point $\vec{r}_n$ inside the solid sample, but we are now concentrating on the atomic eigenfunction corresponding to the eigenvalue E_j). For exactly the same reasons we discussed in point 484 with regard to the periodicity of the hamiltonian operator, also in this case, by virtue of the periodic boundary conditions, the atomic function $\varphi_j(\vec{r})$ is replicated *ad infinitum* on every lattice site of $\mathcal{R}_\mu$, as shown in figure 115. From this it follows that $\varphi_j(\vec{r})$ repeats itself with the same periodicity of $\mathcal{R}_\mu$. Since all the vectors of $\mathcal{R}_M$ are also vectors of $\mathcal{R}_\mu$ (point 304), the conclusion is:

$$\varphi_j(\vec{r} - \vec{s}) = \varphi_j(\vec{r} - (\vec{s} + \vec{T})) \quad \forall \vec{s} \in \mathcal{R}_\mu \quad \forall \vec{T} \in \mathcal{R}_M \quad (945)$$

that is: the values taken by a function φ_j centered on any point $\vec{s} \in \mathcal{R}_\mu$ must be identical to those taken by its replica translated by any vector $\vec{T} \in \mathcal{R}_M$.

492. In the light of the above remarks, let's continue from 944. Based on the remark in point 489, for each value of the index n in the sum of eq. 944 there is a vector $\vec{Q} \in \mathcal{R}_M$ such that, when added to $\vec{r}_n - \vec{R}$, takes us inside the volume of the sample:

$$\forall n \exists! \vec{Q} \in \mathcal{R}_M : \vec{r}_n - \vec{R} + \vec{Q} = \vec{r}_p \in V$$

Note that $\vec{r}_n$ and $\vec{r}_p$, while both being inside the volume of the sample, are not, in general, coincident: look at figure 114.

Based on the remark in point 490 it also must be:

$$\exp \left(i\vec{k} \cdot \left(\vec{r}_n - \vec{R} \right) \right) = \exp \left(i\vec{k} \cdot \left(\vec{r}_n - \vec{R} + \vec{Q} \right) \right) = \exp \left(i\vec{k} \cdot \vec{r}_p \right) \quad \text{with } \vec{r}_p \in V$$

Finally, thanks to the remark in point 491, we have:

$$\varphi_j \left(\vec{r} - \left(\vec{r}_n - \vec{R} \right) \right) = \varphi_j \left(\vec{r} - \left(\vec{r}_n - \vec{R} + \vec{Q} \right) \right) = \varphi_j \left(\vec{r} - \vec{r}_p \right) \quad \text{with } \vec{r}_p \in V$$

Substituting into 944, we can continue the chain of equalities with:

$$\begin{aligned} &= \exp \left(i\vec{k} \cdot \vec{R} \right) \sum_p \exp \left(i\vec{k} \cdot \vec{r}_p \right) \varphi_j \left(\vec{r} - \vec{r}_p \right) \quad \text{with } \vec{r}_p \in V \\ &= \exp \left(i\vec{k} \cdot \vec{R} \right) \Psi_{\vec{k}} \left(\vec{r} \right) \end{aligned}$$

and the perplexity which troubled us in eq. 944 is solved, because now the p sum in the last equality runs over the lattice sites inside the sample volume, as required by the definition of $\Psi_{\vec{k}} \left(\vec{r} \right)$ (eq. 943).

But the final expression is precisely the required condition 528 to satisfy Bloch's theorem.

7.1.6 The Bloch sum is an eigenfunction of the hamiltonian

493. Now that we have established that 943 satisfies Bloch's theorem, we can verify that it is also an eigenfunction of the hamiltonian 936 with eigenvalue E_j (recall that the functions $\varphi_j \left(\vec{r} - \vec{r}_n \right)$, counted by the lattice vectors of the solid sample, which are in a finite number, are all images of the *same* eigenfunction of the isolated atom corresponding to the eigenvalue E_j ; just to make an example, they could be all images of the $1s$ eigenfunction of a perfectly isolated sodium atom, with eigenvalue equal to the $1s$ energy level).

Let's apply the hamiltonian to $\Psi_{\vec{k}} \left(\vec{r} \right)$:

$$\begin{aligned} &\left(-\frac{\hbar^2}{2m} \nabla^2 + \sum_n V_{at} \left(\vec{r} - \vec{r}_n \right) \right) \Psi_{\vec{k}} \left(\vec{r} \right) \\ &= \left(-\frac{\hbar^2}{2m} \nabla^2 + \sum_n V_{at} \left(\vec{r} - \vec{r}_n \right) \right) \sum_m \exp \left(i\vec{k} \cdot \vec{r}_m \right) \varphi_j \left(\vec{r} - \vec{r}_m \right) \\ &\quad \text{constant with respect to } \nabla^2 \\ &= \sum_m -\frac{\hbar^2}{2m} \nabla^2 \overbrace{\exp \left(i\vec{k} \cdot \vec{r}_m \right)}^{\text{does not depend on } \vec{r}} \varphi_j \left(\vec{r} - \vec{r}_m \right) \\ &\quad + \sum_n \left(V_{at} \left(\vec{r} - \vec{r}_n \right) \sum_m \overbrace{\exp \left(i\vec{k} \cdot \vec{r}_m \right)}^{\text{does not depend on } \vec{r}} \varphi_j \left(\vec{r} - \vec{r}_m \right) \right) \\ &= \sum_m \exp \left(i\vec{k} \cdot \vec{r}_m \right) \left(-\frac{\hbar^2}{2m} \nabla^2 \varphi_j \left(\vec{r} - \vec{r}_m \right) \right) \\ &\quad + \sum_n \sum_m \exp \left(i\vec{k} \cdot \vec{r}_m \right) \left(V_{at} \left(\vec{r} - \vec{r}_n \right) \varphi_j \left(\vec{r} - \vec{r}_m \right) \right) \end{aligned}$$

$$\begin{aligned}
& \text{swap the two sums and notice that } \exp(i\vec{k} \cdot \vec{r}_m) \text{ does not depend on } n: \\
& = \sum_m \exp(i\vec{k} \cdot \vec{r}_m) \left(-\frac{\hbar^2}{2m} \nabla^2 \varphi_j(\vec{r} - \vec{r}_m) \right) \\
& + \sum_m \exp(i\vec{k} \cdot \vec{r}_m) \sum_n (V_{at}(\vec{r} - \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_m))
\end{aligned}$$

Based on the same observations we made in point 485, all the terms:

$$V_{at}(\vec{r} - \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_m)$$

are null, except when $n = m$. Therefore in the sum on n only the $n = m$ term survives and we continue with:

$$\begin{aligned}
& = \sum_m \exp(i\vec{k} \cdot \vec{r}_m) \left(-\frac{\hbar^2}{2m} \nabla^2 \varphi_j(\vec{r} - \vec{r}_m) \right) \\
& + \sum_m \exp(i\vec{k} \cdot \vec{r}_m) (V_{at}(\vec{r} - \vec{r}_m) \varphi_j(\vec{r} - \vec{r}_m))
\end{aligned}$$

Now we join the two sums and factor the exponential term out:

$$= \sum_m \exp(i\vec{k} \cdot \vec{r}_m) \overbrace{\left(-\frac{\hbar^2}{2m} \nabla^2 \varphi_j(\vec{r} - \vec{r}_m) + V_{at}(\vec{r} - \vec{r}_m) \varphi_j(\vec{r} - \vec{r}_m) \right)}^{(-\frac{\hbar^2}{2m} \nabla^2 + V_{at}(\vec{r} - \vec{r}_m)) \varphi_j(\vec{r} - \vec{r}_m)}$$

The second term in parentheses is just the hamiltonian for the isolated atom (translated on point $\vec{r}_m$) applied on its eigenfunction $\varphi_j(\vec{r} - \vec{r}_m)$, which has eigenvalue E_j . We thus conclude with:

$$\begin{aligned}
& = \sum_m \exp(i\vec{k} \cdot \vec{r}_m) E_j \varphi_j(\vec{r} - \vec{r}_m) = E_j \sum_m \exp(i\vec{k} \cdot \vec{r}_m) \varphi_j(\vec{r} - \vec{r}_m) \\
& = E_j \Psi_{\vec{k}}(\vec{r})
\end{aligned} \tag{946}$$

7.1.7 In the exaggerated crystal there isn't any dispersion!

494. All that we have seen up to now is for a hypothetical sodium “crystal” where the internuclear distance is so large that each atom is, for all intents and purposes, completely isolated.

What we have found for such system is precisely what we would have expected.

If N is the number of primitive cells in the solid sample, then it will contain $2N$ electrons of type $1s$, $2N$ electrons of type $2s$ and so on. Since each atom is completely isolated from the others (the interatomic distance is 1 cm!) we would expect that all the $1s$ electrons have energy E_{1s} (E_{1s} being the energy of the $1s$ level in an isolated sodium atom and we are assuming that the two possible spin orientations are degenerate), all the $2s$ electrons have energy E_{2s} and so on. And, indeed, this is exactly the result we have found.

In fact, the function 943 is an eigenfunction of the hamiltonian operator with eigenvalue E_j . There are as many eigenfunctions $\Psi_{\vec{k}}(\vec{r})$ (all of them having the same eigenvalue E_j) as allowed $\vec{k}$ points in the first Brillouin zone (eq. 943), that is: N (point 217).

In other words, a set of eigenfunctions of the hamiltonian 936 consists of N degenerate functions with common eigenvalue E_j ; for example, if E_j was the $1s$ level of the isolated sodium atom, the N eigenfunctions (counted by the N allowed wave vectors N in the first Brillouin zone):

$$\Psi_{\vec{k}}(\vec{r}) = \sum_n \exp(i\vec{k} \cdot \vec{r}_n) \varphi_{1s}(\vec{r} - \vec{r}_n) \quad (947)$$

would all have energy E_{1s} .

Each of this N states can host 2 electrons with opposite spin and thus we find what we would have expected: each $1s$ electron of the sodium atoms that make up the solid sample is found at exactly the same energy that it would have in a perfectly isolated atom.

Note that the eigenfunction $\Psi_{\vec{k}}(\vec{r})$ is not the one for the isolated atom: it is a Bloch function with non null values over *all* the volume of the sample, as it must be for a crystal.

Note also that as $\vec{k}$ varies in the first Brillouin zone, we obtain a $1s$ band, a $2s$ band and so on. However, in the present case of a crystal with an exaggerated internuclear distance, the $1s$ band (as well as the $2s$ band and all the other bands) would be perfectly *flat* (equivalently: the eigenvalue $1s$ corresponding to the eigenfunction $\Psi_{\vec{k},1s}(\vec{r})$ would be constant with respect to varying $\vec{k}$ in the first Brillouin zone); $E_{1s}(\vec{k})$ would be a horizontal line (at an energy of E_{1s}): in this case the dispersion relation ... wouldn't show any dispersion at all!

7.2 The electrons in a real crystal and the central idea of the “tight binding” model

495. You might wonder why did we spend efforts to discuss a totally unrealistic system. You will understand the reason.

Look at figure 116, which shows the functions $1s$, $2s$, $2p$, $3s$ centered on two sodium atoms sitting on nearest neighbor sites in *experimental* crystalline sodium (I mean: a *real* sodium crystal, not the imaginary one discussed above).

The first thing to be noticed is that the overlap of the $1s$, $2s$ and $2p$ functions is negligible: that is, with regard to these electronic states everything works as if even in a real sodium crystal the atoms were isolated from each other!

Obviously, in real sodium the interatomic distance ($\approx 3.72 \text{ \AA}$) is such that two atoms in nearest neighbor sites do interact with each other, no doubt. Moreover, from figure 116 you can see that the $3s$ functions (that is, the valence electrons of sodium) have a non negligible overlap: this is reasonable, since, in general, the spatial extension of atomic functions increases with the principal quantum number.

496. Then: the fundamental idea of the “tight binding” model is that the approach that we discussed above for a hypothetical sodium crystal in which all the atoms are effectively isolated from each other can be applied, with some adjustment (which we optimistically hope will be small!) also to a real sodium crystal.

As you will see, the kernel of the model, at least in the super-simplified version that we will discuss, reduces to this: the interaction of an electron on a given atom with the rest of the crystal is not (completely) ignored (as we did, instead, for the exaggerated crystal); however, with the justification that an experimental fact as that shown in figure 116 can afford, such interaction will be limited to the only atoms which are closest to the considered one.

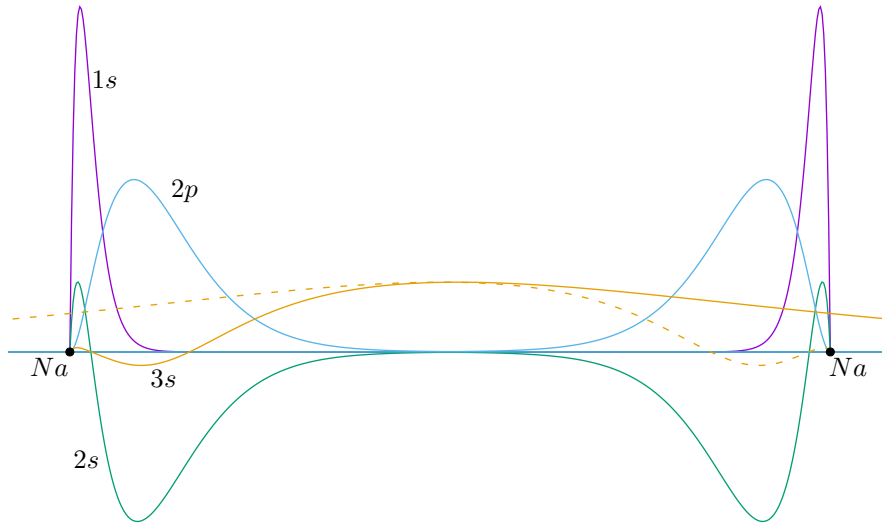


Figure 116: This figure shows the radial part of the $1s$, $2s$, $2p$ and $3s$ orbitals of two sodium atoms in position of nearest neighbors (at a distance of $\approx 3.72 \text{ \AA}$) in crystalline sodium. I have reproduced (in an independent way) figure 10.1 of the book by Ashcroft and Mermin.⁷ For the radial functions of the sodium atom I have used the analytical expressions published by Remy.³⁵ Each function has been multiplied by the radial distance r : this way it easier to visualize the behavior of $r^2|\Psi(r)|^2$ (that is, the radial probability density), but at the same time the four trends remain sufficiently distinct from one another. For the same reason, the $2s$ and $3s$ functions have been multiplied by -1 and the two $3s$ functions have been plotted with a different (filled/dashed) line type, for the sake of better clarity.

7.3 The “tight binding” hamiltonian

497. Let us consider a crystal made by N primitive cells, each containing a single atom (hence, the crystalline structure is based on a Bravais lattice $\mathcal{R}_\mu$ in which there is a single atom on each lattice point).

We will assume that the monoelectronic hamiltonian operator H for this system can be expressed in the form 936:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \sum_n V_{at}(\vec{r} - \vec{r}_n)$$

where the sum is extended to all the N lattice sites $\vec{r}_n$ of the macroscopic sample (and periodically repeated by Born e Von Karman boundary conditions) and V_{at} is the potential operator of the *isolated atom*. This is the first approximation of the model: it is simplistic to assume that the potential felt by an electron in the crystal can be expressed as a sum of the potentials due to all other atoms, *as if they were isolated*.

Our purpose is to derive the band structure for this system: that is, we want to find the relation $\epsilon_i(\vec{k})$ for each value of the band index i .

Identically to what we saw in point 486, we propose form 943 for the eigenfunctions corresponding to eigenvalues close to the value E_j of the perfectly isolated atom:

$$\Psi_{\vec{k}}(\vec{r}) = \sum_n \exp(i\vec{k} \cdot \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_n)$$

$\varphi_j(\vec{r})$ is the eigenfunction of the isolated atom with eigenvalue E_j , $\vec{k}$ is an allowed point inside the first Brillouin zone and the sum runs over all the N lattice sites $\vec{r}_n$ of the sample.

498. As a first thing we rewrite the hamiltonian operator in the following way:

$$\begin{aligned} H &= -\frac{\hbar^2}{2m} \nabla^2 + V_{at}(\vec{r} - \vec{r}_i) + \overbrace{\sum_{\vec{r}_n \neq \vec{r}_i} V_{at}(\vec{r} - \vec{r}_n)}^{v(\vec{r} - \vec{r}_i)} \\ &= \overbrace{-\frac{\hbar^2}{2m} \nabla^2 + V_{at}(\vec{r} - \vec{r}_i)}^{H_{at}(\vec{r} - \vec{r}_i)} + v(\vec{r} - \vec{r}_i) \\ &= H_{at}(\vec{r} - \vec{r}_i) + v(\vec{r} - \vec{r}_i) \end{aligned} \quad (948)$$

that is: we have extracted from the sum the term centered on the lattice site $\vec{r}_i$. In this form the hamiltonian can be thought of as composed by two contributions: the hamiltonian of the isolated atom centered on the lattice site $\vec{r}_i$, $H_{at}(\vec{r} - \vec{r}_i)$, plus a contribution $v(\vec{r} - \vec{r}_i)$ due to all the remaining atoms (different from the one located on site $\vec{r}_i$).

The dependence of the term v from $\vec{r} - \vec{r}_i$ can be rationalized in the following way: if the site $\vec{r}_i$ is the origin, then we have $\vec{r}_i = 0$ and $v(\vec{r} - \vec{r}_i) = v(\vec{r})$ is the energy contribution due to all the sites different from the origin; if $\vec{r}_i$ is any site, then the term v is exactly the same, but *translated* on site $\vec{r}_i$, that is, precisely, $v(\vec{r} - \vec{r}_i)$.

7.4 A general expression for the energy

499. We are now going to find the eigenvalues $\epsilon(\vec{k})$ of the following time-independent and monoelectronic Schrödinger's equation:

$$H\Psi_{\vec{k}}(\vec{r}) = \epsilon(\vec{k})\Psi_{\vec{k}}(\vec{r}) \quad (949)$$

subject to the usual periodic boundary conditions of Born and von Karman.

(I have omitted the indication of the the band index for ϵ : reason is that, as you will see, the band index is determined by the index j which identifies a particular eigenvalue of the isolated atom in the definition of $\Psi_{\vec{k}}(\vec{r})$, eq. 943)

500. If we multiply both sides of 949 by $\Psi_{\vec{k}}^*(\vec{r})$ and integrate over the volume V of the sample, we obtain:

$$\epsilon(\vec{k}) = \frac{\langle \Psi_{\vec{k}} | H | \Psi_{\vec{k}} \rangle}{\langle \Psi_{\vec{k}} | \Psi_{\vec{k}} \rangle} \quad (950)$$

where I have used the “bra-ket” notation for the integrals; that is, for example:

$$\langle \Psi_{\vec{k}} | H | \Psi_{\vec{k}} \rangle = \int_V \Psi_{\vec{k}}^*(\vec{r}) H \Psi_{\vec{k}}(\vec{r}) d\vec{r}$$

501. Note the difference with respect to an atomic/molecular isolated system: in that case the integral that gives the expectation value of the energy would be evaluated over all space, because the state function extends over all space and dies at infinity; on the other hand, in the present case the state function $\Psi_{\vec{k}}(\vec{r})$ is defined only for $\vec{r}$ values inside the sample volume and is extended by periodicity by the Born and von Karman boundary conditions. Since the argument of the integral is periodic on $\mathcal{R}_M$, the integral itself would not be defined if evaluated on all $\mathbb{R}^3$ (in the following, for the sake of a lighter notation, I will omit the indication of V in the integral symbol).

502. Now we plug the expression of $\Psi_{\vec{k}}(\vec{r})$ (eq. 943) into 950:

$$\epsilon(\vec{k}) = \frac{\int \left(\sum_m \exp(i\vec{k} \cdot \vec{r}_m) \varphi_j(\vec{r} - \vec{r}_m) \right)^* H \sum_n \exp(i\vec{k} \cdot \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_n) d\vec{r}}{\int \left(\sum_m \exp(i\vec{k} \cdot \vec{r}_m) \varphi_j(\vec{r} - \vec{r}_m) \right)^* \sum_n \exp(i\vec{k} \cdot \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_n) d\vec{r}} \quad (951)$$

7.4.1 The approximations of the “tight binding” model

7.4.1.1 The denominator

503. Let’s work out the denominator of 951. Perform the complex conjugation, collapse the two sums into a single sum over the two indices m, n and swap the integral with the sum:

$$\begin{aligned} & \sum_{m,n} \int \exp(-i\vec{k} \cdot \vec{r}_m) \varphi_j^*(\vec{r} - \vec{r}_m) \exp(i\vec{k} \cdot \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_n) d\vec{r} \\ &= \sum_{m,n} \int \exp(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m)) \varphi_j^*(\vec{r} - \vec{r}_m) \varphi_j(\vec{r} - \vec{r}_n) d\vec{r} \end{aligned}$$

Here is a first place where the approximations characterizing the “tight binding” model are introduced: assuming that the atomic functions φ_j are sufficiently localized (review point 495 and figure 116), we can neglect all the integrals with $n \neq m$ (because in the region where $\varphi_j^*(\vec{r} - \vec{r}_m)$ is different from zero, $\varphi_j(\vec{r} - \vec{r}_n)$ is effectively null, and viceversa). We are then left with the only terms where $n = m$ and in this case the exponential is equal to 1. Then:

$$= \sum_n \int \varphi_j^*(\vec{r} - \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_n) d\vec{r} = \sum_n 1 = N \quad (952)$$

where N is the number of atoms present in the crystal. The penultimate equality follows because, without loss of generality, we can assume that the atomic functions φ_j are normalized and thus the integral is equal to 1 (the *atomic* functions are defined on the whole space; however, again, thanks to the assumption that they are sufficiently localized, it can be taken for granted that they have decayed to zero outside the volume of the sample, and thus, for the φ_j ’s, the integral over the sample volume is identical to the integral over all $\mathbb{R}^3$).

7.4.1.2 The numerator

504. We now turn to the numerator of 951:

$$\int \left(\sum_m \exp(i\vec{k} \cdot \vec{r}_m) \varphi_j(\vec{r} - \vec{r}_m) \right)^* H \sum_n \exp(i\vec{k} \cdot \vec{r}_n) \varphi_j(\vec{r} - \vec{r}_n) d\vec{r}$$

Perform the complex conjugation:

$$= \int \left(\sum_m \exp \left(-i\vec{k} \cdot \vec{r}_m \right) \varphi_j^* (\vec{r} - \vec{r}_m) \right) H \sum_n \exp \left(i\vec{k} \cdot \vec{r}_n \right) \varphi_j (\vec{r} - \vec{r}_n) d\vec{r}$$

The hamiltonian is linear and thus can be moved to the right of the sum over n . Moreover $\exp \left(i\vec{k} \cdot \vec{r}_n \right)$ does not depend on $\vec{r}$ and therefore it behaves as a constant with respect to the hamiltonian:

$$= \int \left(\sum_m \exp \left(-i\vec{k} \cdot \vec{r}_m \right) \varphi_j^* (\vec{r} - \vec{r}_m) \right) \sum_n \exp \left(i\vec{k} \cdot \vec{r}_n \right) H \varphi_j (\vec{r} - \vec{r}_n) d\vec{r}$$

Now perform the product of the terms in the sum over m with the sum over n and work out the product of the two exponentials:

$$= \int \left(\sum_m \sum_n \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right) \varphi_j^* (\vec{r} - \vec{r}_m) H \varphi_j (\vec{r} - \vec{r}_n) \right) d\vec{r} \quad (953)$$

Swap the integral with the sums noting that $\exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right)$ does not depend on $\vec{r}$ and can thus be factored out of the integral:ⁱⁱ

$$= \sum_{m,n} \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right) \int \varphi_j^* (\vec{r} - \vec{r}_m) H (\vec{r}) \varphi_j (\vec{r} - \vec{r}_n) d\vec{r} \quad (954)$$

(I have emphasized that the hamiltonian is a function of $\vec{r}$)

Now, as we saw in general in eq. 948, we write the hamiltonian as the sum of the hamiltonian of the isolated atom centered on site $\vec{r}_m$ and of the term $v(\vec{r} - \vec{r}_m)$ due the rest of the crystal:

$$\begin{aligned} &= \sum_{m,n} \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right) \times \\ &\quad \times \int \varphi_j^* (\vec{r} - \vec{r}_m) \left(H_{at} (\vec{r} - \vec{r}_m) + \overbrace{\sum_{p \neq m} V_{at} (\vec{r} - \vec{r}_p)}^{v(\vec{r} - \vec{r}_m)} \right) \varphi_j (\vec{r} - \vec{r}_n) d\vec{r} \end{aligned} \quad (955)$$

Separate the terms in both the integral and the sums:

$$\begin{aligned} &= \overbrace{\sum_{m,n} \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right) \int \varphi_j^* (\vec{r} - \vec{r}_m) H_{at} (\vec{r} - \vec{r}_m) \varphi_j (\vec{r} - \vec{r}_n) d\vec{r}}^{S_1} \\ &+ \underbrace{\sum_{m,n} \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right) \int \varphi_j^* (\vec{r} - \vec{r}_m) v (\vec{r} - \vec{r}_m) \varphi_j (\vec{r} - \vec{r}_n) d\vec{r}}_{S_2} \end{aligned} \quad (956)$$

ⁱⁱFrom this point I follow the derivation of Ibach and Lüth.³⁶ Starting exactly from this same point, I have reported in section 7.9 of the extracurricular part also the derivation, a bit longer, which you can find, for example, in the book by Hofmann.³⁷ If you prefer, you can follow that instead of this one.

7.4.1.2.1 The sum S_1

505. This is the second place where the approximations of the “tight binding” model come into play.

In the integral in the first sum of 956 (indicated with S_1) the Hamilton operator of the isolated atom centered on site $\vec{r}_m$ is involved: if the atomic functions φ_j are sufficiently localized, we can assume that such integral is appreciably different from zero only when $m = n$, that is, only when the overlap between atomic functions centered on the *same lattice site* is considered. If you review figure 116, you can realize that this assumption is no doubt defensible for the core states of the sodium atom; it is less defensible for the $3s$ valence functions: in this case we are sure that we are going to have an error, but we hope that such error will be small: the final check (and this applies not only to the “tight binding” model, but to any approximate method in general) will be the comparison of the calculation with the experiment. If we trust this approximation, the sum S_1 can be reduced to a single index (because, as just noted, when $m \neq n$ all the terms are null); moreover, the exponential becomes equal to 1 (because $n = m \implies \vec{r}_n = \vec{r}_m$); we then arrive at:

$$n = m \implies S_1 = \sum_m \int \varphi_j^*(\vec{r} - \vec{r}_m) H_{at}(\vec{r} - \vec{r}_m) \varphi_j(\vec{r} - \vec{r}_m) d\vec{r}$$

Since $\varphi_j(\vec{r} - \vec{r}_m)$ is an eigenfunction of $H_{at}(\vec{r} - \vec{r}_m)$ with eigenvalue E_j , we can continue with:

$$\begin{aligned} &= \sum_m \int \varphi_j^*(\vec{r} - \vec{r}_m) E_j \varphi_j(\vec{r} - \vec{r}_m) d\vec{r} \\ &= \sum_m E_j \int \varphi_j^*(\vec{r} - \vec{r}_m) \varphi_j(\vec{r} - \vec{r}_m) d\vec{r} \end{aligned}$$

The integral must be evaluated over the sample volume V (point 501); however, still based on the assumption that the φ_j 's are strongly localized, its value will be unchanged if the integral is extended to all $\mathbb{R}^3$ (in other words: we assume that the φ_j 's are largely decayed to zero outside the sample volume); but then, with the additional assumption, without loss of generality, that the φ_j 's are normalized, the value of the integral is 1. In conclusion, we arrive at:

$$= \sum_m E_j = E_j \sum_m 1 = N E_j (= S_1) \quad (957)$$

7.4.1.2.2 The sum S_2

506. We are left with sum S_2 of eq. 956.

Also in this case we rely on the assumption that the functions φ_j are very localized; however, since the potential energy term $v(\vec{r} - \vec{r}_m)$ is involved in the integral and the former is due to all the atoms in the sample (except the one on site m , eq. 955), we try to improve the level of approximation and take into account not only the integrals with $n = m$ (as we already did in the case of S_1), but also those in which the lattice site n is a *first neighbor* of site m .

That way the sum S_2 becomes a sum on a single index, say m , which contains only two types of terms: those in which $n = m$ (in these terms the exponential is unit, because $n = m \implies \vec{r}_n = \vec{r}_m$) and those in which n stands for a first neighbor of site m ; the terms of this second type can be grouped together, in turn, into a sum on the index n (the number of terms in this sum on n is the number of first neighbors of a given lattice site: such number depends on the type of Bravais lattice on which the crystalline structure of the solid is based; for example, for a simple cubic lattice with a single atom on every lattice point the number of first neighbors is 6).

We thus have:

$$\begin{aligned}
S_2 = \sum_m & \left[\overbrace{\int \varphi_j^* (\vec{r} - \vec{r}_m) v (\vec{r} - \vec{r}_m) \varphi_j (\vec{r} - \vec{r}_m) d\vec{r}}^{\text{term in which } n = m} \right. \\
& \left. + \underbrace{\sum_n' \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right) \int \varphi_j^* (\vec{r} - \vec{r}_m) v (\vec{r} - \vec{r}_m) \varphi_j (\vec{r} - \vec{r}_n) d\vec{r}}_{\text{terms in which } n \text{ is a first neighbor of } m} \right] \quad (958)
\end{aligned}$$

where the superscript ' on the sum over n reminds us that it runs only over the first neighbors of site m .

507. Now: it is easy to realize that $v (\vec{r} - \vec{r}_m)$ is certainly periodic over $\mathcal{R}_M$. It is defined as the sum of all the potential energy operators V_{at} of the isolated atom, each translated on its own lattice site in the sample volume V ; the sum does not contain the operator on site m (eqs. 955 and 948) and this “hole” makes it not periodic on $\mathcal{R}_\mu$ (at difference with the hamiltonian, which instead is periodic on $\mathcal{R}_\mu$, as we already saw in point 484). However, the periodic boundary conditions ensure that $v (\vec{r} - \vec{r}_m)$ is periodic on $\mathcal{R}_M$, precisely because it is defined on the whole sample volume, which is a primitive cell of $\mathcal{R}_M$.

508. In point 491 we already established that the function φ_j repeats itself with the same periodicity of $\mathcal{R}_\mu$, and thus also of $\mathcal{R}_M$ (because $\mathcal{R}_M$ is commensurate to $\mathcal{R}_\mu$ and the primitive cell of $\mathcal{R}_M$ is a $N_1 \times N_2 \times N_3$ supercell of the primitive cell of $\mathcal{R}_\mu$).

509. Putting together the above remarks, we can say that the integrands of the two integrals present in 958 are periodic on $\mathcal{R}_M$ and the integrals themselves are evaluated on the sample volume, that is, on a primitive cell of $\mathcal{R}_M$. But then, based on what we proved in point 12, the two integrals are invariant with respect to any translation of the function to be integrated.

As m varies, the two integrands undergo a corresponding translation, but their value will remain the same (based on what just said above) (note: in the second integral, the term $\varphi_j (\vec{r} - \vec{r}_n)$ does translate with m , even if it does not contain explicitly the index m , because $\vec{r}_n$ is a first neighbor of site $\vec{r}_m$).

We can thus conclude that the two integrals in 958 *do not depend on m* .

510. There is still a problem.

Even though the second integral does not depend on m , it might nonetheless depend on the index n . Why? Because while it is true that the distance between the lattice sites on which the $\varphi_j^* (\vec{r} - \vec{r}_m)$ and $\varphi_j (\vec{r} - \vec{r}_n)$ functions are centered is independent on n (by definition of first neighbors!), the overlap of the functions may depend on n if their symmetry is *less than* the symmetry with which the first neighbors are positioned around the site m . On the other hand, if the φ_j are s -type atomic orbitals, that is, spherically symmetric, their overlap is totally independent on their reciprocal position. I have tried to explain graphically this idea in figure 117. So: to simplify as much as possible the derivation which we are at, we will suppose that the φ_j 's have spherical symmetry (that is: they are s -type atomic orbitals): note that this assumption is not required by the model, which is perfectly able to include atomic orbitals of any type: s , p , d , f ; it only becomes much more complicated to handle non spherically symmetric orbitals.

Under this last assumption the second integral in 958 becomes independent also on n .

We can then set:

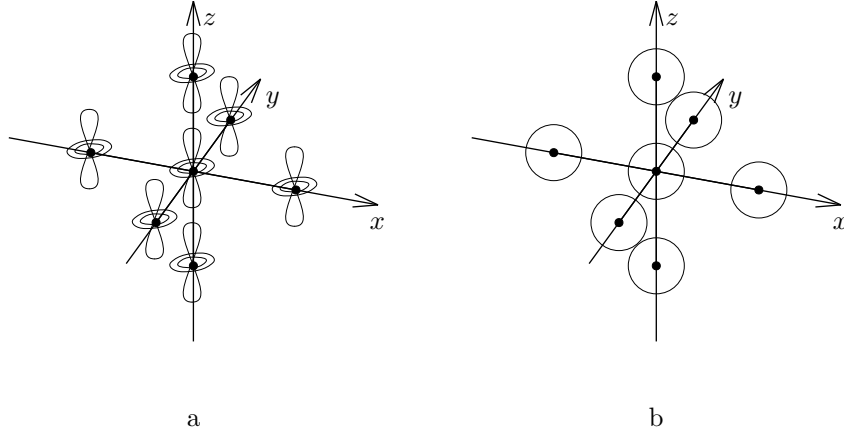


Figure 117: For a given site m , this figure shows the 6 first neighbors in the case of a simple cubic lattice. a: if the atomic function φ_j is, for example, a d_{z^2} orbital, then the overlap integral of the functions centered on the first neighbors and that centered on the site m has the same value for the 4 first neighbors on the xy plane, but will have a different value for the first neighbors located along the z axis (then, in this case, the integral in the sum on n in 958 *depends* on n). b: if the function φ_j has spherical symmetry, then the overlap integral of the functions centered on the first neighbors and that centered on the site m has the same value in any case and thus *does not depend* on n .

$$-A = \int \varphi_j^* (\vec{r} - \vec{r}_m) v (\vec{r} - \vec{r}_m) \varphi_j (\vec{r} - \vec{r}_m) d\vec{r} \quad (959)$$

$$-B = \int \varphi_j^* (\vec{r} - \vec{r}_m) v (\vec{r} - \vec{r}_m) \varphi_j (\vec{r} - \vec{r}_n) d\vec{r} \quad (960)$$

The minus sign on the LHS has been introduced simply because we want the two just defined parameters A and B to be positive, while the two integrals are (almost invariably) negative, since the potential due to the surrounding crystal on a given electron ($v(\vec{r} - \vec{r}_m)$) is of an attractive type.

511. This is an important and peculiar point of the “tight binding” model. The integrals 959 and 960 are not easy to be directly evaluated and are thus expressed by the two parameters A and B , which must be evaluated in some alternative way: either by some other *ad hoc* approximation, or from experimental data.

Note also that in the exaggerated crystal (the one with an internuclear distance of 1 cm) we would have: $A = B = 0$. Indeed, in 959 and 960, $v(\vec{r} - \vec{r}_m)$ is the potential due to the sites *different* from m and thus it would be $v(\vec{r} - \vec{r}_m) = 0$ when $\varphi_j^* (\vec{r} - \vec{r}_m) \neq 0$ and viceversa.

512. With 959 and 960 the sum S_2 (eq. 958) becomes:

$$S_2 = \sum_m \left[(-A) + \sum'_n \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right) (-B) \right]$$

$$= \sum_m \left[(-A) - B \sum'_n \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right) \right]$$

513. It is also trivial to realize that, since the location of the first neighbors around a given lattice site m is always the same (by definition of Bravais lattice!), also the sum on n of the exponentials does not depend on m and takes always the same value. We can thus take for such value the one corresponding to $\vec{r}_m = 0$ (that is, in equivalent words, we evaluate the sum on n for the first neighbors of the origin). This way the expression for S_2 becomes:

$$\begin{aligned} &= \left[-A - B \sum'_n \exp \left(i\vec{k} \cdot \vec{r}_n \right) \right] \sum_m 1 \\ &= N \left(-A - B \sum'_n \exp \left(i\vec{k} \cdot \vec{r}_n \right) \right) \end{aligned} \quad (961)$$

(the $\vec{r}_n$ sites are now first neighbors of the origin)

7.4.2 The final result

514. Substitution into 956 of the results obtained for the two sums S_1 and S_2 (eq. 957 e 961) gives us the expression for the numerator of 950:

$$\text{numerator of eq. 950} = N \left(E_j - A - B \sum'_n \exp \left(i\vec{k} \cdot \vec{r}_n \right) \right) \quad (962)$$

Finally, plugging this and the denominator 952 (which is simply equal to N) into 951 we arrive at the final result:

$$\epsilon(\vec{k}) = E_j - A - B \sum'_n \exp \left(i\vec{k} \cdot \vec{r}_n \right) \quad (963)$$

Eq. 963 relates the energy of an electron described by Schrödinger's equation 949 to the allowed wave vectors $\vec{k}$ in the first Brillouin zone: it is thus the sought dispersion relation given by the “tight binding” model (in the super-simplified version that I have presented).

7.5 Periodicity of the dispersion relation in $\vec{k}$ space

515.

First of all it is easy to verify that $\epsilon(\vec{k})$ is periodic on $\mathcal{R}_\mu^*$ (reciprocal lattice of $\mathcal{R}_\mu$), as required (section 4.6).

For any $\vec{G} \in \mathcal{R}_\mu^*$ we have:

$$\begin{aligned} \epsilon(\vec{k} + \vec{G}) &= E_j - A - B \sum'_n \exp \left(i(\vec{k} + \vec{G}) \cdot \vec{r}_n \right) \\ &= E_j - A - B \sum'_n \exp \left(i\vec{k} \cdot \vec{r}_n \right) \exp \left(i\vec{G} \cdot \vec{r}_n \right) \end{aligned}$$

$$= E_j - A - B \sum_n' \exp \left(i \vec{k} \cdot \vec{r}_n \right)$$

because the scalar product of a reciprocal vector ($\vec{G} \in \mathcal{R}_\mu^*$) and a direct vector ($\vec{r}_n \in \mathcal{R}_\mu$) is always equal to an integer multiple of 2π (eq. 197).

The periodicity of the dispersion relation in the reciprocal space is a necessary condition of the band structure and finding that it is satisfied also in the present case is reassuring about the consistency of the “tight binding” model.

7.6 The bands in the “tight binding” model

516. The set of eigenvalues given by 963 as $\vec{k}$ varies in the first Brillouin zone is what in the previous models (“empty lattice” and “nearly free electron”) we called a “band”.

As I anticipated on p. 341, and differently from the previous models, in the “tight binding” model each band is labelled by a particular electronic level in the isolated atom (the index j in E_j in eq. 963). We have thus s , p , d etc. bands.

The band defined by 963 has been derived with the eigenfunction 943, which contains exclusively atomic eigenfunctions all corresponding to the eigenvalue E_j and each translated on a lattice site of the solid sample. The band is centered on the energy value $E_j - A$ (refer to 963).

The band width is given by the difference between the maximum and minimum values taken by the sum in 963, and is scaled by the factor B :

$$\text{band width} = B \left(\max \left(\sum_n' \exp \left(i \vec{k} \cdot \vec{r}_n \right) \right) - \min \left(\sum_n' \exp \left(i \vec{k} \cdot \vec{r}_n \right) \right) \right)$$

The parameter B (eq. 960) is an overlap integral between the function φ_j centered on the origin and the same function centered on a first neighbor site n of the origin.

From this it follows that bands corresponding to lower energy levels of the isolated atom (that is, corresponding to innermost and thus less expanded atomic orbitals) will be narrower than bands corresponding to higher energy levels, with more expanded orbitals (valence orbitals), able to give larger overlaps.

517. Also the parameter A which appears in eq. 963 is an overlap integral (eq. 959).

If we imagine to expand uniformly the crystal, then the interatomic distance increases and this will make both A and B to decrease correspondingly and tend to zero (in the integral of B this is quite obvious, since the integrand contains φ_j functions centered on different lattice sites; in the case of the integral of A the two φ_j 's are centered on the same lattice site, but the term $v(\vec{r} - \vec{r}_m)$ is the potential due to all lattice sites *different* from site m (eq. 948), and it is this term that tends to zero as the interatomic distance increases). If both A and B tend to zero, then the band width will also tend to zero and $\epsilon(\vec{k}) \rightarrow E_j$, that is (as it must be): we fall back on the result 946 which we found for the exaggerated crystal.

Looking at this from the opposite side, if we imagine to build a crystal by bringing the constituent atoms closer and closer, eq. 963 tells us that each energy level of the isolated atom gets progressively “expanded” into a band whose width is the greater the greater the overlap between the corresponding orbitals and whose “baricenter” moves by A with respect to the eigenvalue of the isolated atom: this is probably the picture of the bands which you were presented with in the first chemistry courses.

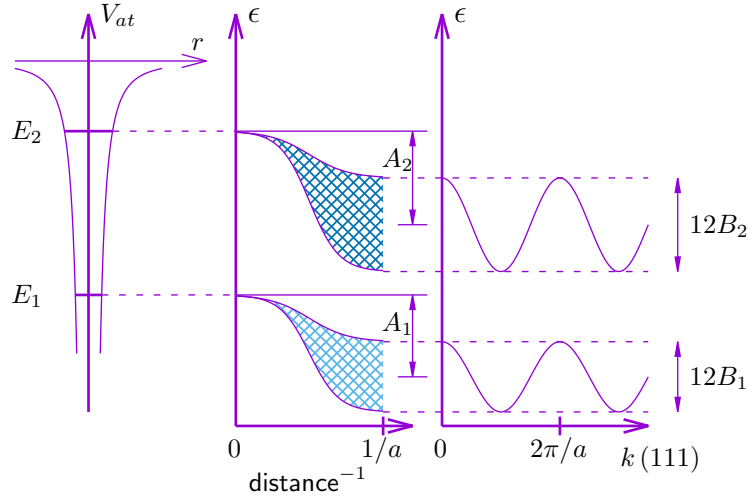


Figure 118: Left: two electronic levels subject to the potential of the isolated atom; center: as the atoms get closer and closer (the inverse distance increases), the levels expand into corresponding bands; right: the behavior of $\epsilon(\vec{k})$ for the two bands along the reciprocal direction $k(111)$.

7.7 “Tight binding” bands for a simple cubic crystal

518. We can get a more tangible feeling with the just obtained result if we use it to explicitly derive the relation $\epsilon(\vec{k})$ for the particular case of a crystal based on a simple cubic Bravais lattice with cell constant a .

In this case there are 6 first neighbors of the origin, at a distance equal to a and thus the vectors $\vec{r}_n$ appearing in the sum of 963 are:

$$(\pm a, 0, 0), (0, \pm a, 0), (0, 0, \pm a)$$

Setting $\vec{k} = (k_x, k_y, k_z)$, the sum in eq. 963 becomes:

$$\begin{aligned} \sum_n' \exp(i\vec{k} \cdot \vec{r}_n) &= \exp(ik_x a) + \exp(-ik_x a) \\ &\quad + \exp(ik_y a) + \exp(-ik_y a) \\ &\quad + \exp(ik_z a) + \exp(-ik_z a) \\ &= 2(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)) \end{aligned}$$

and thus:

$$\epsilon(\vec{k}) = \epsilon(k_x, k_y, k_z) = E_j - A - 2B(\cos(k_x a) + \cos(k_y a) + \cos(k_z a))$$

The sum of the three cosines is always inside the interval $[-3, 3]$ and therefore the band width is $2B \times (3 - (-3)) = 12B$.

The transformation of the electronic levels of the isolated atom into the corresponding bands as the atoms move closer together to form the crystal is shown qualitatively in figure 118.

Note: the graphs of $\epsilon(\vec{k})$ along the direction $k(111)$ of the reciprocal space in the figure are obtained by noting that along such direction one has:

$$k_x = k_y = k_z = k$$

and thus:

$$\epsilon(\vec{k}) = E_j - A - 6B \cos(ka)$$

7.8 Conductors, semiconductors and insulators

519.

All that you have learned in this course is only an infinitesimal part of the theory behind the electronic structure of solids. Regrettably, we have not discussed any application of this theory, due to lack of time.

However, I would like to conclude this course by revisiting, with the very little that we have learned and from a very fundamental standpoint, something that you certainly already have been told about, namely the reason why some elements or compounds are good electrical conductors, others are insulators and still others have intermediate behavior (and for this reason are called semiconductors).

520. First off, recall that for a crystalline solid sample made by N primitive cells, the first Brillouin zone contains N allowed $\vec{k}$ points (point 217). Both the eigenfunctions and the corresponding eigenvalues for a given band index are periodic functions of $\vec{k}$ (point 332): it follows that each band contains N *independent* states (we know that for each $\vec{G} \in \mathcal{R}_\mu^*$ and a given band index, the state $\Psi_{\vec{k}+\vec{G}}(\vec{r})$ is a replica of the state $\Psi_{\vec{k}}(\vec{r})$, with $\vec{k}$ inside the first Brillouin zone, section 4.6).

All over the course we assumed spin degeneracy with respect to $\vec{k}$ (this is indeed the most common situation in practice) and thus two possible states correspond to each single $\vec{k}$ point: this means that each band can “host” $2N$ electrons.

521. In order to keep this discussion as simple as possible let’s limit its scope to crystals made by a single element. Under this assumption, the bands in the ground state will be filled according to the atomic number of the element and to the number of atoms in the primitive cell.

In a crystal made by N primitive cells, each containing N_A atoms of a given element with atomic number Z , there are N_e electrons, with:

$$N_e = NN_A Z \quad (964)$$

At 0 K (ground state) these electrons occupy the bands of the crystal starting from the one at lowest (and in order of increasing) energy.

Based on what we saw for the “tight binding” model we know that the core electrons will occupy bands at lower energy, while the valence electrons will go into bands at higher energy.

The number of occupied bands can be obtained, in general, as:

$$\frac{\text{total number of electrons}}{\text{number of electrons per band}} = \frac{N_e}{2N} \quad (965)$$

If you recall the discussion about the Fermi–Dirac distribution (section 3.14) it should be clear that the electricity conducting properties (as well as many other properties which depend upon electronic excitation) can be explained by considering only the electrons at highest energy (that is, those that are close to the Fermi energy); indeed, the electrons at lower energy lack “nearby” empty energy levels which to make transitions into upon excitation (point 242).

522. In the super-simple case that we are restricting ourselves to in this discussion, we can distinguish two main cases:

1. crystals where the primitive cell contains an *odd number* of electrons, that is:

$$N_A Z = 2n + 1, \quad n \in \mathbb{N} \quad (966)$$

In this case, the occupied bands are given by (eq. 965):

$$\text{occupied bands} = \frac{N_e}{2N} = \frac{N N_A Z}{2N} = \frac{N_A Z}{2} = \frac{2n + 1}{2} = n + \frac{1}{2} \quad (967)$$

that is: the first $n = (N_A Z - 1) / 2$ bands will be completely filled while the highest energy band will be half filled.

This is the example of aluminum, which has $Z = 13$ and a single atom in the primitive cell, $N_A = 1$; so:

$$N_A Z = 2n + 1 \implies n = \frac{N_A Z - 1}{2} = \frac{1 \times 13 - 1}{2} = 6 \quad (968)$$

In crystalline *Al* the first 6 bands are completely filled, the 7-th band is half filled and the remaining bands (band index ≥ 8) will be empty.

In “tight binding” “language”:

$1s, 2s, 2p_x, 2p_y, 2p_z, 3s$	completely filled
$3p_x$	half-occupied
$3p_y, \dots$	empty

2. crystals where the primitive cell contains an *even number* of electrons, that is:

$$N_A Z = 2n, \quad n \in \mathbb{N} \quad (969)$$

In this case, the occupied bands are given by (eq. 965):

$$\text{occupied bands} = \frac{N_e}{2N} = \frac{N N_A Z}{2N} = \frac{N_A Z}{2} = \frac{2n}{2} = n \quad (970)$$

which is to say that the first $n = N_A Z / 2$ bands will be completely filled while bands with band index $\geq n + 1$ will be empty.

This is the case of selenium, with $Z = 34$, whose primitive cell, in one of its allotropic crystalline forms, contains a single atom, $N_A = 1$; thus, for selenium we have:

$$N_A Z = 2n \implies n = \frac{N_A Z}{2} = \frac{1 \times 34}{2} = 17 \quad (971)$$

which means that the lowest energy bands with band index ≤ 17 are completely filled, while those at higher energy, with band index > 17 will be empty.

Using the “tight binding” language:

$$\begin{array}{ll}
 1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z, & \\
 3d_{xy}, 3d_{xz}, 3d_{yz}, 3d_{z^2}, 3d_{x^2-y^2}, 4s, 4p_x, 4p_y & \text{completely filled} \\
 4p_z, \dots & \text{empty}
 \end{array}$$

523. Note: for the simplest case that we are considering here (a crystal with a single atom sitting on each Bravais lattice site), band occupation in the ground state works identically to electronic level occupation of an isolated single atom; in the case of the latter you know very well how to sort out the ground state configuration: you assign to each electronic level 2 electrons with opposite spin in order of increasing energy: $1s, 2s, 2p_x, 2p_y, \dots$ (Aufbau principle); in the case of the crystalline system we assign $2N$ electrons (partitioned in 2 groups of opposite spin) to each *band* in increasing energy order.

524. The highest energy *occupied* band is called *valence band* (you should easily realize the origin of the name if you refer to the “tight binding” model).

The lowest energy *unoccupied* band is called *conduction band*.

If in a crystal the valence band is not completely filled (it is half occupied, or, in general, only partially occupied), then the Fermi energy will be within the band’s limits (section 5.6.3) and there will be electrons with empty levels immediately accessible.ⁱⁱⁱ

If the solid is subjected to an electrical potential difference, the electrons close to the Fermi energy can be accelerated (thus increasing their energy and making transitions to the available empty levels) and the solid will behave as an electrical conductor.

525. If, on the other hand, the valence band is completely filled and separated from the conduction band by a band gap, then switching on a potential difference at opposite ends of the solid will not cause current flow because electrons cannot (easily) access higher energy states: in this case the solid will behave as an insulator.

526. Aluminum has an odd atomic number ($Z = 13$) and a single atom per primitive cell in the crystalline state ($N_A = 1$): as seen above, this means that the valence band of aluminium is half occupied; indeed, aluminum is a very good electrical conductor. The same holds for all alkali metals, which have an odd number of electrons.

527. Carbon has an even number of electrons ($Z = 6$) and, in the diamond crystalline form, has 2 atoms per primitive cell ($N_A = 2$): in such conditions the valence band is completely filled and diamond is an insulator.

528. The alkali earth metals are good conductors, despite having an even number of electrons. This is possible because, in these elements, the completely filled valence band overlaps the following (empty) band: there is no band gap between valence and conduction band and this allows the highest energy electrons to acquire energy in the presence of an applied electric field.

ⁱⁱⁱRecall also that, as we saw in point 216, the spacing of the levels belonging to the same band is of the order of:

$$\frac{\hbar^2 \left(\sqrt[3]{\frac{8\pi^3}{V}} \right)^2}{2m}$$

where V is the sample volume and m the mass of the electron; this number is so small that the energy levels in the same band can be considered practically continuous.

529. If the valence band is completely filled and separated by a band gap from the conduction band the solid is not necessarily an insulator. If the energy gap between valence and conduction band is small (say, of the order of 1 – 2 eV or less) then at ordinary temperature a small fraction of electrons (which would be found in the valence band at 0 K) can populate the conduction band: review the estimate of the broadening of the Fermi–Dirac distribution which we derived in section 3.14.3. In this case the electrons in the conduction band (and the electronic vacancies left in the valence band) can determine an appreciable electrical conductivity. The systems of this type are called *semiconductors*.

An example is selenium, in which, as we saw above, the valence band is completely filled; the band gap which separates it from the empty conduction band is only 1.60 eV and this makes selenium a typical semiconductor.

Figure 119 shows schematically the relation between the reciprocal position of the valence and conduction bands, their occupancy and the behavior as a conductor, semiconductor or insulator.

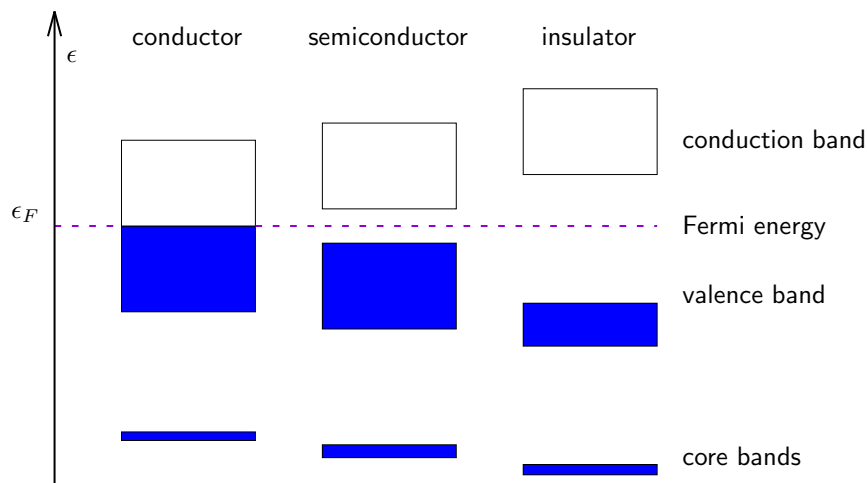


Figure 119: The relative position of the valence and conduction bands in a conductor, semiconductor and insulator.

7.9 Una derivazione alternativa della relazione di dispersione per il modello “tight binding”

530. A partire dalla 953, scambio di posto l’integrale e le somme, osservando che $\exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right)$ non dipende da $\vec{r}$ e quindi si può portare fuori dal segno di integrale:

$$= \sum_m \overbrace{\left(\sum_n \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right) \int \varphi_j^* (\vec{r} - \vec{r}_m) H \varphi_j (\vec{r} - \vec{r}_n) d\vec{r} \right)}^{\text{generico addendo della somma su } m} \quad (972)$$

Ho messo in evidenza che la somma su m è fatta da addendi che, a loro volta, sono somme su n . Ora considerate attentamente il generico addendo della somma su m :

$$\sum_n \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_m) \right) \int \varphi_j^* (\vec{r} - \vec{r}_m) H \varphi_j (\vec{r} - \vec{r}_n) d\vec{r} \quad (973)$$

Per un dato m , questa e' una somma su tutti i siti reticolari del campione, indicizzati da n .

531. Riutilizzando quanto detto ai punti 489–491, possiamo dimostrare che tutte le somme 973 sono indipendenti dal particolare vettore $\vec{r}_m$ che compare in ciascuna di esse e quindi hanno sempre lo stesso valore.

In altre parole, presi due indici qualsiasi m_1 ed m_2 della somma su m , dimostriamo che:

$$\begin{aligned} & \overbrace{\sum_n \exp \left(i\vec{k} \cdot (\vec{r}_n - \vec{r}_{m_1}) \right) \int \varphi_j^* (\vec{r} - \vec{r}_{m_1}) H \varphi_j (\vec{r} - \vec{r}_n) d\vec{r}}^{\text{per brevit\`a: } S(m_1)} \\ &= \underbrace{\sum_n \exp \left( i\vec{k} \cdot (\vec{r}_n - \vec{r}_{m_2}) \right) \int \varphi_j^* (\vec{r} - \vec{r}_{m_2}) H \varphi_j (\vec{r} - \vec{r}_n) d\vec{r}}_{\text{per brevit\`a: } S(m_2)} \end{aligned} \quad (974)$$

532. Consideriamo l'addendo s -esimo della somma $S(m_1)$:

$$\exp \left(i\vec{k} \cdot (\vec{r}_s - \vec{r}_{m_1}) \right) \int \varphi_j^* (\vec{r} - \vec{r}_{m_1}) H \varphi_j (\vec{r} - \vec{r}_s) d\vec{r} \quad (975)$$

Per il termine esponenziale possiamo fare le seguenti due osservazioni.

533. Osservazione n. 1. Utilizzando un argomento identico a quello esposto al punto 489, e' abbastanza semplice realizzare che esiste (ed e' unico) un vettore $\vec{Q} \in \mathcal{R}_M$ tale che, sommato a $\vec{r}_s - \vec{r}_{m_1}$, produce il vettore $\vec{r}_p - \vec{r}_{m_2}$, con $\vec{r}_p \in V$. In matematiche:

$$\forall s, m_1, m_2 \exists! \vec{Q}_{m_1 m_2 s} \in \mathcal{R}_M : \vec{r}_s - \vec{r}_{m_1} + \vec{Q}_{m_1 m_2 s} = \vec{r}_p - \vec{r}_{m_2} \quad \text{con } \vec{r}_p \in V \quad (976)$$

(i tre indici per $\vec{Q}$ significano semplicemente che il vettore $\vec{Q}$ e' un (unico) vettore *opportuno* che dipende da m_1, m_2 ed s)

Per verificarlo, riscrivete la 976 come:

$$\overbrace{\vec{r}_s - \vec{r}_{m_1} + \vec{r}_{m_2}}^{\in \mathcal{R}_\mu} + \vec{Q}_{m_1 m_2 s} = \vec{r}_p \quad (\in V) \quad (977)$$

Essendo una combinazione lineare di vettori di $\mathcal{R}_\mu$, il vettore $\vec{r}_s - \vec{r}_{m_1} + \vec{r}_{m_2}$ e' esso stesso un vettore di $\mathcal{R}_\mu$. Ma allora vale l'osservazione gia' fatta al punto 489, e quindi esiste un (unico) vettore di $\mathcal{R}_M$ che connette quel punto con la sua immagine *all'interno* della cella primitiva di $\mathcal{R}_M$ (cioe' V); ma questo significa che la 977, e quindi la 976, sono vere. (Ovviamente, se $\vec{r}_s - \vec{r}_{m_1} + \vec{r}_{m_2}$ e' gia' contenuto in V , sara' $\vec{Q}_{m_1 m_2 s} = 0$, il vettore nullo di $\mathcal{R}_M$).

Ho cercato di illustrare il ragionamento nella figura 120.

Per alleggerire, nel seguito sottintendero' i tre indici in $\vec{Q}_{m_1 m_2 s}$ e scrivero' semplicemente $\vec{Q}$.

534. Osservazione n. 2. Come gia' detto al punto 490, l'esponenziale:

$$\exp \left(i\vec{k} \cdot (\vec{r}_s - \vec{r}_{m_1}) \right) \quad (978)$$

e' periodico su $\mathcal{R}_M$, ovvero:

$$\exp \left(i\vec{k} \cdot (\vec{r}_s - \vec{r}_{m_1} + \vec{T}) \right) = \exp \left(i\vec{k} \cdot (\vec{r}_s - \vec{r}_{m_1}) \right) \quad \forall \vec{T} \in \mathcal{R}_M \quad (979)$$

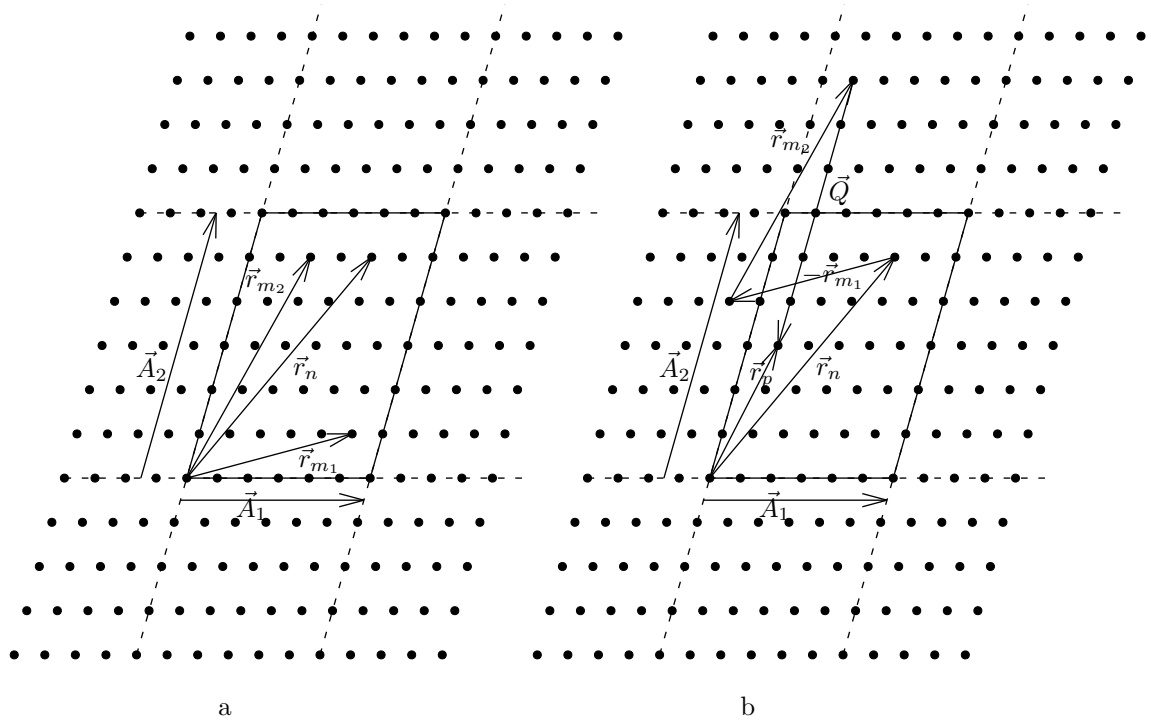


Figure 120: a: i vettori $\vec{r}_n$, $\vec{r}_{m_1}$ ed $\vec{r}_{m_2}$ interni alla cella primitiva di $\mathcal{R}_M$ che costituisce il campione solido (realizzate che l'origine dei vettori puo' essere scelta in modo totalmente arbitrario); b: la somma vettoriale $\vec{r}_n - \vec{r}_{m_1} + \vec{r}_{m_2}$ produce un vettore *esterno* al volume del campione; tuttavia, sommando a tale vettore il vettore $\vec{Q} = -\vec{A}_2 \in \mathcal{R}_M$ si ottiene il vettore $\vec{r}_p$ *interno* al volume del campione.

535. Allora, preso il vettore $\vec{Q} \in \mathcal{R}_M$ che gode della proprieta' 976 e facendo uso della 979 si ha:

$$\begin{aligned} & \exp \left(i\vec{k} \cdot (\vec{r}_s - \vec{r}_{m_1}) \right) \\ &= \exp \left(i\vec{k} \cdot (\vec{r}_s - \vec{r}_{m_1} + \vec{Q}) \right) \quad (\text{per la 979}) \\ &= \exp \left(i\vec{k} \cdot (\vec{r}_p - \vec{r}_{m_2}) \right) \quad \text{con } \vec{r}_p \in V \quad (\text{per la 976}) \end{aligned}$$

E questo mostra che il termine esponenziale dell'addendo s -esimo della somma $S(m_1)$ e' uguale al termine esponenziale dell'addendo p -esimo della somma $S(m_2)$.

536. E ora mostriamo che anche l'integrale dell'addendo s -esimo della somma $S(m_1)$ e' uguale al corrispondente integrale dell'addendo p -esimo della somma $S(m_2)$.

L'integrando della 975 e' periodico su $\mathcal{R}_M$ perche' sia le φ_j (punto 491) che l'hamiltoniano sono periodici su $\mathcal{R}_M$ (l'hamiltoniano e' periodico anche su $\mathcal{R}_\mu$, punto 332). L'integrale e' fatto sul volume del campione, che e' una cella primitiva di $\mathcal{R}_M$. Ma allora, per quanto visto a suo tempo (punto 12), l'integrale e' invariante rispetto a una traslazione arbitraria della funzione integranda. Quindi possiamo applicare la traslazione $\vec{r}_{m_1} - \vec{r}_{m_2}$ all'argomento dell'integrale senza cambiare il suo valore e ottenere (evidenzio che l'integrale e' fatto sul volume V del campione e anche che l'hamiltoniano e' funzione di $\vec{r}$):

$$\begin{aligned} & \int_V \varphi_j^* (\vec{r} - \vec{r}_{m_1}) H(\vec{r}) \varphi_j (\vec{r} - \vec{r}_s) d\vec{r} \\ & \text{l'integrale e' invariante rispetto a una traslazione di } \vec{r}_{m_1} - \vec{r}_{m_2}: \\ &= \int_V \varphi_j^* (\vec{r} - \vec{r}_{m_2}) H(\vec{r} + \vec{r}_{m_1} - \vec{r}_{m_2}) \varphi_j (\vec{r} - (\vec{r}_s - \vec{r}_{m_1} + \vec{r}_{m_2})) d\vec{r} \\ & \text{l'hamiltoniano e' periodico su } \mathcal{R}_\mu \text{ (e } \vec{r}_{m_1} - \vec{r}_{m_2} \in \mathcal{R}_\mu): \\ &= \int_V \varphi_j^* (\vec{r} - \vec{r}_{m_2}) H(\vec{r}) \varphi_j (\vec{r} - (\vec{r}_s - \vec{r}_{m_1} + \vec{r}_{m_2})) d\vec{r} \\ & \text{in base alla 976:} \\ &= \int_V \varphi_j^* (\vec{r} - \vec{r}_{m_2}) H(\vec{r}) \varphi_j \left(\vec{r} - (\vec{r}_p - \vec{Q}) \right) d\vec{r} \\ & \varphi_j \text{ e' periodica su } \mathcal{R}_M \text{ (punto 491):} \\ &= \int_V \varphi_j^* (\vec{r} - \vec{r}_{m_2}) H(\vec{r}) \varphi_j (\vec{r} - \vec{r}_p) d\vec{r} \quad (\text{con } \vec{r}_p \in V) \end{aligned} \tag{980}$$

(il vettore $\vec{Q}$ e' sempre quello che gode della proprieta' 976)

537. Abbiamo cosi' dimostrato che l'intero addendo s -esimo della somma $S(m_1)$ e' uguale all'addendo p -esimo della somma $S(m_2)$.

E siccome s era un indice qualsiasi, cio' che abbiamo appena trovato deve valere *per tutti* gli addendi di $S(m_1)$.

Ovviamente, a ciascun addendo di $S(m_1)$ corrispondera' un diverso addendo di $S(m_2)$; ma cio' che conta e' che ogni addendo di $S(m_1)$ e' mappato su un addendo di $S(m_2)$ che ha esattamente *lo stesso valore numerico*. Ho cercato di illustrare graficamente l'idea nella figura 121.

Ma questo significa proprio che la somma $S(m_1)$ ha lo stesso valore della somma $S(m_2)$, ovvero la validita' della 974.

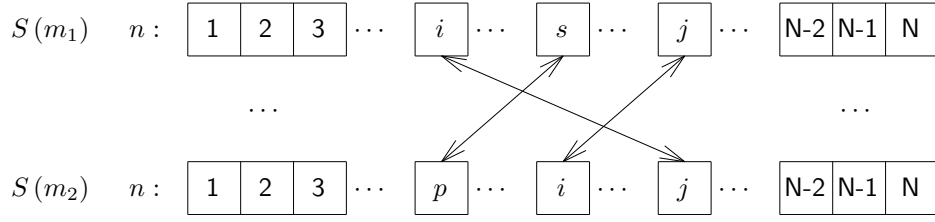


Figure 121: Ogni addendo della somma $S(m_1)$ e' mappato su un corrispondente addendo della somma $S(m_2)$ avente un *identico valore numerico*. "Chi viene mappato su chi" dipende da m_1 ed m_2 e non ha alcuna importanza nel presente contesto: la cosa importante e' che in ogni caso i vettori delle due somme sono *interni* al volume V del campione, come deve essere in base alla definizione delle somme stesse. Nella figura l'addendo s -esimo di $S(m_1)$ e' mappato sull'addendo p -esimo di $S(m_2)$ (cioe' gli addendi s e p hanno lo stesso valore numerico); l'addendo i -esimo di $S(m_1)$ e' mappato sull'addendo j -esimo di $S(m_2)$ e cosi' via.

Infine, siccome m_1 ed m_2 erano due indici qualsiasi, rimane definitivamente provato che tutte le somme 973 hanno un identico valore comune.

538. Ma allora, nella 972, la somma su m e' una somma di addendi tutti uguali e quindi possiamo sostituirla con un semplice fattore N (ricordate che N e' il numero di celle primitive del campione, cioe' dei suoi siti reticolari e quindi e' anche il numero degli addendi che compaiono nelle somme su m ed n). Inoltre, siccome gli N addendi hanno tutti lo stesso valore, possiamo prendere come valore comune quello dell'addendo corrispondente a $\vec{r}_m = 0$. Possiamo cosi' continuare riprendendo dalla 972:

$$= N \sum_n \exp(i\vec{k} \cdot \vec{r}_n) \int \varphi_j^*(\vec{r}) H \varphi_j(\vec{r} - \vec{r}_n) d\vec{r} \quad (981)$$

539. Ora estraggo il termine con $\vec{r}_n = 0$ dalla somma su n .

Nel termine estratto dalla sommatoria l'esponenziale e' diventato 1 (perche' $\vec{r}_n = 0$) e anche $\varphi_j(\vec{r} - \vec{r}_n) \rightarrow \varphi_j(\vec{r})$:

$$= N \left(\overbrace{\int \varphi_j^*(\vec{r}) H \varphi_j(\vec{r}) d\vec{r}}^{\vec{r}_n=0} + \sum_{\vec{r}_n \neq 0} \exp(i\vec{k} \cdot \vec{r}_n) \int \varphi_j^*(\vec{r}) H \varphi_j(\vec{r} - \vec{r}_n) d\vec{r} \right) \quad (982)$$

540. Per il primo integrale della 982, scrivendo l'hamiltoniano come (punto 498):

$$\begin{aligned} H &= -\frac{\hbar^2}{2m} \nabla^2 + V_{at}(\vec{r}) + \overbrace{\sum_{\vec{r}_n \neq 0} V_{at}(\vec{r} - \vec{r}_n)}^{v(\vec{r})} \\ &= H_{at}(\vec{r}) + v(\vec{r}) \end{aligned} \quad (983)$$

(cioe' ho estratto dalla sommatoria il termine corrispondente a $\vec{r}_n = 0$) e ricordando che φ_j e' autofunzione di H_{at} con autvalore E_j , si ha:

$$\begin{aligned}
\int \varphi_j^*(\vec{r}) H \varphi_j(\vec{r}) d\vec{r} &= \int \varphi_j^*(\vec{r}) (H_{at} + v) \varphi_j(\vec{r}) d\vec{r} \\
&= \overbrace{\int \varphi_j^*(\vec{r}) H_{at} \varphi_j(\vec{r}) d\vec{r}}^{E_j} + \overbrace{\int \varphi_j^*(\vec{r}) v(\vec{r}) \varphi_j(\vec{r}) d\vec{r}}^{-A} \\
&= E_j - A
\end{aligned} \tag{984}$$

dove abbiamo definito:

$$\int \varphi_j^*(\vec{r}) v(\vec{r}) \varphi_j(\vec{r}) d\vec{r} = -A \tag{985}$$

(il segno $-$ e' semplicemente perche' vogliamo che A , che e' un parametro del modello, sia positivo, mentre l'integrale e' (quasi invariabilmente) negativo, visto che il potenziale esercitato sull'elettrone dal resto del cristallo, $v(\vec{r})$, e' di tipo attrattivo)

Nel ricavare la 984 ho anche sfruttato il fatto che le φ_j sono normalizzate.

541. Questo e' un punto in cui si manifesta un'altro aspetto peculiare del modello "tight binding": l'integrale con l'operatore dell'energia potenziale dovuta al cristallo, $v(\vec{r})$, e' qualche cosa che, in generale, e' difficile da calcolare in modo esplicito. Per cui lo poniamo uguale a una costante, $-A$, che deve essere in qualche modo introdotta nel modello come parametro: potra' essere calcolata in modo approssimato, oppure ricavata in modo empirico da dati sperimentali.

Notate che nel cristallo con distanza internucleare di 1 cm si avrebbe $A = 0$. Infatti nella 983 $v(\vec{r})$ e' il potenziale dovuto a siti *diversi* dall'origine e quindi il termine $v(\vec{r}) \varphi_j(\vec{r})$ sarebbe nullo ($v(\vec{r}) = 0$ quando $\varphi_j(\vec{r}) \neq 0$ e viceversa).

La nostra catena di uguaglianze puo' continuare con:

$$= N \left(E_j - A + \sum_{\vec{r}_n \neq 0} \exp(i\vec{k} \cdot \vec{r}_n) \int \varphi_j^*(\vec{r}) H \varphi_j(\vec{r} - \vec{r}_n) d\vec{r} \right) \tag{986}$$

542. Ci rimane l'ultima sommatoria. Nella versione super-semplice del modello "tight binding" che stiamo sviluppando, facciamo due ulteriori assunzioni che ci permettono di arrivare al risultato finale senza troppo sforzo.

543. La prima e' che l'integrale che compare nella sommatoria sia apprezzabilmente diverso da zero solo quando il sito reticolare su cui e' centrata la funzione $\varphi_j(\vec{r} - \vec{r}_n)$ e' un primo vicino (punto 145) dell'origine (dove e' centrata la funzione $\varphi_j^*(\vec{r})$). Questa assunzione e' alla base del modello: stiamo assumendo che gli elettroni siano molto localizzati e quindi l'overlap fra funzioni atomiche centrate su siti diversi decade rapidamente a zero con la distanza fra i siti reticolari. Notate che nel cristallo con distanza internucleare di 1 cm integrali di questo tipo sarebbero nulli anche per funzioni centrate su primi vicini.

544. La seconda assunzione che facciamo e' che le funzioni φ_j abbiano simmetria sferica (e quindi siano orbitali atomici di tipo s). Questa non e' un'assunzione essenziale e il modello "tight binding" e' in grado di trattare orbitali atomici di qualsiasi tipo (s , p , d , f). Ma, come vedrete fra un attimo, assumere che le φ_j siano orbitali di tipo s a simmetria sferica ci semplifichera' molto la vita.

545. Grazie alla prima assunzione la sommatoria nella 986 puo' essere limitata ai soli primi vicini. Inoltre, grazie alla seconda assunzione (φ_j con simmetria sferica), l'integrale assume sempre lo stesso valore, perche' la distanza del sito $\vec{r}_n$ dall'origine e' sempre la stessa (il sito $\vec{r}_n$ e' sempre

e solo un primo vicino dell'origine) e l'overlap fra $\varphi_j^*(\vec{r})$ e $v(\vec{r})\varphi_j(\vec{r})$ e' indipendente da come il sito $\vec{r}_n$ e' orientato rispetto all'origine (per la simmetria sferica) (figura 117). Possiamo cosi' introdurre un secondo parametro del modello:

$$\int \varphi_j^*(\vec{r}) H \varphi_j(\vec{r} - \vec{r}_n) d\vec{r} = -B \quad (987)$$

Per il parametro B ora introdotto valgono le stesse considerazioni fatte a proposito del parametro A . Usiamo il segno $-$ per avere $B > 0$, visto che ci si aspetta che il potenziale esercitato sull'elettrone dal resto del cristallo, $v(\vec{r})$, sia di tipo attrattivo, e quindi il valore dell'integrale sia negativo. Il calcolo effettivo dell'integrale e' complesso (questo e' il motivo per cui il modello lo tratta come un parametro da introdurre "dall'esterno", ottenendolo, per esempio, da dati sperimentali).

Di nuovo, come era il caso per A ed esattamente per gli stessi motivi, anche il valore di B in un cristallo in cui gli atomi siano effettivamente e completamente isolati gli uni dagli altri, sarebbe nullo.

546. Arriviamo dunque a:

$$= N \left(E_j - A - B \sum_n' \exp \left(i\vec{k} \cdot \vec{r}_n \right) \right) \quad (988)$$

dove l'indice sulla sommatoria ci ricorda che ora essa corre solo sui primi vicini dell'origine.

Infine, sostituendo il risultato appena ottenuto e il denominatore 952 nella 951 arriviamo al risultato finale:

$$\epsilon(\vec{k}) = E_j - A - B \sum_n' \exp \left(i\vec{k} \cdot \vec{r}_n \right)$$

che e' la 963, cioe' la relazione di dispersione cercata.

A questo punto potete riprendere dal punto 515.

References

- [1] Andre' Nicolas Integral of periodic function over the length of the period is the same everywhere. 2012; <https://math.stackexchange.com/questions/98409/integral-of-periodic-function-over-the-length-of-the-period-is-the-same-everywhere>, [Online; accessed 24-August-2019]
- [2] Wikipedia contributors Euler's formula — Wikipedia, The Free Encyclopedia. 2019; https://en.wikipedia.org/w/index.php?title=Euler%27s_formula&oldid=904652298, [Online; accessed 24-August-2019]
- [3] G. Balducci Calculate Fourier series. 2021; <http://www.dschi.units.it/~balducci/sss/figures/fourier-series>
- [4] Wikipedia Fourier series — Wikipedia, The Free Encyclopedia. <http://en.wikipedia.org/w/index.php?title=Fourier%20series&oldid=1036551447>, 2021; [Online; accessed 12-September-2021]
- [5] Kittel, C. Introduction To Solid State Physics, 7th ed.; John Wiley & Sons: New York, 1996
- [6] Ref. 5, ch. 2
- [7] Ashcroft, N. W.; Mermin, N. D. Solid State Physics; Harcourt Brace College Publishers, 1976
- [8] Ref. 7, app. D
- [9] G. Balducci 1D progressive wave. 2021; http://www.dschi.units.it/~balducci/sss/figures/progr_wave/progr_wave.html
- [10] G. Balducci v - λ - T relation. 2021; <http://www.dschi.units.it/~balducci/sss/figures/v-lambda-T>
- [11] Ron Horgan Brillouin zones pictures. 2012; <http://www.damtp.cam.ac.uk/user/rrh/notes/bzpics.pdf>
- [12] G. Balducci The unit-cell-o-scope. 2021; <http://www.dschi.units.it/~balducci/sss/figures/1stbz/1stbz.php>
- [13] Harris, J. W.; Stocker, H. The Handbook of Mathematics and Computational Science; Springer-Verlag: Berlin, Heidelberg, 1998
- [14] G. Balducci Periodic Boundary Conditions. 2021; <http://www.dschi.units.it/~balducci/sss/figures/pbc/>
- [15] Ref. 7, p. 40-42
- [16] Schroeder, D. V. An Introduction To Thermal Physics; Addison Welsey Longman, 2000
- [17] Ref. 16, p.223
- [18] Ref. 16, p.247
- [19] Ref. 7, ch. 8
- [20] Ref. 5, ch. 7

- [21] Ibach, H.; Lüth, H. Solid-State Physics: An Introduction to Principles of Materials Science, 3rd ed.; Springer: Berlin, 2003
- [22] Ref. 21, ch. 7
- [23] McQuarrie, D. Quantum chemistry; University Science Books, 1983
- [24] Ref. 5, ch. 7, fig. 8
- [25] Ref. 21, fig. 7.3
- [26] Ref. 5, ch. 9, figg. 6, 7, 8 e 9
- [27] Ref. 5, pp. 189-192
- [28] Ref. 21, sec. 7.2
- [29] Ref. 7, pp. 156-159
- [30] Ref. 5, ch. 7, fig. 3a
- [31] Ref. 21, fig. 7.4
- [32] Richard Lyons Sum of two sinusoids. 2011; http://dspguru.com/sites/dspguru/files/Sum_of_Two_Sinusoids.pdf
- [33] Wikipedia atan2 — Wikipedia, The Free Encyclopedia. <https://en.wikipedia.org/wiki/Atan2>, 2025
- [34] Ref. 7, p. 144
- [35] Remy, M. Physics Letters A **1973**, 44, 203–204
- [36] Ref. 21, sec. 7.3
- [37] Hofmann, P. Solid-State Physics: An Introduction, 2nd ed.; Wiley-VCH: Weinheim, 2015