"Complementi di Fisica" Lectures 13,14

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In these lectures

- **Contents**
  - Introduction to periodic potentials: Bloch theorem
  - Simplified Kronig-Penney model for an electron in a periodic potential ("Dirac-comb", infinite crystal: detailed calculations):
    - dispersion relation *E:K*; reduced representation, 1st Brillouin zone
    - allowed and forbidden energy bands
    - crystal momentum
  - Better approximations:
    - Finite crystal, effect of boundary conditions: discrete en. levels
    - Finite barriers instead of Dirac delta-functions (results only)
  - Interpretation of forbidden bands in terms of Bragg reflections
- **Reference textbooks**
  - D.J.Griffiths, Introduction to Quantum Mechanics, Prentice-Hall, 1995, p. 198-203 ("5.3.2 Band structure"); p.61-64
  - D.A. Neamen, Semiconductor Physics and Devices, McGraw-Hill, 3rd ed., 2003, p.56-70 ("3.1 Allowed and forbidden energy bands")
  - Ch.Kittel, Introduction to Solid State Physics, J.Wiley & Sons, 7th ed., p. 176-179 ("Origin of the energy gap")

Free and bound particles: "dispersion" *E(k)*

Free: continuous energy eigenvalues

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

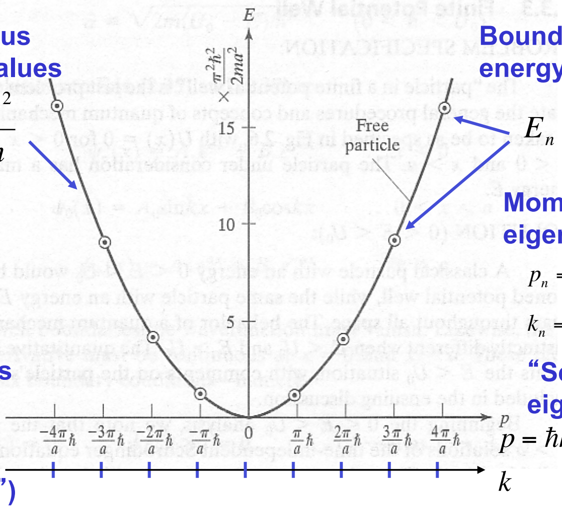
Momentum eigenvalues

$$p = \hbar k$$

"Separable" eigenfunctions

$$\psi(x) \propto e^{ikx}$$

("plane waves")



Bound: discrete energy eigenvalues

$$E_n = \frac{p_n^2}{2m}$$

Momentum eigenvalues

$$p_n = \hbar k_n$$

$$k_n = \pm n\frac{\pi}{a}$$

"Separable" eigenfunctions

$$p = \hbar k$$

$$\psi_n(x) \propto \left[e^{ik_n x} - e^{-ik_n x}\right] \propto \sin k_n x$$

Why is *E(k)* relevant? What are our plans?

Partially localized (free) particles: wave packets, superpositions of plane waves in a limited k-interval

$$\Psi(x,t) = \psi(x) e^{-i\frac{E}{\hbar}t} \propto e^{i\left(kx - \frac{\hbar k^2}{2m}t\right)} \qquad \omega \equiv \frac{E}{\hbar} = \frac{\hbar k^2}{2m}$$

The particle velocity is well represented by the group velocity

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar}\frac{dE}{dk} = \frac{\hbar k}{m} = \frac{p}{m}$$

Now:
for a particle (electron) in a periodic potential (≈ a crystal):
- **wave functions structure (periodic too ? Bloch's theorem)**
- **allowed energy eigenvalues *E* ? ⇒ "energy bands"**
- **momentum (or wave number): new "crystal momentum" concept !**
- **new (different) dispersion relation *E(K)*, similar meaning**

This is the basis for the study of the motion of electrons in crystals

Bloch's Theorem

Bloch's Theorem

Consider a single particle subject to a periodic potential energy:

$$U(x+a) = U(x)$$

The solutions ψ to the Schrödinger equation: $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi = E\psi$

are not themselves periodical, but satisfy one of the two following equivalent conditions, for some "constant" *K* depending on *E*:

Wave function, 1 period apart — Wave function

$$\psi(x+a) = e^{iKa}\psi(x) \quad \Leftrightarrow \quad \psi(x) = e^{iKx}u_K(x), \quad u_K(x+a) = u_K(x)$$

phase factor — Plane wave — Periodic amplitude

NB: although $\psi(x)$ is not periodical itself, $|\psi(x)|^2$ is periodical

$$|\psi(x+a)|^2 = |\psi(x)|^2$$

Bloch's Theorem: proof (1)

The "Translation operator" T_a changes the argument *x* by quantity *a*
It leaves the periodic potential function U(x) (period *a*) unchanged

What is its effect on the wave functions?
Just multiplication by a number… (exponential!)

$$T_a U(x) = U(x+a) = U(x) \quad \Rightarrow \quad [T_a, H] = 0$$

$$\Rightarrow \quad \text{if } \psi \text{ solution of } H\psi = E\psi \text{ then } \psi \text{ also eigenfunction of } T_a$$

$$\Rightarrow \quad T_a\psi(x) = \lambda_a \psi(x) \qquad \lambda_a = \text{eigenvalue of } T_a$$

$$\Rightarrow \quad \text{composition of two arbitrary (additive) translations:}$$

$$T_{a'}(T_a\psi(x)) = \lambda_{a'}\lambda_a\psi(x) = \lambda_{a+a'}\psi(x)$$

$$\Rightarrow \quad \lambda_a = e^{\alpha a}$$

$$\text{where: } a = \text{ displacement}, \ \alpha = \text{"constant"}, \ \alpha = \alpha(E)$$

Bloch's Theorem: proof (2)

Can we say something more about this number $\lambda_a = \exp(\alpha a)$?
From the normalization condition:

$$\int_{-\infty}^{+\infty} |T_a\psi(x)|^2 dx = \int_{-\infty}^{+\infty} |e^{\alpha a}\psi(x)|^2 dx = 1 = |e^{\alpha a}|^2 \Rightarrow$$

$$\Rightarrow \quad \alpha \quad \text{imaginary} \quad \Rightarrow \quad \alpha = iK \quad \Rightarrow \quad T_a = e^{iKa}, \quad K = K(E)$$

$$\Rightarrow \quad \boxed{\psi_E(x+a) = e^{iK(E)a}\psi_E(x)}$$

First form of the theorem: **for wave functions, the translation by the period *a* is equivalent to the multiplication by a phase *exp(iKa)*, where *K* depends on the chosen eigenvalue *E* and eigenfunction ψ_E**

Bloch's Theorem: proof (3)

OK. Can we now isolate a truly periodic part inside the wave function? Let's try, calling $u_K(x)$ the periodic function

(Equivalent question: can we isolate a term that represents a plane wave?)

$$\psi(x) \equiv A_K(x)\, u_K(x), \qquad u_K(x) = u_K(x+a)$$

$$\psi(x+a) = A_K(x+a)\, u_K(x+a) = $$
$$= A_K(x+a)\, u_K(x) =$$
$$= T_a \psi(x) =$$
$$= e^{iKa} A_K(x)\, u_K(x)$$

$$A_K(x+a) = e^{iKa} A_K(x) \quad \Leftrightarrow \quad \Leftrightarrow \quad A_K(x) = e^{iKx}$$

$$\Rightarrow \boxed{\psi(x) = e^{iKx} u_K(x), \qquad u_k(x+a) = u_k(x)}$$

Yes! This is the second form of the theorem…

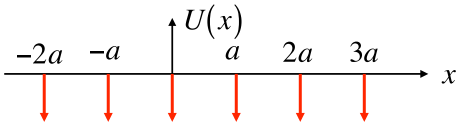
Electrons in crystals: periodic potential

A simplified model:
"Kronig-Penney",
with delta functions ("Dirac comb")

Dirac comb

A (negative) electron travelling in a crystal "sees" a periodic sequence of "traps" (positive ions: attractive forces approximately represented by static Coulomb potential wells)

To find its qualitative quantum behaviour, extreme approximation of the periodic attractive potential: "Dirac comb" with period *a*

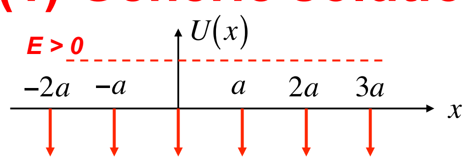


$$U(x) = -\eta \sum_{j=-\infty}^{j=+\infty} \delta(x - ja)$$

Our strategy (similar to what we did for steps and barriers):

1. Write down generic eigenfunction for one interval (e.g. $0 < x < a$)
2. Fix the unknown coefficients by applying continuity boundary conditions (periodic in this case ⇒ Bloch's theorem!)
3. Find the allowed *E* eigenvalues, and the dispersion relation *E(K)*, representing the effect of the interaction with the crystal

(1) Generic solution in an interval



$$U(x) = -\eta \sum_{j=-\infty}^{j=+\infty} \delta(x - ja)$$

time - independent Schrodinger equation : for $x \neq ja$, $U(x) = 0$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \quad \Rightarrow \quad \frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0; \quad \text{for } E > 0, \quad q^2 = \frac{2mE}{\hbar^2} > 0$$

$$\left(\text{for } E < 0, \quad q = i\alpha, \quad \alpha = \sqrt{-\frac{2mE}{\hbar^2}} > 0\right)$$

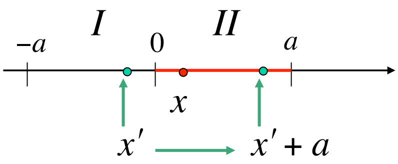
generic solution in $0 < x < a$

$\psi(x) = A\sin(qx) + B\cos(qx)$ or, completely equivalent :

$$\psi(x) = Ce^{iqx} + De^{-iqx}$$

for $x < 0$, $x > a$: Bloch's theorem and continuity conditions

(2) Effect of Bloch's theorem



Bloch:
$$\psi(x'+a) = e^{iKa}\psi(x')$$
$$\psi(x') = e^{-iKa}\psi(x'+a)$$

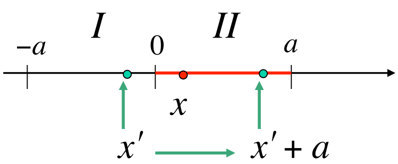
$(II) \quad 0 < x < a$

$$\psi_{II}(x) = A\sin(qx) + B\cos(qx)$$
$$\frac{d\psi_{II}}{dx} = qA\cos(qx) - qB\sin(qx)$$

$(I) \quad -a < x' < 0$

$$\psi_I(x') = e^{-iKa}\psi_{II}(x'+a) = e^{-iKa}\left[A\sin(qx'+qa) + B\cos(qx'+qa)\right]$$
$$\frac{d\psi_I}{dx'} = e^{-iKa}\left[qA\cos(qx'+qa) - qB\sin(qx'+qa)\right]$$

(3) (dis)continuity conditions at *x = 0*



Bloch:
$$\psi(x'+a) = e^{iKa}\psi(x')$$
$$\psi(x') = e^{-iKa}\psi(x'+a)$$

$x \to 0, \quad x' \to 0 \quad (x'+a \to a)$

$$\lim_{x'\to 0}\psi_I(x') = \lim_{x\to 0}\psi_{II}(x)$$
$$e^{-iKa}\left[A\sin(qa) + B\cos(qa)\right] = B$$

(1) Wave function continuity at *x = 0*

$$\left.\frac{d\psi_{II}}{dx}\right|_{x=0^+} - \left.\frac{d\psi_I}{dx'}\right|_{x'=0^-} = -\frac{2m\eta}{\hbar^2}\psi(0)$$

(2) derivative discontinuity at *x = 0*
(see Dirac-delta well)

$$qA - e^{-iKa}\left[qA\cos(qa) - qB\sin(qa)\right] = -\frac{2m\eta}{\hbar^2}B$$

(4) Find $E \Leftrightarrow q \Leftrightarrow K$

2 equations: eliminating A, B determine the relationship:

$$E = \frac{\hbar^2 q^2}{2m} \quad \leftrightarrow \quad q = \frac{\sqrt{2mE}}{\hbar} \quad \leftrightarrow \quad K$$

Energy eigenvalue

Wave number (free particle) $\left(\psi(x) \propto e^{iqx}\right)$

"Crystal" Wave number

$$\psi(x) = e^{iKx} u_K(x), \quad u_K(x) \text{ periodic}$$

$$\left(\begin{array}{c}\text{for instance:} \\ u_K(x) = Ce^{i(q-K)x} + De^{-i(q+K)x}\end{array}\right)$$

(5) Find an equation for $q \Leftrightarrow K$

2 equations: eliminating A, B determine the relationship:

$$E = \frac{\hbar^2 q^2}{2m} \quad \leftrightarrow \quad q = \frac{\sqrt{2mE}}{\hbar} \quad \leftrightarrow \quad K$$

From eq.(1): $A = B\dfrac{e^{iKa} - \cos(qa)}{\sin(qa)}$

Subst. in (2): after some rather lenghty algebra, the q ⇔ K relation is:

$$e^{iKa} + e^{-iKa} = 2\cos(qa) - \frac{2m\eta a}{\hbar^2}\frac{\sin(qa)}{qa}$$

$$\boxed{\cos(Ka) = \cos(qa) - P'\frac{\sin(qa)}{qa} = f(qa)}, \quad P' = \frac{m\eta a}{\hbar^2}$$

Particle mass (m), **Interaction strength** (η), **Lattice period** (a)

(6) Solving to find *E(K)*

Equation to be solved to find *E* for a given *K*:

$$\cos(Ka) = f(qa) = \cos(qa) - P'\frac{\sin(qa)}{qa}, \qquad P' = \frac{m\eta a}{\hbar^2}$$

$$K \;\Rightarrow\; \cos(Ka) \;\Rightarrow\; f(qa) \;\Rightarrow\; q \;\Rightarrow\; E(K)$$

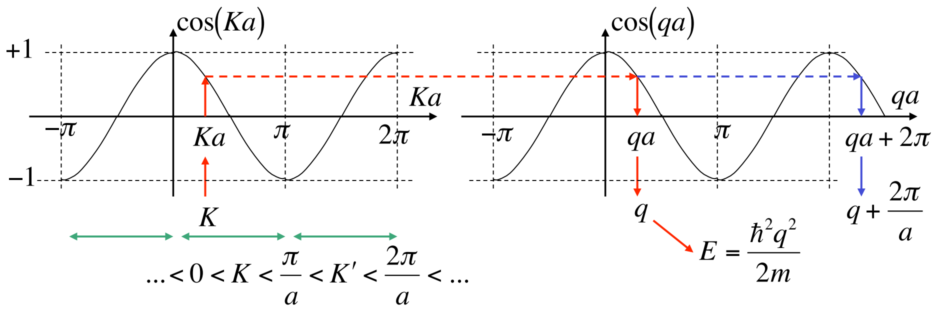
We'll see how this works in two special cases:

1. **"easy" (almost free particle: $\eta \to 0$, $P' \to 0$)**
2. **"simple to draw" (P' = 1)**

and discuss the corresponding dispersion relation E(K) (periodic, $2\pi/a$)

Special case (1): "free" particle ($\eta \to 0$)

Easy: $P' \to 0 \;\Rightarrow\; \cos(Ka) = \cos(qa) + \ldots \;\Rightarrow\; q \approx K \Rightarrow\; E(K) \approx \frac{\hbar^2 K^2}{2m}$



NB: solved piece-wise in intervals of K

changing *Ka* or *qa* by 2π give the same solutions!

Limit case (1): "free" particle ($\eta \to 0$)

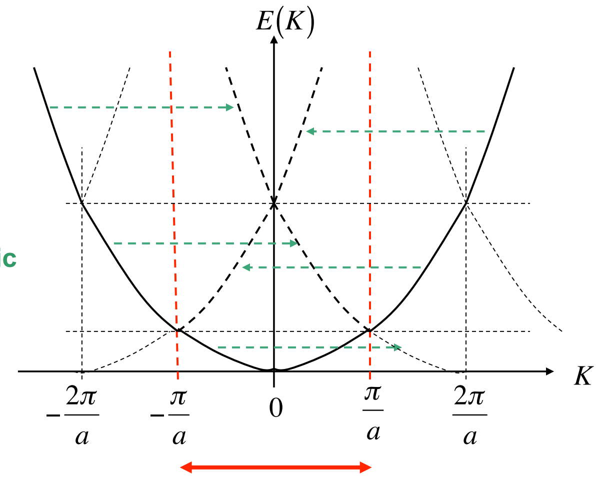
Result:

$$E(K) \to \frac{\hbar^2 K^2}{2m}$$

But:

E(K) is periodic

Period = $2\pi/a$

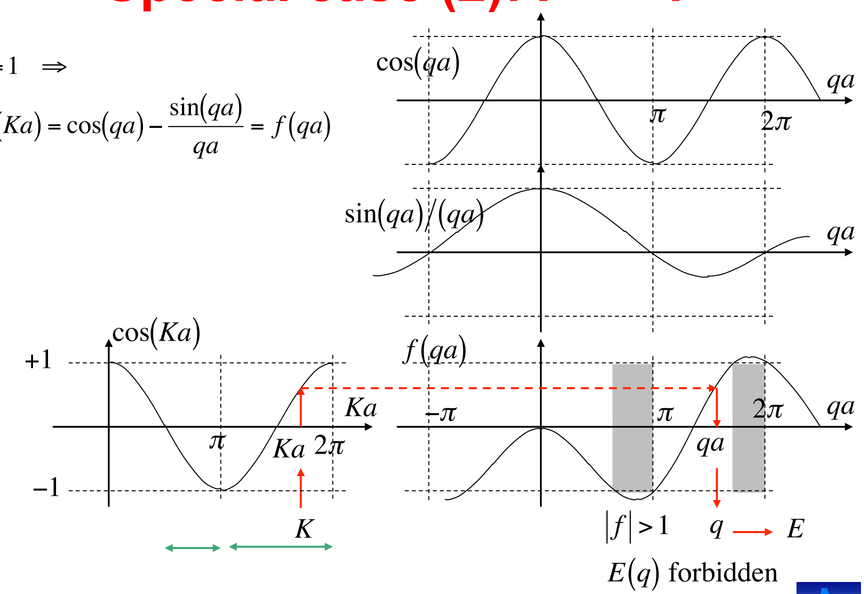


This interval ("first Brillouin zone") can be taken as representative

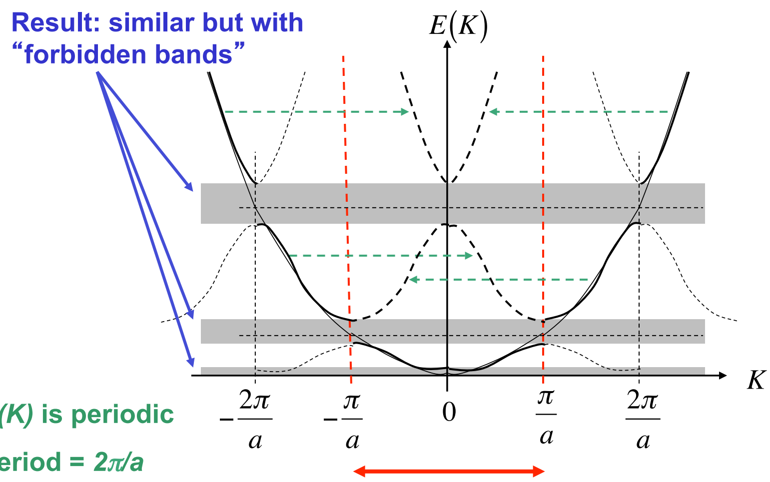
Special case (2): *P' = 1*

$$P' = 1 \quad \Rightarrow$$

$$\cos(Ka) = \cos(qa) - \frac{\sin(qa)}{qa} = f(qa)$$



Special case (2): *P’ = 1*

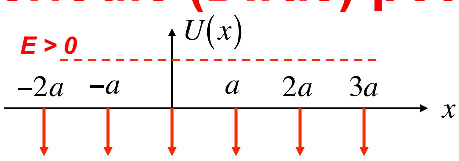


E(K) is periodic

Period = $2\pi/a$

This interval (“first Brillouin zone”) can be taken as representative

Periodic (Dirac) potential: summary



$$U(x) = -\eta \sum_{j=-\infty}^{j=+\infty} \delta(x - ja)$$

Conclusions:

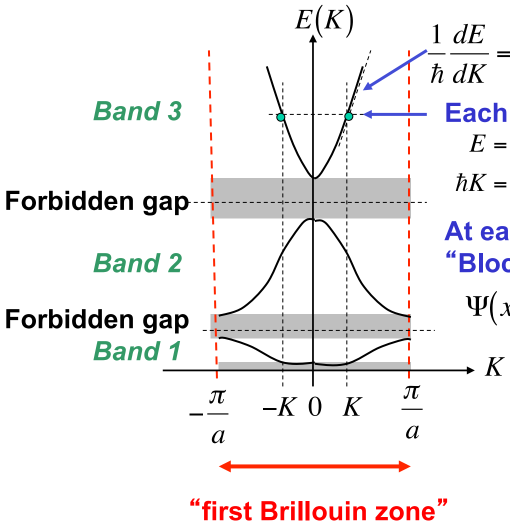
1. Wave functions: “Bloch waves” $\psi(x) = e^{iKx} u_K(x)$
2. For a given K (“crystal wave number”) NOT ALL the positive energies E > 0 are allowed
3. K is similar to the free particle wave number, but due to the periodicity of the potential:

$$K, \quad K \pm n\frac{2\pi}{a} \quad (n = 0, 1, 2, ...) \quad \text{are equivalent}$$

$$\text{for a given} \quad -\frac{\pi}{a} < K < \frac{\pi}{a} \quad \text{several } E \text{ values are possible}$$

"Band structure" diagrams

For a particle (electron) interacting with an ideal (perfect) crystal



$$\frac{1}{\hbar}\frac{dE}{dK} = v_g$$ Group velocity of a "Bloch" wave packet

Each point: one "state"

$E =$ energy

$\hbar K =$ "crystal momentum"

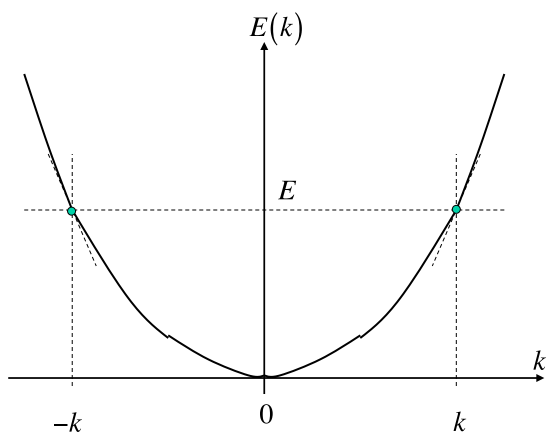
At each allowed E: two "Bloch" plane waves

$$\Psi(x,t) = u_K(x)e^{\pm iKx}e^{-i\frac{E}{\hbar}t}$$

Periodic in x

Comparison with a truly free particle

For a free particle (electron): $P' \equiv 0$ ($\eta \equiv 0$)



$$\frac{1}{\hbar}\frac{dE}{dk} = v_g$$ Group velocity of a wave packet

Each point: one "state"

$E =$ energy $= \frac{\hbar^2 k^2}{2m}$

$\hbar k =$ momentum

At each E: two plane waves

$$\Psi_\pm(x,t) = A_\pm e^{\pm ikx}e^{-i\frac{E}{\hbar}t} =$$
$$= A_\pm e^{\pm ikx}e^{-i\frac{\hbar k^2}{2m}t}$$

Extreme approximations ?

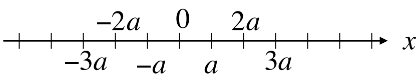
Approximations in representing the interaction with the crystal:

1. Infinite crystal ⇒ boundary conditions if finite ? ***See next*** **!**
2. "Dirac comb" ⇒ what about a more realistic (Coulomb) potential? **See applet for examples of solutions: qualitatively similar (allowed bands, forbidden gaps, etc)**
3. Perfectly periodic crystal ⇒ what about realistic defects that spoil the periodicity (impurities, dislocations, vibrations) ?

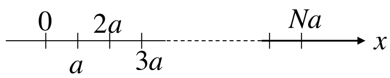
   A "perfect" crystal is "transparent" for a Bloch wave packet (electron) propagating through it, but

   Defects cause "scattering" of the Bloch wave packet, similar to isolated potential steps or barriers/wells: we will discuss this later

Finite crystal



infinite



large, but finite

N ≈ 10^{23}

Two equivalent approaches (infinite → finite):

Boundary conditions

$$\psi(0) = \psi(Na) = 0$$

$$\Rightarrow \psi(x) = A u(x) \frac{e^{iKx} - e^{-iKx}}{2i}$$

$$= A\, u(x) \sin(Kx)$$

$$\Rightarrow K\,Na = n\pi \quad \Rightarrow \quad K_n = \frac{n}{N}\frac{\pi}{a}$$

Periodic boundary conditions

$$\psi(0) = \pm\psi(Na)$$

$$\text{Bloch: } \psi(Na) = e^{iKNa}\psi(0)$$

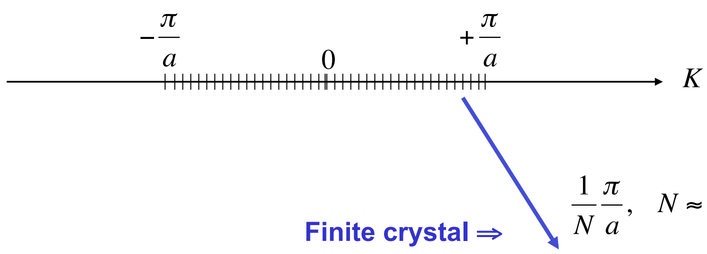
$$\Rightarrow \quad e^{iKNa} = \pm 1 \quad \Rightarrow \quad K\,Na = n\pi$$

$$\Rightarrow \quad K_n = \frac{n}{N}\frac{\pi}{a}$$

$$(n = 0, \pm 1, \pm 2, \ldots)$$

Finite crystal

in *K*-space: *N* discrete *K*-values (states) in the first Brillouin zone



$\frac{1}{N}\frac{\pi}{a}, \quad N \approx 10^{23}$

Finite crystal ⇒
⇒ *K* discrete, but small spacing

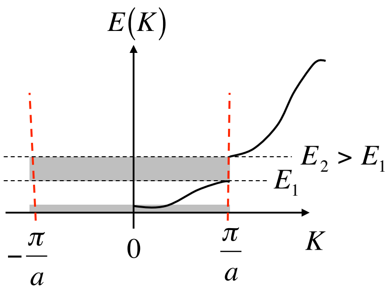
Two separate facts
(do not confuse!)

Periodic crystal (period *a*) ⇒
⇒ Periodic *E(K)*, with period *2π/a*

Forbidden bands: why?

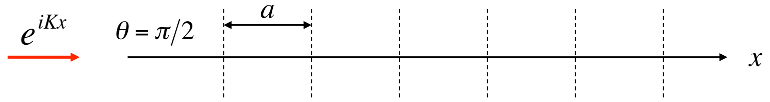
One last comment: do we qualitatively understand
the *physical meaning* of the *forbidden energy bands* ?

In other terms: why does the *E(K)* function split at *K* → ± *π/a*,
so that *E* → two different limits ($E_1 \neq E_2$)?



Answer: Bragg condition

In a 1-dimensional crystal, electrons can only propagate at right angles ($\theta = \pi/2$) with respect to the crystal "planes" spaced by period *a* $\Rightarrow$ constructive interference Bragg condition:



$$2a\sin\theta = n\lambda \quad \Leftrightarrow \quad 2a\sin\frac{\pi}{2} = 2a = n\lambda = n\frac{2\pi}{K} \quad \Leftrightarrow \quad K = n\frac{\pi}{a}$$

in the limit $n = 1, \quad K \to \frac{\pi}{a}$ two independent solutions:

$$\psi_1 \propto e^{iKx} + e^{-iKx} \propto \cos(Kx) = \cos\left(\frac{\pi}{a}x\right) \qquad |\psi_1|^2 \propto \left[\cos\left(\frac{\pi}{a}x\right)\right]^2 \qquad E_1$$

Electron preferentially close to x= 0, a, 2a, …

$$\psi_2 \propto e^{iKx} - e^{-iKx} \propto \sin(Kx) = \sin\left(\frac{\pi}{a}x\right) \qquad |\psi_2|^2 \propto \left[\sin\left(\frac{\pi}{a}x\right)\right]^2 \qquad E_2 > E_1$$

Lectures 16, 17: summary

We understood the qualitative behaviour of a particle (electron) in a periodic Dirac potential (in a crystal):

- wave functions: similar to plane waves with wave number *K*, but modulated by a periodic function (Bloch's theorem)

- allowed energy eigenvalues: "energy bands" and "forbidden gaps"

- new periodic "dispersion relations" *E(K)* describing the available states corresponding to Bloch waves, and the group velocity of Bloch wave packets

More realistic potentials give qualitatively similar results (see applet)

Next:
still ideal crystals: semi-classical electrons' motion in an external field $\Rightarrow$ "effective mass" for electrons
Then: introduce the concept of holes, and more realistic crystal