Electron levels in a periodic potential: general remarks

Outline

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

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

Mathematical toos

Plane-wave expansion of periodic functions

Fourier series expansion

- Plane waves are a complete set and orthogonal:

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

  - v: volume of the primitive cell C
  - $\boldsymbol{K}$: reciprocal lattice vector
- For a periodic function $f(\boldsymbol{r}+\boldsymbol{R}) = f(\boldsymbol{r}), \forall\boldsymbol{r}, \forall\boldsymbol{R}$:
  - $\boldsymbol{R}$: Bravais lattice vectors
- Plane-wave expansion: $f(\boldsymbol{r}) = \sum_{\boldsymbol{K}} f_{\boldsymbol{K}} e^{i\boldsymbol{K}\cdot\boldsymbol{r}}$
  - only p.w. with the periodicity of the Bravais lattice ($\boldsymbol{k}=\boldsymbol{K}$)
  - $f_{\boldsymbol{K}}$: Fourier coefficients

Mathematical toos

Plane-wave expansion of periodic functions

Fourier series expansion

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

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

- Therefore:

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

Mathematical toos

Plane-wave expansion of periodic functions

Applications

- For a periodic function in k-space with reciprocal-lattice periodicity:
  - $\phi(\boldsymbol{k}+\boldsymbol{K}) = \phi(\boldsymbol{k}), \forall \boldsymbol{k}, \forall \boldsymbol{K}$
  - $\boldsymbol{K}$: reciprocal lattice vectors
- Plane-wave expansion: $\phi(\boldsymbol{k}) = \sum_{\boldsymbol{R}} \phi_{\boldsymbol{R}} e^{i\boldsymbol{R}\cdot\boldsymbol{k}}$
  - The reciprocal of the reciprocal lattice is the direct lattice
- The Fourier coefficients $\phi_{\boldsymbol{R}}$ are:

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

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

Mathematical toos

Plane-wave expansion of periodic functions

Applications

- For a periodic function with the periodicity dictated by the Born-von Karman conditions:
  - $f(\boldsymbol{r}+N_i\boldsymbol{a}_i)=f(\boldsymbol{r}),\ i=1,2,3$
- Primitive vectors of the direct lattice: $N_i\boldsymbol{a}_i,\ i=1,2,3$
- Primitive vectors of its reciprocal lattice: $\frac{\boldsymbol{b}_i}{N_i}$
- Reciprocal lattice vectors: $\boldsymbol{k}=\sum_{i=1}^{3}\frac{m_i}{N_i}\boldsymbol{b}_i$
  - m_i integers
- Volume of the primitive cell: volume of the crystal, V

Mathematical toos

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:

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

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

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4 General remarks about Bloch's theorem

5 The Fermi surface

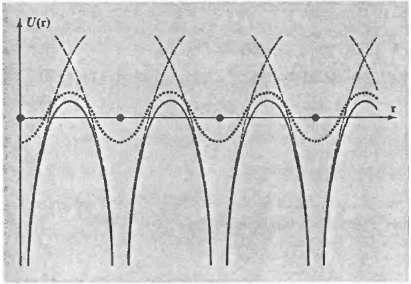
6 Density of Levels

The periodic potential

The independent electron approximation

General remarks

- A lattice is a periodic array of atoms
- Hence the effective potential felt by an electron is periodic:
    - $U(\boldsymbol{r}+\boldsymbol{R}) = U(\boldsymbol{r}),\ \forall \boldsymbol{R}$
    - $\boldsymbol{R}$: Bravais lattice vector



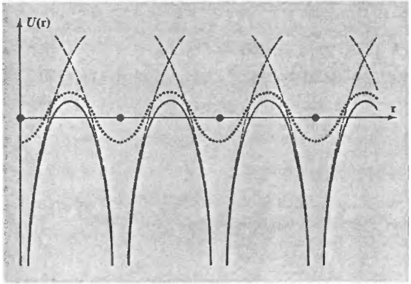
a typical crystalline periodic potential

The periodic potential

The independent electron approximation

General remarks

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



a typical crystalline periodic potential

The periodic potential

The independent electron approximation

Bloch electrons

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

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

- $U(\boldsymbol{r}) = 0$ for free electrons
- We will examine the general properties of ψ

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

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Bloch's theorem

Statement and proofs

Theorem

- The solution of the TISE with periodic $U(\boldsymbol{r})$ can be written as:

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

  - a plane wave times a periodic function $u_{n\boldsymbol{k}}(\boldsymbol{r})$
  - $u_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = u_{n\boldsymbol{k}}(\boldsymbol{r})$, $\forall \boldsymbol{R}$ Bravais lattice vectors
  - n: band index
- Implying:
  - $\psi_{n\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi_{n\boldsymbol{k}}(\boldsymbol{r})$

Bloch's theorem

Statement and proofs

Theorem

- The theorem can also be stated as:

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

- This implies all above results:
  - $u(\boldsymbol{r}) = e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\psi(\boldsymbol{r})$ is periodic: $u(\boldsymbol{r}+\boldsymbol{R}) = u(\boldsymbol{r})$
  - $\psi(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u(\boldsymbol{r})$

Bloch's theorem

Statement and proofs

Proof

- $\forall \boldsymbol{R}$ define a translation operator $T_{\boldsymbol{R}}$:
    - $T_{\boldsymbol{R}} f(\boldsymbol{r}) = f(\boldsymbol{r} + \boldsymbol{R})$
- Every $T_{\boldsymbol{R}}$ commutes with the Hamiltonian H:
    - $T_{\boldsymbol{R}}(H\psi) = H(\boldsymbol{r} + \boldsymbol{R})\psi(\boldsymbol{r} + \boldsymbol{R}) = H(\boldsymbol{r})\psi(\boldsymbol{r} + \boldsymbol{R}) = H(T_{\boldsymbol{R}}\psi)$
- Furthermore:

$$\begin{aligned} T_{\boldsymbol{R}} T_{\boldsymbol{R}'} \psi(\boldsymbol{r}) &= \psi(\boldsymbol{r} + \boldsymbol{R} + \boldsymbol{R}') = T_{\boldsymbol{R}+\boldsymbol{R}'} \psi(\boldsymbol{r}) \\ &= T_{\boldsymbol{R}'} T_{\boldsymbol{R}} \psi(\boldsymbol{r}) \end{aligned}$$

Bloch's theorem

Statement and proofs

Proof

- $\{H, T_{\boldsymbol{R}}\}\ \forall \boldsymbol{R}$ is a set of commuting operators
- Eigenstates of H are also eigenstates of $T_{\boldsymbol{R}}$, $\forall \boldsymbol{R}$:
  - $H\psi = \varepsilon\psi$
  - $T_{\boldsymbol{R}}\psi = c(\boldsymbol{R})\psi$
- Since
$$T_{\boldsymbol{R}} T_{\boldsymbol{R}'} = T_{\boldsymbol{R}+\boldsymbol{R}'} \Longrightarrow c(\boldsymbol{R}+\boldsymbol{R}') = c(\boldsymbol{R})c(\boldsymbol{R}')$$
- It follows that:
$$c(\boldsymbol{a}_i) = e^{2\pi i x_i}$$
  - x_i: complex number

Bloch's theorem

Statement and proofs

Proof

- If $\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$:

$$c(\boldsymbol{R}) = c(\boldsymbol{a}_1)^{n_1} c(\boldsymbol{a}_2)^{n_2} c(\boldsymbol{a}_3)^{n_3} = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}$$

  - $k = x_1\boldsymbol{b}_1 + x_2\boldsymbol{b}_2 + x_3\boldsymbol{b}_3$
  - $\boldsymbol{b}_i$: reciprocal lattice vectors ($\boldsymbol{b}_i \cdot \boldsymbol{a}_j = 2\pi\delta_{ij}$)
- Therefore:

$$T_{\boldsymbol{R}}\psi = \psi(\boldsymbol{r} + \boldsymbol{R}) = c(\boldsymbol{R})\psi = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi(\boldsymbol{r})$$

Bloch's theorem

Statement and proofs

Born-von Karman boundary conditions

- Assume bulk properties are not affected by boundary conditions
- Choose a macroscopic region commensurate with the primitive cell
- Impose macroscopic periodicity of the wave function:
  - $\psi(\boldsymbol{r} + N_i \boldsymbol{a}_i) = \psi(\boldsymbol{r})$, $i = 1, 2, 3$
  - $N = N_1 N_2 N_3$: total number of cells ($N_i \sim O(N^{\frac{1}{3}})$)
- From Bloch's theorem:

$$\psi_{n\boldsymbol{k}}(\boldsymbol{r} + N_i \boldsymbol{a}_i) = e^{iN_i \boldsymbol{k}\cdot\boldsymbol{a}_i}\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \psi_{n\boldsymbol{k}}(\boldsymbol{r})$$

Bloch's theorem

Statement and proofs

Born-von Karman boundary conditions

- It follows that:

$$e^{iN_i \boldsymbol{k}\cdot\boldsymbol{a}_i} = 1 \Longrightarrow e^{2\pi i N_i x_i} = 1 \Longrightarrow x_i = \frac{m_i}{N_i}$$

  - m_i integers
  - Block wave vectors: $\boldsymbol{k} = \sum_{i=1}^{3} \frac{m_i}{N_i}\boldsymbol{b}_i$
  - x_i are real due to the cyclic boundary conditions

Bloch's theorem

Statement and proofs

Born-von Karman boundary conditions

- Volume per allowed $\boldsymbol{k}$ in k-space, $\Delta\boldsymbol{k}$:

$$\begin{aligned}\Delta\boldsymbol{k} &= \frac{\boldsymbol{b}_1}{N_1}\cdot\left(\frac{\boldsymbol{b}_2}{N_2}\times\frac{\boldsymbol{b}_3}{N_3}\right)\\ &= \frac{1}{N}\boldsymbol{b}_1\cdot(\boldsymbol{b}_2\times\boldsymbol{b}_3) = \frac{(2\pi)^3}{vN}\\ &= \frac{(2\pi)^3}{V}\end{aligned}$$

  - As in the free electron case
  - The number of allowed $\boldsymbol{k}$ in a primitive cell is equal to the number of sites in the crystal

Bloch's theorem

Statement and proofs

Proof of Bloch's theorem by explicit construction

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

$$\psi(\boldsymbol{r}) = \sum_{\boldsymbol{q}} c_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$$

  - $\boldsymbol{q} = \sum_{i=1}^{3} \frac{m_i}{N_i} \boldsymbol{b}_i$
  - $c_{\boldsymbol{q}} = \frac{1}{V} \int_V e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \psi(\boldsymbol{r}) d\boldsymbol{r}$
  - V volume of the crystal

Bloch's theorem

Statement and proofs

Proof of Bloch's theorem by explicit construction

- $U(\boldsymbol{r})$ has the periodicity of the lattice:

$$U(\boldsymbol{r}) = \sum_{\boldsymbol{K}} U_{\boldsymbol{K}} e^{i\boldsymbol{K}\cdot\boldsymbol{r}}$$

  - $\boldsymbol{K}$: reciprocal lattice vectors
  - $U_{\boldsymbol{K}} = \frac{1}{v}\int_C e^{-i\boldsymbol{K}\cdot\boldsymbol{r}} U(\boldsymbol{r}) d\boldsymbol{r}$ (C volume of the primitive cell)
  - Fix the energy scale by setting $U_{\boldsymbol{0}} = \frac{1}{v}\int_C U(\boldsymbol{r}) d\boldsymbol{r} = 0$
- Since $U(\boldsymbol{r}) = U(\boldsymbol{r})^*$, and assuming inversion symmetry:
  - $\sum_{\boldsymbol{K}}(U_{\boldsymbol{K}} - U^*_{-\boldsymbol{K}}))e^{i\boldsymbol{K}\cdot\boldsymbol{r}} = 0 \Longrightarrow U_{\boldsymbol{K}} = U^*_{-\boldsymbol{K}}$
  - $U_{\boldsymbol{K}} = U_{-\boldsymbol{K}} \Longrightarrow U_{\boldsymbol{K}}$ is real

Bloch's theorem

Statement and proofs

Proof of Bloch's theorem by explicit construction

- For the kinetic term:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\nabla^2[\sum_{\boldsymbol{q}} c_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}}] = \frac{\hbar^2}{2m}\sum_{\boldsymbol{q}} c_{\boldsymbol{q}} q^2 e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$$

- For the potential term:

$$\begin{aligned} U\psi(\boldsymbol{r}) &= (\sum_{\boldsymbol{K}} U_{\boldsymbol{K}} e^{i\boldsymbol{K}\cdot\boldsymbol{r}})(\sum_{\boldsymbol{q}} c_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}}) \\ &= \sum_{\boldsymbol{K}\boldsymbol{q}} U_{\boldsymbol{K}} c_{\boldsymbol{q}} e^{i(\boldsymbol{K}+\boldsymbol{q})\cdot\boldsymbol{r}} \\ &= \sum_{\boldsymbol{K}'\boldsymbol{q}} U_{\boldsymbol{K}'} c_{\boldsymbol{q}-\boldsymbol{K}'} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \end{aligned}$$

Bloch's theorem

Statement and proofs

Proof of Bloch's theorem by explicit construction

- Collecting all terms:

$$\sum_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \left[\left(\frac{\hbar^2}{2m} q^2 - \varepsilon \right) c_{\boldsymbol{q}} + \sum_{\boldsymbol{K}'} U_{\boldsymbol{K}'} c_{\boldsymbol{q}-\boldsymbol{K}'} \right] = 0$$

- Using $\int_V e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = 0$ for $\boldsymbol{k} \neq 0$:

$$\left(\frac{\hbar^2}{2m} q^2 - \varepsilon \right) c_{\boldsymbol{q}} + \sum_{\boldsymbol{K}'} U_{\boldsymbol{K}'} c_{\boldsymbol{q}-\boldsymbol{K}'} = 0$$

- Putting $\boldsymbol{q} = \boldsymbol{k} - \boldsymbol{K}$ so that $\boldsymbol{k} \in$ 1st BZ:

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

Bloch's theorem

Statement and proofs

Proof of Bloch's theorem by explicit construction

- Putting $\boldsymbol{K}'' = \boldsymbol{K} + \boldsymbol{K}'$ and later $\boldsymbol{K}'' \to \boldsymbol{K}'$:

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

- Couples coefficients $c_{\boldsymbol{k}'}$ whose wavevector $\boldsymbol{k}'$ differ from $\boldsymbol{k}$ by a reciprocal lattice vector $\boldsymbol{K}$
- N independent problems
  - one for each allowed wavevector $\boldsymbol{k}$ in the 1st BZ
  - for fixed $\boldsymbol{k}$ there are an ∞ number of solutions (secular equations)

Bloch's theorem

Statement and proofs

Proof of Bloch's theorem by explicit construction

- Therefore, for fixed $\boldsymbol{k}$:

$$\psi(\boldsymbol{r}) = \sum_{\boldsymbol{K}} c_{\boldsymbol{k}-\boldsymbol{K}} e^{i(\boldsymbol{k}-\boldsymbol{K})\cdot\boldsymbol{r}} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u(\boldsymbol{r})$$

- with

$$u(\boldsymbol{r}) = \sum_{\boldsymbol{K}} c_{\boldsymbol{k}-\boldsymbol{K}} e^{-i\boldsymbol{K}\cdot\boldsymbol{r}}$$

  - $u(\boldsymbol{r})$ has the periodicity of the direct lattice

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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

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

    - $\boldsymbol{k}$ is called crystal momentum

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.
- $\psi(\boldsymbol{r} + \boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi(\boldsymbol{r})$ is the same for both $\boldsymbol{k}$ and $\boldsymbol{k}'$
- In summary

$$\begin{aligned} \psi_{n,\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}) &= \psi_{n\boldsymbol{k}}(\boldsymbol{r}) \\ \varepsilon_{n,\boldsymbol{k}+\boldsymbol{K}} &= \varepsilon_{n\boldsymbol{k}} \end{aligned}$$

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 $\psi(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u(\boldsymbol{r})$:

$$\begin{aligned} H\psi(\boldsymbol{r}) &= He^{i\boldsymbol{k}\cdot\boldsymbol{r}} u(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\nabla^2(e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u(\boldsymbol{r})) + U(\boldsymbol{r})e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u(\boldsymbol{r}) \\ &= e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \underbrace{\left[\frac{\hbar^2}{2m}\left(\frac{1}{i}\nabla + \boldsymbol{k}\right)^2 + U(\boldsymbol{r})\right]}_{H_{\boldsymbol{k}}} u(\boldsymbol{r}) \end{aligned}$$

- Therefore $u(\boldsymbol{r})$ satisfy $H_{\boldsymbol{k}} u_{\boldsymbol{k}}(\boldsymbol{r}) = \varepsilon_{\boldsymbol{k}} u_{\boldsymbol{k}}(\boldsymbol{r})$
- with boundary conditions $u(\boldsymbol{r} + \boldsymbol{R}) = u(\boldsymbol{r})$

Bloch's theorem

General remarks

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

- From $H_{\boldsymbol{k}} u_{\boldsymbol{k}}(\boldsymbol{r}) = \varepsilon_{\boldsymbol{k}} u_{\boldsymbol{k}}(\boldsymbol{r})$, and $u(\boldsymbol{r}+\boldsymbol{R}) = u(\boldsymbol{r})$
  - the Hermitean eigenvalue problem is restricted to a primitive cell in k-space
  - 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:

$$\begin{aligned} \psi_{n,\boldsymbol{k}+\boldsymbol{K}}(\boldsymbol{r}) &= \psi_{n\boldsymbol{k}}(\boldsymbol{r}) \\ \varepsilon_{n,\boldsymbol{k}+\boldsymbol{K}} &= \varepsilon_{n\boldsymbol{k}} \end{aligned}$$

- If we label appropriately the levels with n
- Leads to a description of energy levels in term of continuous functions $\varepsilon_{n\boldsymbol{k}} \equiv \varepsilon_n(\boldsymbol{k})$
  - band structure of the solid
  - for fixed n, $\varepsilon_n(\boldsymbol{k})$ is called energy band
  - any energy band is limited (upper and lower bounds)

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

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The Fermi surface

Ground state of N Bloch electrons

Filling the one-electron levels

- Each state is labeled by two quantum numbers n and $\boldsymbol{k}$
  - each level accomodates two electrons
- $\boldsymbol{k}$ 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: $\Delta\varepsilon >> k_B T$
- Intrinsic semiconductors: $\Delta\varepsilon \sim k_B T$

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 $\varepsilon_n(\boldsymbol{k}) = \varepsilon_F$
- 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

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6. **Density of Levels**

Density of levels

Density of levels in the *n*-th band

Definitions

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

$$q = \lim_{V\to\infty} \frac{Q}{V} = \lim_{V\to\infty} 2\frac{1}{(2\pi)^3}\sum_{n\boldsymbol{k}} Q_n(\boldsymbol{k})\Delta\boldsymbol{k} = \sum_n \int \frac{d\boldsymbol{k}}{4\pi^3} Q_n(\boldsymbol{k})$$

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

Density of levels

Density of levels in the *n*-th band

Definitions

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

$$\begin{aligned} q &= \sum_n \int \frac{d\boldsymbol{k}}{4\pi^3} Q(\varepsilon_n(\boldsymbol{k})) \\ &= \sum_n \int \int \frac{d\boldsymbol{k}}{4\pi^3} Q(\varepsilon)\delta(\varepsilon - \varepsilon_n(\boldsymbol{k}))d\varepsilon \\ &= \sum_n \int g_n(\varepsilon)Q(\varepsilon)d\varepsilon \\ &= \int g(\varepsilon)Q(\varepsilon)d\varepsilon \end{aligned}$$

- $g(\varepsilon) = \sum_n g_n(\varepsilon)$: 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 $g_n(\varepsilon) = \int \frac{d\boldsymbol{k}}{4\pi^3}\delta(\varepsilon - \varepsilon_n(\boldsymbol{k}))$
    - integral over a primitive cell of k-space
- In other words:

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

Density of levels

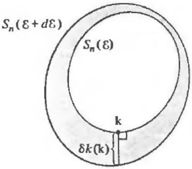
Density of levels in the n-th band

Definitions

- Consider the volume enclosed between the surfaces $\varepsilon = \varepsilon_n(\boldsymbol{k})$ ($S_n(\varepsilon)$) and $S_n(\varepsilon + d\varepsilon)$

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

  - in the primitive cell



a two-dimensional illustration

Density of levels

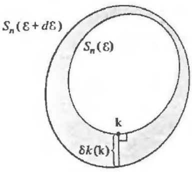
Density of levels in the *n*-th band

Definitions

- From $\varepsilon + d\varepsilon = \varepsilon + |\nabla\varepsilon_n(\boldsymbol{k})|\delta k(\boldsymbol{k})$:

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

  - note that $\nabla\varepsilon_n(\boldsymbol{k}) \perp S_n(\varepsilon)$
  - esplicit relation btw density of states and band structure



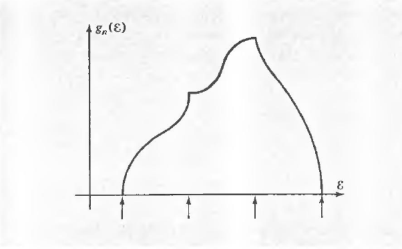
a two-dimensional illustration

Density of levels

Density of levels in the *n*-th band

Definitions

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



typical van-Hove singularities in the density of levels