Electron levels in a periodic potential: general remarks

Outline

Mathematical tools

Plane-wave expansion of periodic functions

Fourier series expansion

- Plane waves (p.w.) are a complete and orthogonal set of functions:

$$\int_C e^{i(\boldsymbol{K}-\boldsymbol{K}_0)\cdot\boldsymbol{r}}\, d\boldsymbol{r} = \begin{cases} v & \boldsymbol{K}=\boldsymbol{K}_0 \\ 0 & \boldsymbol{K}\neq\boldsymbol{K}_0 \end{cases}$$

  - v: volume of the primitive cell C of the direct lattice $\mathcal{R}$
  - $\boldsymbol{K}$: reciprocal lattice vector, $\boldsymbol{K}\in\mathcal{R}^*$
- If $f(\boldsymbol{r}+\boldsymbol{R}) = f(\boldsymbol{r})$, $\forall\boldsymbol{r}\in\mathbb{R}^3, \forall\boldsymbol{R}\in\mathcal{R}$:

$$f(\boldsymbol{r}) = \sum_{\boldsymbol{K}} f_{\boldsymbol{K}} e^{i\boldsymbol{K}\cdot\boldsymbol{r}}$$

  - only pw with the periodicity of $\mathcal{R} \Longrightarrow \boldsymbol{k}=\boldsymbol{K}\in\mathcal{R}^*$
  - $f_{\boldsymbol{K}}$: Fourier coefficients

Mathematical tools

Plane-wave expansion of periodic functions

Fourier series expansion

- If $f(\boldsymbol{r}) = \sum_{\boldsymbol{K}_0} f_{\boldsymbol{K}_0} e^{i\boldsymbol{K}_0\cdot\boldsymbol{r}}$

$$\begin{aligned}\int_C e^{-i\boldsymbol{K}\cdot\boldsymbol{r}} f(\boldsymbol{r})\, d\boldsymbol{r} &= \sum_{\boldsymbol{K}_0} f_{\boldsymbol{K}_0} \int_C e^{i(\boldsymbol{K}_0-\boldsymbol{K})\cdot\boldsymbol{r}}\, d\boldsymbol{r} \\ &= \sum_{\boldsymbol{K}_0} f_{\boldsymbol{K}_0} v \delta_{\boldsymbol{K}_0,\boldsymbol{K}} = f_{\boldsymbol{K}} v\end{aligned}$$

- Therefore:

$$f_{\boldsymbol{K}} = \frac{1}{v} \int_C e^{-i\boldsymbol{K}\cdot\boldsymbol{r}} f(\boldsymbol{r})\, d\boldsymbol{r}$$

Mathematical tools

Plane-wave expansion of periodic functions

Applications

- For a periodic function in k-space with reciprocal-lattice periodicity:
    - $\phi(\boldsymbol{k}+\boldsymbol{K}) = \phi(\boldsymbol{k}), \quad \forall \boldsymbol{k} \in \mathbb{R}^3, \forall \boldsymbol{K} \in \mathcal{R}^*$
- Plane-wave expansion: $\phi(\boldsymbol{k}) = \sum_{\boldsymbol{R}} \phi_{\boldsymbol{R}} e^{i\boldsymbol{R}\cdot\boldsymbol{k}}$
    - $(\mathcal{R}^*)^* = \mathcal{R} \Longrightarrow \boldsymbol{R} \in \mathcal{R}$
- The Fourier coefficients are:

$$\phi_{\boldsymbol{R}} = \frac{v}{(2\pi)^3} \int d\boldsymbol{k}\, e^{-i\boldsymbol{R}\cdot\boldsymbol{k}} \phi(\boldsymbol{k})$$

- volume of the primitive cell in k-space: $\frac{(2\pi)^3}{v}$

Mathematical tools

Plane-wave expansion of periodic functions

Applications

- For a periodic function with the periodicity dictated by the Born-von Karman conditions:
  - $f(\boldsymbol{r} + N_i \boldsymbol{a}_i) = f(\boldsymbol{r}), \quad \forall \boldsymbol{k} \in \mathbb{R}^3 \quad i = 1, 2, 3$
- Primitive vectors of the direct Bravais lattice: $N_i \boldsymbol{a}_i$, $i = 1, 2, 3$
- Primitive vectors of its reciprocal lattice: $\boldsymbol{b}_i / N_i$
- Reciprocal lattice vectors:

$$\boldsymbol{k} = \sum_{i=1}^{3} \frac{m_i}{N_i} \boldsymbol{b}_i \quad m_i \in \mathbb{Z}$$

- Volume of the primitive cell of the Bravais lattice: volume of the crystal, V

Mathematical tools

Plane-wave expansion of periodic functions

Applications

- Plane-wave expansion: $f(\boldsymbol{r}) = \sum_{\boldsymbol{k}} f_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$
- The Fourier coefficients $f_{\boldsymbol{k}}$ are:

$$f_{\boldsymbol{k}} = \frac{1}{V}\int_V e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} f(\boldsymbol{r})\, d\boldsymbol{r}$$

- $\int_V e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\, d\boldsymbol{r} = 0 \quad \text{for } \boldsymbol{k} \neq 0$

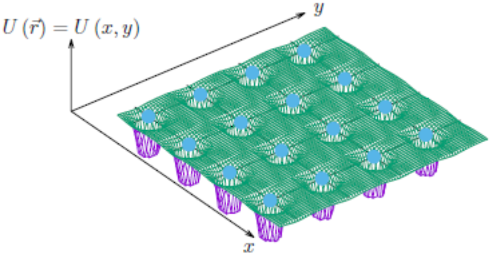
The periodic potential

The independent electron approximation

General remarks

- A lattice is a periodic array of atoms/ions
- Hence the effective potential felt by an electron is periodic:

$$U(\boldsymbol{r}+\boldsymbol{R}) = U(\boldsymbol{r}), \quad \forall \boldsymbol{R} \in \mathcal{R}, \quad \forall \boldsymbol{r} \in \mathbb{R}^3$$



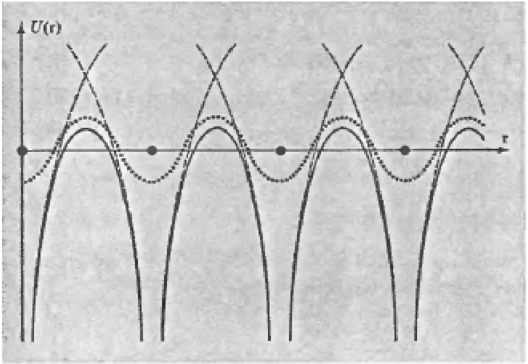
Bidimensional periodic potential

The periodic potential

The independent electron approximation

The periodic potential $U(\boldsymbol{r})$

- Essentially atomic in the region of the ionic core
- Relatively flat in the regions between fixed cores



Several sections of a crystalline periodic potential

The periodic potential

The independent electron approximation

Bloch electrons

- Satisfy the one-electron TISE for a periodic potential $U(\boldsymbol{r})$:

$$H\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r})$$

- $U(\boldsymbol{r}) = 0$ for free electrons
- The ions are assumed to be stationary
- $U(\boldsymbol{r})$ can include an effective potential to describe electron-electron interaction (mean field theories such as DFT)
- We will examine the general properties of $\psi(\boldsymbol{r})$ subject to such a potential
    - due to the translational symmetry of the problem

The periodic potential

The independent electron approximation

General remarks

- Perfect periodicity is an idealization:
  - solids are never pure
  - finite (thermal) probability of vacancies or misplaced ions
  - ion cores are never stationary (vibrations)
- Accounted as small perturbations to the problem (perturbation theory)

1. Mathematical tools
2. The periodic potential
3. Bloch's theorem and Born-von Karman boundary conditions
4. General remarks about Bloch's theorem
5. The Fermi surface
6. Density of levels

Bloch's theorem

Statements and proof

Theorem

- The solution of the TISE with a periodic potential $U(\boldsymbol{r})$ with the periodicity of the Bravais lattice $\mathcal{R}$, can be written as the product of a plane wave and a function which is $\mathcal{R}$-periodic:

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$$

- $u_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = u_{n\boldsymbol{k}}(\boldsymbol{r}), \quad \forall \boldsymbol{R} \in \mathcal{R}$
    - n: band index (vide infra)
- $\Longrightarrow \psi_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi_{n\boldsymbol{k}}(\boldsymbol{r})$

Bloch's theorem

Statements and proof

Theorem

- Equivalent form:

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi_{n\boldsymbol{k}}(\boldsymbol{r})$$

Equivalency of the two statements

- $\Longrightarrow$ follows from the periodicity of $u_{n\boldsymbol{k}}(\boldsymbol{r})$
- $\Longleftarrow$ Let $\psi_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi_{n\boldsymbol{k}}(\boldsymbol{r})$
  - $\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\psi_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\left[e^{-i\boldsymbol{k}\cdot(\boldsymbol{R}+\boldsymbol{r})}\psi_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R})\right]$
  - $u_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\psi_{n\boldsymbol{k}}(\boldsymbol{r})$ is periodic on $\mathcal{R}$: $u(\boldsymbol{r}+\boldsymbol{R}) = u(\boldsymbol{r})$
  - $\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u_{n\boldsymbol{k}}(\boldsymbol{r})$

Bloch's theorem

Statements and proof

Proof of Bloch's theorem

- $\forall \boldsymbol{R} \in \mathcal{R}$ define a translation operator $T_{\boldsymbol{R}}$:

$$T_{\boldsymbol{R}} f(\boldsymbol{r}) = f(\boldsymbol{r} + \boldsymbol{R})$$

- $T_{\boldsymbol{R}}$ is such that: $T_{\boldsymbol{R}} H(\boldsymbol{r}) = H(\boldsymbol{r} + \boldsymbol{R}) = H(\boldsymbol{r})$
  - $H = -\frac{\hbar^2}{2m}\nabla^2 + U(\boldsymbol{r})$
  - $T_{\boldsymbol{R}} U(\boldsymbol{r}) = U(\boldsymbol{r} + \boldsymbol{R}) = U(\boldsymbol{r})$ by hypothesis
  - $T_{\boldsymbol{R}} \nabla^2_{\boldsymbol{r}} = \nabla^2_{\boldsymbol{r}+\boldsymbol{R}} = \nabla^2_{\boldsymbol{r}}$ $\forall \boldsymbol{R}$ (not necessarily $\boldsymbol{R} \in \mathcal{R}$)
- Every $T_{\boldsymbol{R}}$ commutes with the Hamiltonian H:

$$T_{\boldsymbol{R}}(H\psi) = H(\boldsymbol{r} + \boldsymbol{R})\psi(\boldsymbol{r} + \boldsymbol{R}) = H(\boldsymbol{r})\psi(\boldsymbol{r} + \boldsymbol{R}) = H(T_{\boldsymbol{R}}\psi)$$

Bloch's theorem

Statements and proof

Proof of Bloch's theorem

- Furthermore:

$$T_{\boldsymbol{R}} T_{\boldsymbol{R}'} \psi(\boldsymbol{r}) = \psi(\boldsymbol{r} + \boldsymbol{R} + \boldsymbol{R}') = T_{\boldsymbol{R}+\boldsymbol{R}'} \psi(\boldsymbol{r}) = T_{\boldsymbol{R}'} T_{\boldsymbol{R}} \psi(\boldsymbol{r})$$

- $\{H, T_{\boldsymbol{R}}\}$ $\forall \boldsymbol{R} \in \mathcal{R}$ is a set of commuting operators
    - $\longrightarrow$ we can find eigenstates of H that are also eigenstates of $T_{\boldsymbol{R}}$, $\forall \boldsymbol{R} \in \mathcal{R}$
- Therefore:

$$H\psi = \varepsilon\psi$$

$$T_{\boldsymbol{R}}\psi = c(\boldsymbol{R})\psi$$

Bloch's theorem

Statement and proofs

Proof of Bloch's theorem (cont.)

- Since $T_{\boldsymbol{R}+\boldsymbol{R}'} = T_{\boldsymbol{R}} T_{\boldsymbol{R}'} \Rightarrow c(\boldsymbol{R}+\boldsymbol{R}') = c(\boldsymbol{R})c(\boldsymbol{R}')$
- $c(\sum_{i=1}^{n} \boldsymbol{R}_i) = \prod_{i=1}^{n} c(\boldsymbol{R}_i)$
- If $T_{\boldsymbol{a}_i}\psi(\boldsymbol{r}) = c(\boldsymbol{a}_i)\psi(\boldsymbol{r})$, let $c(\boldsymbol{a}_i) = e^{2\pi i x_i}$
  - $x_i \in \mathbb{C}$ $(\forall z \in \mathbb{C},\ z = |z|e^{i\theta} = e^{(\ln|z|+i\theta)} = e^{i2\pi x} \to x = \frac{\theta}{2\pi} - \frac{i}{2\pi}\ln|z|)$
- $\forall \boldsymbol{R} \in \mathcal{R}$: $\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3,\ n_i \in \mathbb{Z}$
- Therefore: $c(\boldsymbol{R}) = c(\boldsymbol{a}_1)^{n_1}c(\boldsymbol{a}_2)^{n_2}c(\boldsymbol{a}_3)^{n_3} = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}$
  - $\boldsymbol{k} = x_1\boldsymbol{b}_1 + x_2\boldsymbol{b}_2 + x_3\boldsymbol{b}_3$
  - $\boldsymbol{b}_i$: reciprocal lattice vectors $(\boldsymbol{b}_i \cdot \boldsymbol{a}_j = 2\pi\delta_{ij})$
- $T_{\boldsymbol{R}}\psi = \psi(\boldsymbol{r}+\boldsymbol{R}) = c(\boldsymbol{R})\psi = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi(\boldsymbol{r})$

Bloch's theorem

Statement and proofs

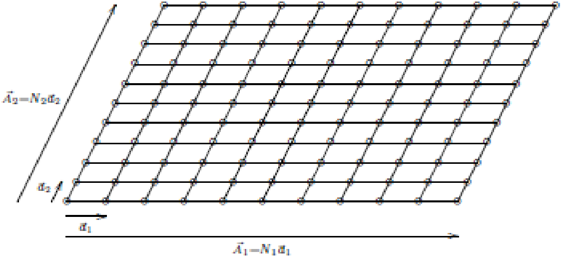
Born-von Karman boundary conditions

- Assume bulk properties are not affected by boundary conditions
- Choose a macroscopic region (of volume V) commensurate with the primitive cell
    - defined by vectors $\boldsymbol{A}_i = N_i \boldsymbol{a}_i \quad (i = 1, 2, 3) \quad N_i \sim O(N^{1/3})$, $N \sim N_A$
    - V will contain $N = N_1 N_2 N_3$ primitive cells of $\mathcal{R}$
- $\mathcal{R}$: Bravais lattice of the crystal structure $\longrightarrow \mathcal{R}_\mu$
    - C_μ denotes its primitive cell of volume v
- Bravais lattice on which $\psi(\boldsymbol{r})$ is periodic $\longrightarrow \mathcal{R}_M$
    - C_M denotes its primitive cell of volume V
    - $\Longrightarrow V = Nv$

Bloch's theorem

Statement and proofs

Born-von Karman boundary conditions



Commensurability of Bravais lattices $\mathcal{R}_\mu$ and $\mathcal{R}_M$

Bloch's theorem

Statement and proofs

Born-von Karman boundary conditions

- Impose macroscopic periodicity of the wave function:

$$\psi(\boldsymbol{r} + N_i \boldsymbol{a}_i) = \psi(\boldsymbol{r}), \quad i = 1, 2, 3$$

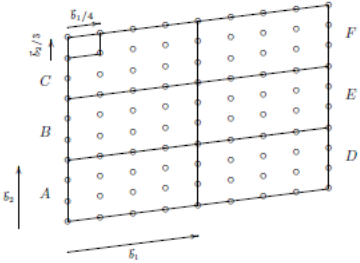
- From Bloch's theorem: $\psi_{n\boldsymbol{k}}(\boldsymbol{r} + N_i \boldsymbol{a}_i) = e^{iN_i \boldsymbol{k}\cdot\boldsymbol{a}_i}\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \psi_{n\boldsymbol{k}}(\boldsymbol{r})$
- $\Longrightarrow e^{iN_i \boldsymbol{k}\cdot\boldsymbol{a}_i} = 1 \Rightarrow e^{2\pi i N_i x_i} = 1 \Rightarrow x_i = \frac{m_i}{N_i}$ with $m_i \in \mathbb{Z}$
  - $\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij}$
- Quantization of the Bloch wave vector: $\boldsymbol{k} = \sum_{i=1}^{3} \frac{m_i}{N_i} \boldsymbol{b}_i$
  - $x_i \in \mathbb{R}$ due to the cyclic boundary conditions imposed on $\psi_{n\boldsymbol{k}}(\boldsymbol{r})$
- allowed wave vector become countable (but infinite) $\Longrightarrow$ all lattice points of $\mathcal{R}_M^*$

Bloch's theorem

Statement and proofs

Born-von Karman boundary conditions

- $\boldsymbol{k} = m_1 \boldsymbol{B}_1 + m_2 \boldsymbol{B}_2 + m_3 \boldsymbol{B}_3,\ m_i \in \mathbb{Z}$
- $\boldsymbol{B}_1 = 2\pi \frac{\boldsymbol{A}_2 \times \boldsymbol{A}_3}{\boldsymbol{A}_1 \cdot \boldsymbol{A}_2 \times \boldsymbol{A}_3} = \frac{1}{N_1} \boldsymbol{b}_1,\ \boldsymbol{B}_2 = \frac{1}{N_2} \boldsymbol{b}_2,\ \boldsymbol{B}_3 = \frac{1}{N_3} \boldsymbol{b}_3$
  - $\boldsymbol{B}_i,\ i = 1, 2, 3$ primitive vectors of $\mathcal{R}^*_M$
  - $\boldsymbol{b}_i,\ i = 1, 2, 3$ primitive vectors of $\mathcal{R}^*_\mu$



Relation between the reciprocal Bravais lattices $\mathcal{R}^*_\mu$ and $\mathcal{R}^*_M$

Bloch's theorem

Statement and proofs

Observations

- $\mathcal{R}_\mu$ and $\mathcal{R}_M$ are commensurate: $\mathcal{R}_M$ is less denser than $\mathcal{R}_\mu$
    - $\forall \boldsymbol{Q} \in \mathcal{R}_M$, $\boldsymbol{Q} \in \mathcal{R}_\mu$, the converse is not true
- $\mathcal{R}^*_\mu$ and $\mathcal{R}^*_M$ are also commensurate: $\mathcal{R}^*_\mu$ is less denser than $\mathcal{R}^*_M$.
    - $\boldsymbol{b}_i = N_i \boldsymbol{B}_i \ i = 1, 2, 3 \Longrightarrow \mathcal{R}^*_\mu \subset \mathcal{R}^*_M$
- C^*_μ contains $N = N_1 N_2 N_3$ primitive cells of $\mathcal{R}^*_M \Longrightarrow v^* = NV^*$
- Volume per allowed k in k-space: $\Delta \boldsymbol{k} = \frac{(2\pi)^3}{V}$

The central equation

Proof of Bloch's theorem by explicit construction

Derivation of the central equation

- Find solutions of the one-electron TISE for a periodic potential $U(\boldsymbol{r})$:

$$H\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r})$$

- $\psi(\boldsymbol{r})$ has a macroscopic periodicity (Born-von Karman conditions):

$$\psi(\boldsymbol{r}) = \sum_{\boldsymbol{k}} C_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

- $\boldsymbol{k} \in \mathcal{R}^*_M$: $\boldsymbol{k} = \sum_{i=1}^{3} \frac{m_i}{N_i}\boldsymbol{b}_i$
- $\longrightarrow$ find the coefficients $C_{\boldsymbol{k}}$ (and eigenvalues)

The central equation

Proof of Bloch's theorem by explicit construction

Derivation of the central equation

- $U(\boldsymbol{r})$ has the periodicity of $\mathcal{R}_\mu$: $U(\boldsymbol{r}) = \sum_{\boldsymbol{G}} U_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$

$$U_{\boldsymbol{G}} = \frac{1}{v}\int_{C_\mu} e^{-i\boldsymbol{G}\cdot\boldsymbol{r}} U(\boldsymbol{r})\, d\boldsymbol{r}$$

- Not needed for the proof but later:
    - fix the energy scale by setting $U_0 = \frac{1}{v}\int_{C_\mu} U(\boldsymbol{r})\, d\boldsymbol{r} = 0$
    - $U(\boldsymbol{r}) = U(\boldsymbol{r})^*$ and assuming inversion symmetry $U_{\boldsymbol{G}} \in \mathbb{R}$

The central equation

Proof of Bloch's theorem by explicit construction

Derivation of the central equation

- For the kinetic term:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\nabla^2\left[\sum_{\boldsymbol{k}} C_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\right] = \frac{\hbar^2}{2m}\sum_{\boldsymbol{k}} C_{\boldsymbol{k}} k^2 e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

- For the potential term:

$$U\psi(\boldsymbol{r}) = \left(\sum_{\boldsymbol{G}} U_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}\right)\left(\sum_{\boldsymbol{k}} C_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\right) = \sum_{\boldsymbol{G},\boldsymbol{k}} U_{\boldsymbol{G}} C_{\boldsymbol{k}} e^{i(\boldsymbol{G}+\boldsymbol{k})\cdot\boldsymbol{r}}$$

$$= \sum_{\boldsymbol{G},\boldsymbol{k}'} U_{\boldsymbol{G}} C_{\boldsymbol{k}'-\boldsymbol{G}} e^{i\boldsymbol{k}'\cdot\boldsymbol{r}} = \sum_{\boldsymbol{G},\boldsymbol{k}} U_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

The central equation

Proof of Bloch's theorem by explicit construction

Derivation of the central equation

- Collecting all terms:

$$\sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \left[\left(\frac{\hbar^2}{2m} k^2 - \varepsilon \right) C_{\boldsymbol{k}} + \sum_{\boldsymbol{G}} U_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} \right] = 0$$

- Using the orthogonality of plane waves:

$$\left(\frac{\hbar^2}{2m} k^2 - \varepsilon \right) C_{\boldsymbol{k}} + \sum_{\boldsymbol{G}} U_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} = 0$$

- $\forall \boldsymbol{k} \in \mathcal{R}^*_M \longrightarrow$ infinite set of equations!

The central equation

Proof of Bloch's theorem by explicit construction

Structure of the central equation

- In a given equation (indexed by $\boldsymbol{k}$) only $C_{\boldsymbol{k}'}$ with $\boldsymbol{k}'$ differing from $\boldsymbol{k}$ by a reciprocal lattice vector $\boldsymbol{G} \in \mathcal{R}_{\mu}^{*}$ enter:

$$\left(\frac{\hbar^2}{2m} k^2 - \varepsilon \right) C_{\boldsymbol{k}} + \sum_{\boldsymbol{G}} U_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} = 0$$

- N independent subsystems: the number of $\boldsymbol{k}$ points inside the primitive cell of $\mathcal{R}_{\mu}^{*}$
    - one subsystem for each allowed $\boldsymbol{k}$ in the 1st BZ of $\mathcal{R}_{\mu}^{*}$
- For fixed $\boldsymbol{k} \in$ 1st BZ of $\mathcal{R}_{\mu}^{*}$ there are an ∞ number of solutions (secular equations)

The central equation

Proof of Bloch's theorem by explicit construction

Structure of subsystem j, $j = 1, \ldots, N$

- $\boldsymbol{k}_j \in \mathcal{R}^*_M$ be a $\boldsymbol{k}$ vector inside the 1st BZ of $\mathcal{R}^*_\mu$.
- $\boldsymbol{G}_i \in \mathcal{R}^*_\mu$ enumerated such that $\boldsymbol{G}_1 = 0$.

$$\begin{cases} \left(\frac{\hbar^2}{2m} k_j^2 - \varepsilon\right) C_{\boldsymbol{k}_j} + \sum_{\boldsymbol{G}} U_{\boldsymbol{G}} C_{\boldsymbol{k}_j - \boldsymbol{G}} = 0 \\ \left(\frac{\hbar^2}{2m} |\boldsymbol{k}_j - \boldsymbol{G}_2|^2 - \varepsilon\right) C_{\boldsymbol{k}_j - \boldsymbol{G}_2} + \sum_{\boldsymbol{G}} U_{\boldsymbol{G}} C_{\boldsymbol{k}_j - \boldsymbol{G}_2 - \boldsymbol{G}} = 0 \\ \ldots \\ \left(\frac{\hbar^2}{2m} |\boldsymbol{k}_j - \boldsymbol{G}_i|^2 - \varepsilon\right) C_{\boldsymbol{k}_j - \boldsymbol{G}_i} + \sum_{\boldsymbol{G}} U_{\boldsymbol{G}} C_{\boldsymbol{k}_j - \boldsymbol{G}_i - \boldsymbol{G}} = 0 \\ \ldots \end{cases}$$

- Contains only coeffs. corresponding to reciprocal lattice vectors $\boldsymbol{k} \in S_j$:
  - $S_j = \{\boldsymbol{k} : \boldsymbol{k} = \boldsymbol{k}_j - G_i, \boldsymbol{k}_j \in \mathit{1st\ BZ} \quad \forall \boldsymbol{G}_i \in \mathcal{R}^*_\mu\}$

The central equation

Proof of Bloch's theorem by explicit construction

Structure of subsystem j, $j = 1, \dots, N$

- Each subsystem can be solved independently from the others
- The N independent subsystems constitute a partition of the full system
- Each subsystem has an ∞ number of solutions $\Longrightarrow$ need another index n to enumerate the particular solutions: $\psi_{n\boldsymbol{k}}(\boldsymbol{r})$, $\varepsilon_{n\boldsymbol{k}}$.
- n is called band index
    - enumerates the solutions in order of increasing energy: $\varepsilon_{1,\boldsymbol{k}} \leq \varepsilon_{2,\boldsymbol{k}} \leq \varepsilon_{3,\boldsymbol{k}} \dots$
- Eigenvector n can be written in the form:

$$\psi_{n\boldsymbol{k}_j}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \left(C_{\boldsymbol{k}_j - \boldsymbol{G}}\right)_n e^{i(\boldsymbol{k}_j - \boldsymbol{G})\cdot\boldsymbol{r}}$$

Bloch's theorem

Statement and proofs

Proof of Bloch's theorem by explicit construction

- For fixed $\boldsymbol{k} \in$ 1st BZ:

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \left(C_{\boldsymbol{k}-\boldsymbol{G}}\right)_n e^{i(\boldsymbol{k}-\boldsymbol{G})\cdot\boldsymbol{r}} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$$

- with $u_{n\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \left(C_{\boldsymbol{k}-\boldsymbol{G}}\right)_n e^{-i\boldsymbol{G}\cdot\boldsymbol{r}}$
- One can prove that $u_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = u_{n\boldsymbol{k}}(\boldsymbol{r})$

Bloch's theorem

General remarks

$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$

- $\boldsymbol{k}$ is not proportional to the electron's momentum
- $U(\boldsymbol{r})$ breaks the complete translational invariance of H

$$\boldsymbol{p}\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \frac{\hbar}{i}\nabla\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \hbar\boldsymbol{k}\psi_{n\boldsymbol{k}}(\boldsymbol{r}) + e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\frac{\hbar}{i}\nabla u_{n\boldsymbol{k}}(\boldsymbol{r}) \neq c \times \psi_{n\boldsymbol{k}}(\boldsymbol{r})$$

- $\boldsymbol{k} \Longrightarrow$ crystal momentum
  - full resemblance to $\frac{\boldsymbol{p}}{\hbar}$ appears when considering the response to external E.M. fields

Bloch's theorem

General remarks

$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$

- $\boldsymbol{k}$ can always be restricted to a primitive cell in k-space (often but not always taken as the 1st BZ).
- If $\boldsymbol{k}' \notin$ 1st BZ then for a given $\boldsymbol{K}$, $\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{K}$ with $\boldsymbol{k} \in$ 1st BZ: $\longrightarrow$ $\psi_{n,\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r})$ and $\varepsilon_{n,\boldsymbol{k}+\boldsymbol{K}}$ are periodic in $\boldsymbol{k}$ space:

$$\psi_{n,\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}) = \psi_{n\boldsymbol{k}}(\boldsymbol{r})$$

$$\varepsilon_{n,\boldsymbol{k}+\boldsymbol{K}} = \varepsilon_{n\boldsymbol{k}}$$

Bloch's theorem

General remarks

$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$

- Index n (band index) counts all solutions for a given $\boldsymbol{k}$.
- For solutions of the TISE of the form $\psi(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u(\boldsymbol{r})$:

$$H\psi(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \left[\frac{\hbar^2}{2m} \left(\frac{1}{i}\nabla + \boldsymbol{k} \right)^2 + U(\boldsymbol{r}) \right] u(\boldsymbol{r}) \equiv e^{i\boldsymbol{k}\cdot\boldsymbol{r}} H_{\boldsymbol{k}} u(\boldsymbol{r})$$

- $u_{\boldsymbol{k}}(\boldsymbol{r})$ satisfy

$$H_{\boldsymbol{k}} u_{\boldsymbol{k}}(\boldsymbol{r}) = \varepsilon_{\boldsymbol{k}} u_{\boldsymbol{k}}(\boldsymbol{r})$$

- b.c.: $u(\boldsymbol{r} + \boldsymbol{R}) = u(\boldsymbol{r}) \; \forall \boldsymbol{R} \in \mathcal{R}_\mu$

Bloch's theorem

General remarks

$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$

$$\begin{cases} H_{\boldsymbol{k}} u_{\boldsymbol{k}}(\boldsymbol{r}) = \varepsilon_{\boldsymbol{k}} u_{\boldsymbol{k}}(\boldsymbol{r}) \\ u(\boldsymbol{r} + \boldsymbol{R}) = u(\boldsymbol{r}) \end{cases}$$

- The eigenvalue problem is restricted to a primitive cell of $\mathcal{R}_\mu$
- The energy spectrum is discrete: levels are indexed by n
- the Hamiltonian $H_{\boldsymbol{k}}$ depends on $\boldsymbol{k}$ parametrically
- $\varepsilon_{n\boldsymbol{k}} \equiv \varepsilon_n(\boldsymbol{k})$ is a continuous function of $\boldsymbol{k}$

Bloch's theorem

General remarks

$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$

- Eigenstates and eigenvalues are periodic functions of $\boldsymbol{k}$ in the reciprocal lattice:

$$\psi_{n,\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}) = \psi_{n\boldsymbol{k}}(\boldsymbol{r})$$

$$\varepsilon_{n,\boldsymbol{k}+\boldsymbol{K}} = \varepsilon_{n\boldsymbol{k}}$$

- Leads to a description of energy levels in terms of continuous functions:

$$\varepsilon_{n\boldsymbol{k}} \equiv \varepsilon_n(\boldsymbol{k})$$

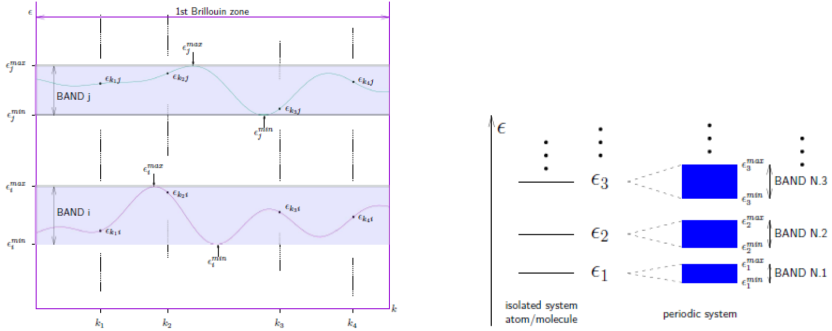
- For fixed n, $\varepsilon_n(\boldsymbol{k})$ is called energy band
- Any energy band is limited (upper and lower bounds):

$$\varepsilon_n^{\min} \leq \varepsilon_n(\boldsymbol{k}) \leq \varepsilon_n^{\max}$$

Bloch's theorem

General remarks

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$$



Bloch's theorem

General remarks

$\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n\boldsymbol{k}}(\boldsymbol{r})$

- For a $(n\boldsymbol{k})$ level, the electron mean velocity is:

$$\boldsymbol{v}_n(\boldsymbol{k}) = \frac{1}{\hbar}\nabla_{\boldsymbol{k}}\varepsilon_n(\boldsymbol{k})$$

- The electrons move without degradation of the mean velocity

1 Mathematical tools

2 The periodic potential

3 Bloch's theorem and Born-von Karman boundary conditions

4 General remarks about Bloch's theorem

5 The Fermi surface

6 Density of levels

The Fermi surface

Ground state of N Bloch electrons

Filling the one-electron levels

- Each state is labeled by two quantum numbers n and $\mathbf{k}$
  - each level accommodates two electrons
- $\mathbf{k}$ is confined to the 1st BZ
  - for a proper counting of levels
- Two possible scenarios when the N lowest-energy levels are filled:
  - a certain number of bands are completely filled, all other are empty
  - a number of bands are partially filled

The Fermi surface

Ground state of N Bloch electrons

Completely filled bands

- Band gap: $\Delta\varepsilon$ between the highest occupied level and the lowest unoccupied level
  - i.e. between the top of the highest occupied band and the bottom of the lowest empty band
- Insulators: $\Delta\varepsilon \gg k_B T$
- Intrinsic semiconductors: $\Delta\varepsilon \sim k_B T$
- Nr. of states in a band = nr. of primitive cells in the crystal

The Fermi surface

Ground state of N Bloch electrons

Partially filled bands

- ε_F (Fermi energy) of the highest occupied level lies within the energy range of one or more bands
- For each partially filled band there is a surface in k-space
  - separating occupied from empty states
  - branch of the Fermi surface in the nth band
  - analytically described by $\varepsilon_n(\mathbf{k}) = \varepsilon_F$
- The set of all branches is called Fermi surface
  - set of constant-energy surfaces
  - usually restricted to a single band of a fairly small number of bands
  - periodic in k-space with the periodicity of the reciprocal lattice
  - not present in a solid with a gap
  - metallic properties require a Fermi surface to exist

Density of levels

Density of levels in the *n*-th band

Definitions

- Consider weighted sums of one-electron properties of the form $Q = 2\sum_{n\mathbf{k}} Q_n(\mathbf{k})$
  - $\mathbf{k} = \sum_i \frac{m_i}{N_i}\mathbf{b}_i$ in the 1st BZ
  - very dense mesh in the limit of infinite V
- It is:

$$q = \lim_{V\to\infty} \frac{Q}{V} = \lim_{V\to\infty} \frac{2}{(2\pi)^3} \sum_{n\mathbf{k}} Q_n(\mathbf{k})\Delta\boldsymbol{k} = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} Q_n(\mathbf{k})$$

- Often $Q_n(\mathbf{k})$ depends on n and $\mathbf{k}$ only through the energy $\varepsilon = \varepsilon_n(\mathbf{k})$:
  - If $q = n = N/V \to Q(\varepsilon) = f(\varepsilon)$
  - If $q = u = E/V \to Q(\varepsilon) = \varepsilon f(\varepsilon)$

Density of levels

Density of levels in the *n*-th band

Definitions

- If $Q_n(\mathbf{k}) = Q(\varepsilon_n(\mathbf{k}))$:

$$q = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} Q(\varepsilon_n(\mathbf{k})) = \sum_n \int\int \frac{d\mathbf{k}}{4\pi^3} Q(\varepsilon)\delta(\varepsilon - \varepsilon_n(\mathbf{k}))\, d\varepsilon$$

$$= \sum_n \int g_n(\varepsilon) Q(\varepsilon)\, d\varepsilon = \int g(\varepsilon) Q(\varepsilon)\, d\varepsilon$$

- $g(\varepsilon) = \sum_n g_n(\varepsilon)$ density of levels (per unit volume)
- $g_n(\varepsilon)$: density of levels in the *n*-th band

Density of levels

Density of levels in the *n*-th band

Definitions

- It follows that

$$g_n(\varepsilon) = \int \frac{d\mathbf{k}}{4\pi^3}\delta(\varepsilon - \varepsilon_n(\mathbf{k}))$$

  - integral over a primitive cell of *k*-space
- In other words:

$$g_n(\varepsilon)\, d\varepsilon = \frac{2}{V} \times \begin{cases} nr.\ \ of\ allowed\ \mathbf{k}\ \ in\ the\ n\text{-}th\ band \\ in\ the\ energy\ range\ (\varepsilon, \varepsilon + d\varepsilon) \end{cases}$$

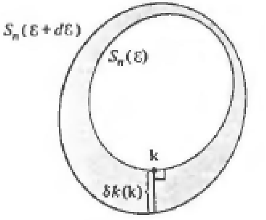
Density of levels

Density of levels in the n-th band

Definitions

- Consider the volume enclosed between the surfaces $S_n(\varepsilon)$ and $S_n(\varepsilon + d\varepsilon)$ in the primitive cell of $\mathcal{R}^*_\mu$:

$$g_n(\varepsilon)\, d\varepsilon = \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3} \delta k(\mathbf{k})$$



Density of levels

Density of levels in the *n*-th band

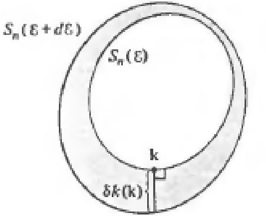
Definitions

- From

$$\varepsilon + d\varepsilon = \varepsilon + |\nabla\varepsilon_n(\mathbf{k})|\delta k(\mathbf{k})$$

$$g_n(\varepsilon) = \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3}\frac{1}{|\nabla\varepsilon_n(\mathbf{k})|}$$

  - $\nabla\varepsilon_n(\mathbf{k}) \perp S_n(\varepsilon)$
- Explicit relation between density of states and band structure

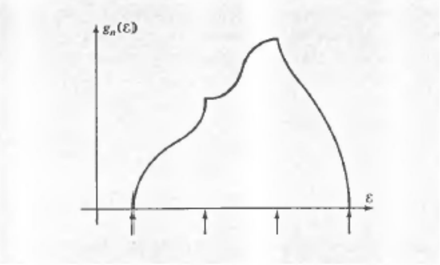


Density of levels

Density of levels in the *n*-th band

Definitions

- In each primitive cell there must be stationary points
  - points at which $|\nabla \varepsilon_n(\mathbf{k})| = 0$ (e.g. max, min)
  - since $\varepsilon_n(\mathbf{k})$ is continuous and periodic
- The integrand diverges (integrable in 3D giving finite g_n)
- Shows up as divergences in the slope (van-Hove singularities)



Typical van-Hove singularities in the density of levels