Electron in a periodic potential

"Bloch electron"

Theorem that establishes general properties of a quantum particle in a Bravais lattice: $U(\vec{r}+\vec{R}) = U(\vec{r})$

(F. Bloch, 1929) extremely important!

$$\hat{H} = \frac{\hat{\vec{p}}^2}{2m} + U(\vec{r})$$

$\hat{\vec{p}} = -i\hbar\vec{\nabla}_{\vec{r}}$

↙ Breaks translational invariance:

$$[\hat{\vec{p}}, \hat{H}] = -i\hbar \frac{\partial U}{\partial \vec{r}} \neq 0$$

↓

force

$\hat{\vec{p}}$ is no longer an integral of the motion

$\Rightarrow$ no conserved quantum # $\vec{p}$

no conserved momentum in $U(\vec{r})$

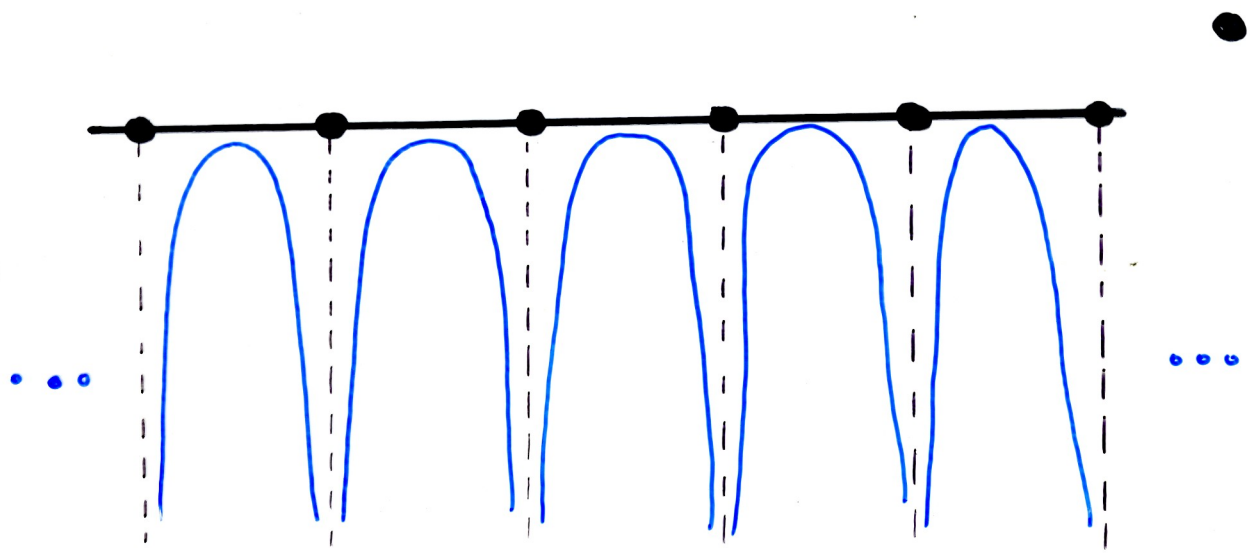
Question:

$$\hat{H}\,\psi(\vec{r}) = \varepsilon\,\psi(\vec{r})$$

How to classify states?

$$U(\vec{r}+\vec{R}) = U(\vec{r}) \qquad \vec{R} \in BL$$

When <u>crystal</u> translational symmetry is present.



what are e^- energy levels?

$\Downarrow$

energy bands $\varepsilon_s(\vec{k})$

electron crystal momentum $\vec{k}$

Brillouin zones

Theorem. $\hat{H} = \frac{\hat{\vec{p}}^2}{2m} + U(\vec{r})$,

when $U(\vec{r}+\vec{R}) = U(\vec{r})$, $\vec{R} \in BL$

$$\psi(\vec{r}) = \psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \cdot u_{\vec{k}}(\vec{r})$$

$$\hat{H}\psi_{\vec{k}}(\vec{r}) = \varepsilon(\vec{k})\,\psi_{\vec{k}}(\vec{r})$$

- eigenstates of $\hat{H}$ are labeled by electron crystal momentum $\vec{k}$
- $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \cdot u_{\vec{k}}(\vec{r})$

Bloch function is periodic $u_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r})$

$$\psi_{\vec{k}}(\vec{r}+\vec{R}) = \exp(i\vec{k}\cdot[\vec{r}+\vec{R}]) \cdot u_{\vec{k}}(\vec{r}+\vec{R})$$

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

- All physically distinct $\vec{k} \in$ 1st Brillouin zone
- $\exists$ N different $\vec{k}$ there $\equiv$ number of primitive cells

1st Proof: Based on general symmetry considerations

Translation operator $\hat{T}_{\vec{R}}$:

$$\hat{T}_{\vec{R}}\,\psi(\vec{r}) = \psi(\vec{r}+\vec{R})$$

explicit form $\hat{T}_{\vec{R}} = \exp(\vec{R}\cdot\vec{\nabla}_{\vec{r}})$

expansion in Taylor series:

$$\hat{T}_{\vec{R}}\,\psi(\vec{r}) = \sum_{n=0}^{\infty} \frac{1}{n!}(\vec{R}\cdot\vec{\nabla}_r)^n\,\psi(\vec{r})$$

$$\boxed{\hat{T}_{\vec{R}} = \exp\left(\tfrac{1}{\hbar} i\vec{R}\cdot\hat{\vec{p}}\right)}$$

Momentum operator $\hat{\vec{p}} = -i\hbar\vec{\nabla}_{\vec{r}}$: $\hbar$

is a generator of translations in real space $\vec{r}$.

$$\left[\hat{\vec{p}}, \hat{H}\right] \neq 0 \Rightarrow \text{for arbitrary } \vec{R}$$

$$\left[\hat{T}_{\vec{R}}, \hat{H}\right] \neq 0$$

2. Crystal translations $\vec{R} = \sum_i n_i \vec{a}_i \in BL$

$$\hat{T}_{\vec{R}} \hat{H} \psi(\vec{r}) = \hat{H}(\vec{r}+\vec{R}) \psi(\vec{r}+\vec{R}) = \hat{H}(\vec{r}) \hat{T}_{\vec{R}} \psi(\vec{r})$$

$$\hat{T}_{\vec{R}} \psi(\vec{r})$$

$$\forall \psi(\vec{r}) \quad \left(\hat{T}_{\vec{R}} \hat{H} - \hat{H} \hat{T}_{\vec{R}}\right) \psi(\vec{r}) = 0$$

$$\left[\hat{T}_{\vec{R}}, \hat{H}\right] \psi(\vec{r}) = 0$$

$$\Rightarrow \quad \boxed{\left[\hat{T}_{\vec{R}}, \hat{H}\right] = 0}$$

$\Updownarrow$

some symmetry exists!

Bravais lattice translations $\hat{T}_{\vec{R}}$ } a set of

Hamiltonian $\hat{H}$

+Hermiticity! of $\hat{H}$

commuting operators

$\Rightarrow$ a complete set of common eigenstates can be found

$$\hat{H}\psi = \varepsilon\psi$$

Eigenvalues

$$\hat{T}_{\vec{R}}\psi(\vec{r}) = \psi(\vec{r}+\vec{R}) = c(\vec{R})\,\psi(\vec{r})$$

$\psi(\vec{r})$ is an eigenfunction simultaneously for $\hat{H}$ and $\hat{T}_{\vec{R}}$

Repeated translations

$$\hat{T}_{\vec{R}_2}\hat{T}_{\vec{R}_1}\phi(\vec{r}) = \hat{T}_{R_2}\phi(\vec{r}+\vec{R}_1) = \phi(\vec{r}+\vec{R}_2+\vec{R}_1)$$

$$= \hat{T}(\vec{R}_1+\vec{R}_2)\phi(\vec{r})$$

$$\hat{T}_{\vec{R}_1}\phi(\vec{r}+\vec{R}_2) = \hat{T}_{\vec{R}_1}\hat{T}_{\vec{R}_2}\phi(\vec{r})$$

$$\forall\,\phi(\vec{r}) \qquad \left(\hat{T}_{\vec{R}_2}\hat{T}_{\vec{R}_1} - \hat{T}_{\vec{R}_1}\hat{T}_{\vec{R}_2}\right)\phi(\vec{r}) = 0$$

$$\Rightarrow \boxed{\left[\hat{T}_{\vec{R}_1}, \hat{T}_{\vec{R}_2}\right] = 0}$$

translations commute $\equiv$

form an Abelian group of transformations
[all elements of the group commute with each other]

Eigenvalues $C(\vec{R})$: $\hat{T}_{\vec{R}}\,\psi(\vec{r}) = C(\vec{R})\,\psi(\vec{r})$

$$\hat{T}_{\vec{R}_2}\hat{T}_{\vec{R}_1}\psi(\vec{r}) = \hat{T}_{\vec{R}_2}\,C(\vec{R}_1)\,\psi(\vec{r})$$

$$\| \qquad\qquad\qquad\qquad \|$$

$$\hat{T}_{\vec{R}_1+\vec{R}_2}\,\psi(\vec{r}) \qquad\qquad C(\vec{R}_2)\,C(\vec{R}_1)\,\psi(\vec{r})$$

$$\|$$

$$C(\vec{R}_1+\vec{R}_2)\,\psi(\vec{r})$$

used

$$\boxed{\hat{T}_{\vec{R}_2}\hat{T}_{\vec{R}_1} = \hat{T}_{\vec{R}_1+\vec{R}_2}}$$

$$\boxed{C(\vec{R}_1)\,C(\vec{R}_2) = C(\vec{R}_1+\vec{R}_2)}$$

it must be:

① $C(\vec{R}) = e^{\vec{\mu}\cdot\vec{R}} \quad \forall\ \vec{R}$ $\Rightarrow$ some vector $\vec{\mu}$ appears

② $\vec{\mu} = i\vec{k}$, $\vec{k}$ real

$\Leftrightarrow$ $e^{\vec{\mu}\cdot\vec{R}}\,\psi(\vec{r})$

suppose no $\rightarrow$ exponentially growing in some direction

For an ∞ crystal is not admissible

$$\forall \vec{R} \qquad \hat{T}_{\vec{R}}\,\psi(\vec{r}) = c(\vec{R})\,\psi(\vec{r})$$

$$c(\vec{R}) = \exp(i\vec{k}\cdot\vec{R})$$

a simultaneous eigenfunction of all translation operators satisfying the Boundary conditions for an infinite crystal

↓ No exponential growth

$\vec{k}$ is a wave vector

a general form

$$\vec{k} = x_1\cdot\vec{b}_1 + x_2\cdot\vec{b}_2 + x_3\vec{b}_3$$

primitive RL vectors

$$\vec{a}_i\cdot\vec{b}_j = 2\pi\delta_{ij}$$

BL primitive vectors

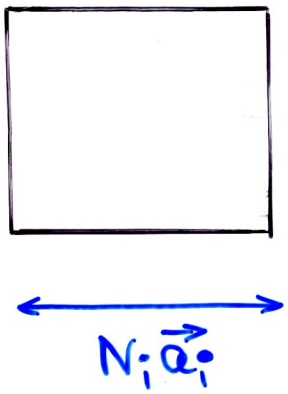
All physically distinct $\vec{k} \in$ 1st Brillouin zone

Finite (macroscopically large) crystals

$\Downarrow$

we need to impose Boundary cond.

The Born - von Karman B.C.



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

$$\psi_{\vec{k}}(\vec{r} + N_i \vec{a}_i) = e^{i \vec{k} \cdot N_i \vec{a}_i} \psi_{\vec{k}}(\vec{r})$$

$$\vec{k} \cdot N_i \vec{a}_i = 2\pi \cdot m_i \qquad m_i = 0, \pm 1, \ldots$$

$$\vec{k} = \sum_{j=1}^{3} x_j \vec{b}_j$$

$$\sum_{j=1}^{3} x_j \vec{b}_j \cdot N_i \vec{a}_i = 2\pi \cdot N_i x_i = 2\pi \cdot m_i$$

$\vec{b}_j \cdot \vec{a}_i = 2\pi \delta_{ij}$

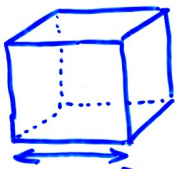
$$x_i = \frac{m_i}{N_i}$$

m_i integer

$$\vec{k} = \sum_{j=1}^{3} \frac{m_j}{N_j} \cdot \vec{b}_j$$

allowed Bloch wavevectors

$\Delta\vec{k}$, Volume in $\vec{k}$-space per 1 allowed state



$$\Delta\vec{k}_i = \frac{\vec{b}_i}{N_i}$$

$$\Delta m_i = 1$$

$$\Delta\vec{k} = \Delta\vec{k}_1 \circ \Delta\vec{k}_2 \times \Delta\vec{k}_3$$

$$\Delta\vec{k} = \frac{\vec{b}_1}{N_1} \circ \left(\frac{\vec{b}_2}{N_2} \times \frac{\vec{b}_3}{N_3} \right)$$

$$\Delta\vec{k} = \frac{\vec{b}_1 \circ (\vec{b}_2 \times \vec{b}_3)}{N_1 \cdot N_2 \cdot N_3} = \frac{v_{RL}}{N} = \frac{(2\pi)^3}{v \cdot N}$$

$$\boxed{\Delta\vec{k} = \frac{(2\pi)^3}{V}}$$ ← crystal volume

same as in the free electron case

Bloch's theorem: further development of ideas

$\hbar\vec{k}$ is crystal momentum.

it does not coincide with the momentum of the electron!

physical meaning of $\vec{k}$?

Bloch wave function $\psi_{\vec{k}} = e^{i\vec{k}\cdot\vec{r}} \cdot u_{\vec{k}}(\vec{r})$

$$\hat{\vec{p}}\,\psi_{\vec{k}} = (-i\hbar\vec{\nabla})\,\psi_{\vec{k}} = \hbar\vec{k}\cdot\psi_{\vec{k}} + e^{i\vec{k}\cdot\vec{r}}(-i\hbar)\frac{\partial u_{\vec{k}}}{\partial \vec{r}}$$

$\psi_{\vec{k}}$ is not an eigenstate of $\hat{\vec{p}}$.

Bloch electron does not have a specific momentum $\vec{p}$.

$$\updownarrow \left[\hat{\vec{p}}, \hat{H}\right] \neq 0 .$$

$\vec{k}$ is extremely important for

1. classification of states
2. studying dynamics of an electron in crystal + external fields.

All Non-equivalent $\vec{k} \in$ 1st Brillouin zone:

$$\hat{T}_{\vec{R}}\,\psi_{\vec{k}+\vec{K}}(\vec{r}) = \exp\left(i[\vec{k}+\vec{K}]\cdot\vec{R}\right)\psi_{\vec{k}+\vec{K}}(\vec{r}) .$$

$\vec{k}' = \vec{k}+\vec{K} \notin$ 1st BZ, $\vec{K} \in RL$.

$\psi_{\vec{k}+\vec{K}}$ and $\psi_{\vec{k}}$ are equivalent under translations.

Electron Bands

$\psi_{n\vec{k}}(\vec{r})$

n — discrete quantum #: Band index

$$\hat{H}\psi_{\vec{k}}(\vec{r}) = \left[\frac{\hat{\vec{p}}^2}{2m} + U(\vec{r})\right]\psi_{\vec{k}}(\vec{r})$$

$$\hat{\vec{p}}\,\psi_{\vec{k}}(\vec{r}) = \left(-i\hbar\frac{\partial}{\partial\vec{r}}\right)e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})$$

$$= e^{i\vec{k}\cdot\vec{r}}\left(\hbar\vec{k} + \hat{\vec{p}}\right)u_{\vec{k}}(\vec{r})$$

$$\hat{\vec{p}}\,\psi_{\vec{k}} \longrightarrow \left(\hat{\vec{p}} + \hbar\vec{k}\right)u_{\vec{k}}$$

$$\hat{H}\,\psi_{\vec{k}} \longrightarrow \hat{H}_{\vec{k}}\,u_{\vec{k}}$$

$$\boxed{\hat{H}_{\vec{k}} = \frac{1}{2m}\left(\hat{\vec{p}} + \hbar\vec{k}\right)^2 + U(\vec{r})}$$

$$\hat{H}_{\vec{k}}\,u_{\vec{k}}(\vec{r}) = \varepsilon_{\vec{k}}\,u_{\vec{k}}(\vec{r})$$

eigenvalue problem +

$$u_{\vec{k}}(\vec{r}+\vec{R}) = u_{\vec{k}}(\vec{r})$$

boundary conditions.

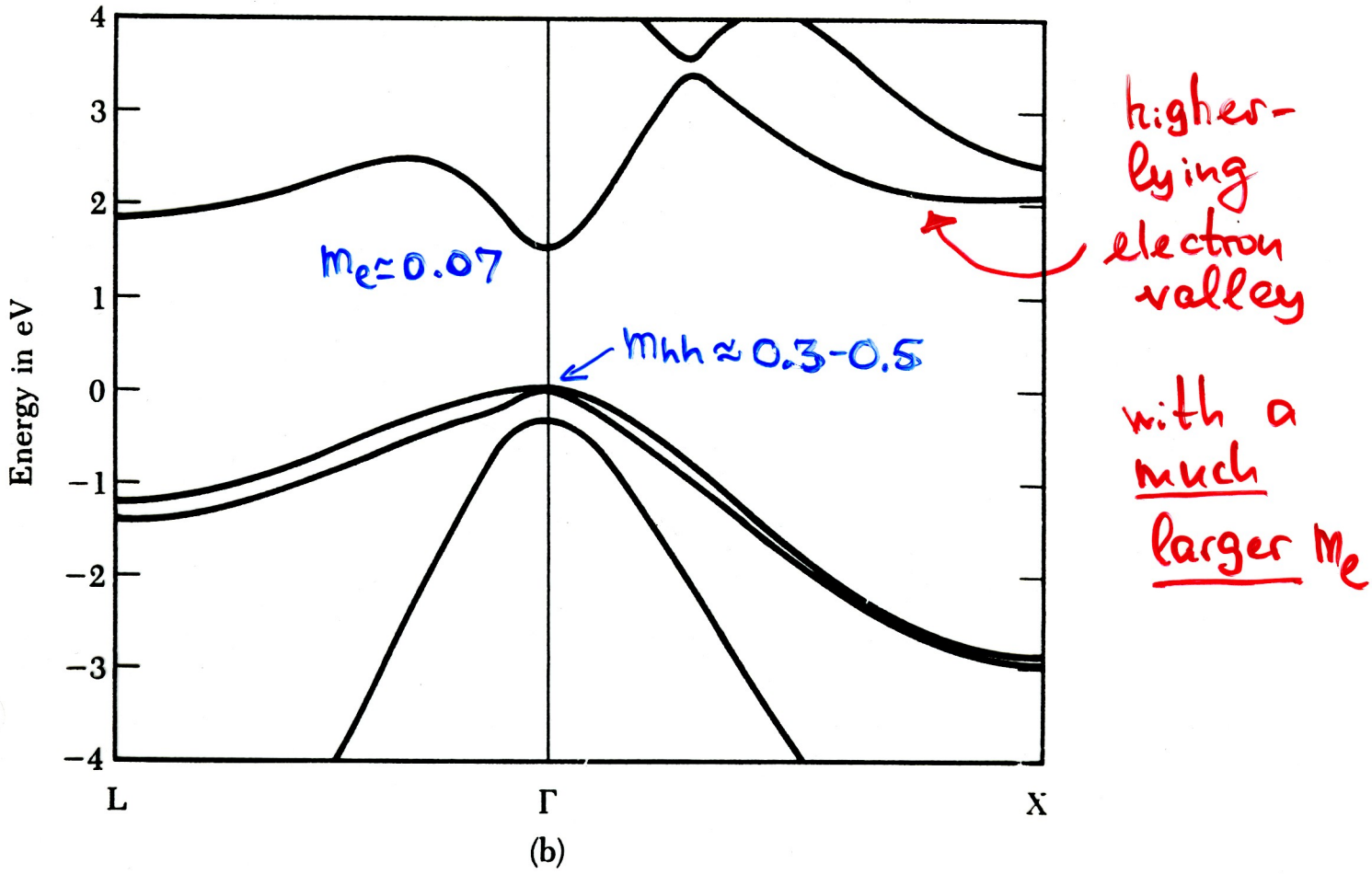


Figure 17b Band structure of GaAs, after S. G. Louie.

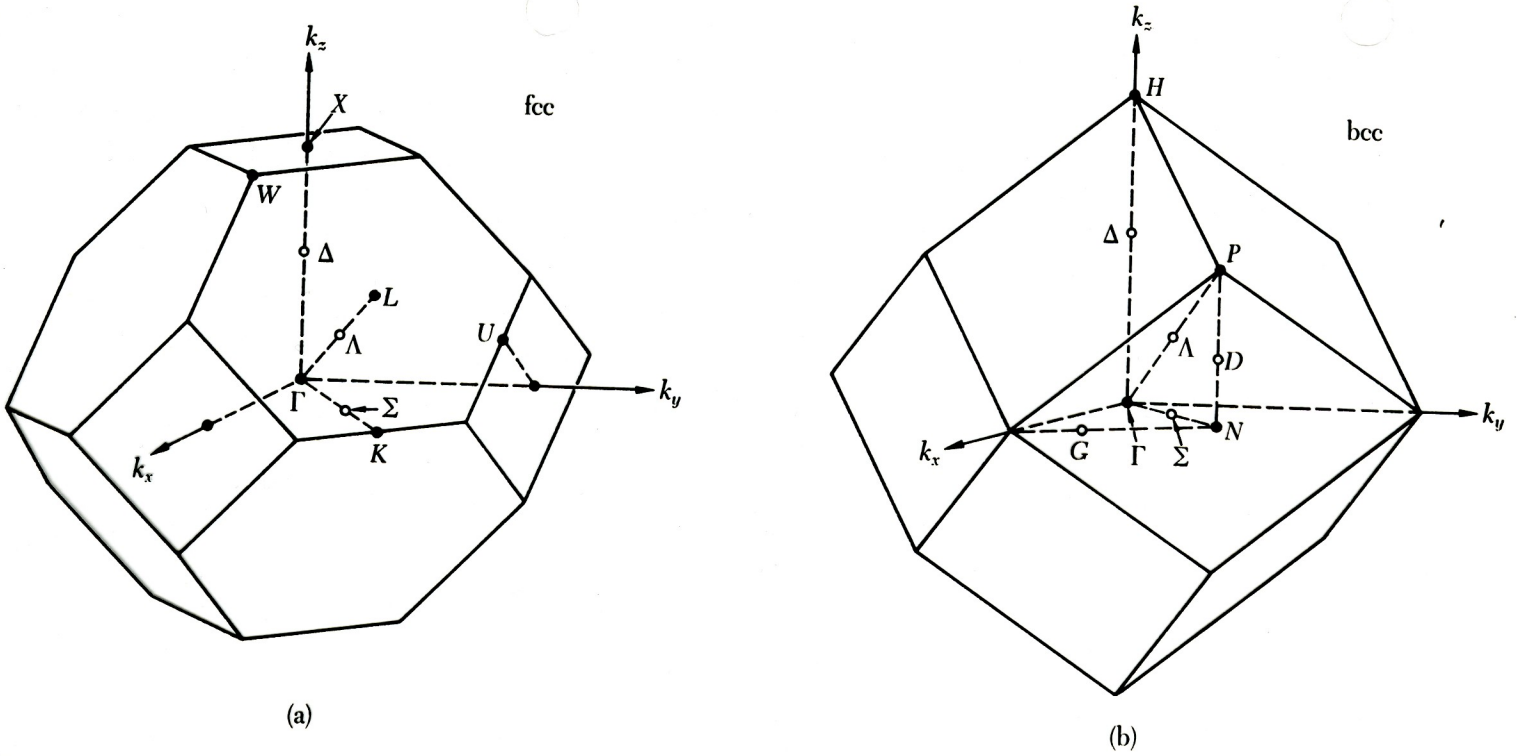


Figure 15 Standard labels of the symmetry points and axes of the Brillouin zones of the fcc and bcc lattices. The zone centers are Γ. In (a) the boundary point at $(2\pi/a)(100)$ is X; the boundary point at $(2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ is L; the line Δ runs between Γ and X. In (b) the corresponding symbols are H, P and Δ.

$u_{\vec{k}}(\vec{r})$ can be restricted to a single primitive cell $\Rightarrow$

- electron in a Box $\longrightarrow$ discrete set of states (n)

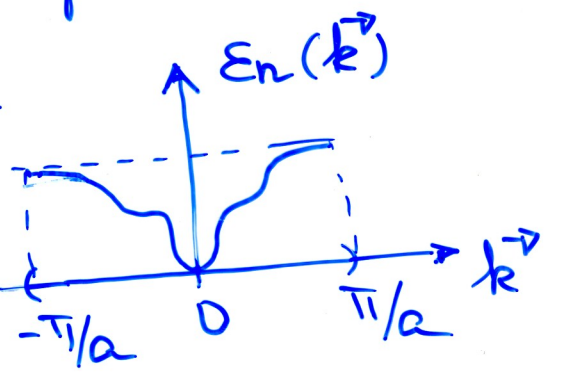
for each fixed $\vec{k}$

$$\hat{H}_{\vec{k}}\, u_{n\vec{k}}(\vec{r}) = \varepsilon_{n\vec{k}}\, u_{n\vec{k}}(\vec{r})$$

$\hat{H}_{\vec{k}}$: Hamiltonian depends on $\vec{k}$ as on a parameter

$\varepsilon_n(\vec{k})$ continuous dependence on $\vec{k}$

$\uparrow$ fixed Band index n



Periodicity in $\vec{k}$

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

$$\varepsilon_n(\vec{k}+\vec{K}) = \varepsilon_n(\vec{k})$$

$$\vec{K} \in RL$$

$\Rightarrow \vec{k}$ may be restricted to the 1st BZ

Electron energy levels in a crystal:

a family of $\varepsilon_n(\vec{k})$

crystal momentum

n: discrete band index

$\vec{k}$: continuous function of $\vec{k}$ for each n.

Band structure

$\varepsilon_n(\vec{k})$ ↑ fixed n

- continuous
- periodic in $\vec{k}$

} has lower and upper Bounds

Velocity of a Bloch electron

$$\vec{V}_n(\vec{k}) = \frac{1}{\hbar}\frac{\partial}{\partial \vec{k}}\varepsilon_n(\vec{k})$$

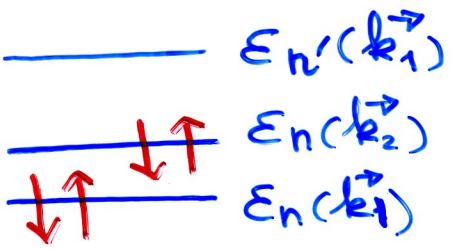
non-vanishing mean velocity !

$$\langle \psi_{n\vec{k}} | \hat{\vec{r}} | \psi_{n\vec{k}} \rangle = \vec{V}_n(\vec{k})$$

stationary states. Bloch electron does not experience scattering by static ions arranged in a crystal

The Fermi surface

Ground state of $N^* Z$ valence non-interacting electrons constructed:

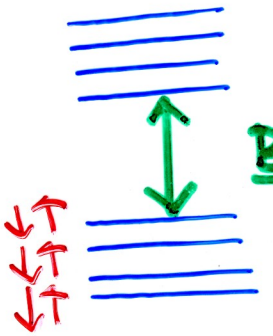


Filling of $\frac{N}{2}$ lowest one-electron levels

$+ \vec{k}_i \in$ 1st BZ ($\vec{k}_i$ must be non-equivalent for any fixed Band n)

$i = 1, \ldots N$

I.



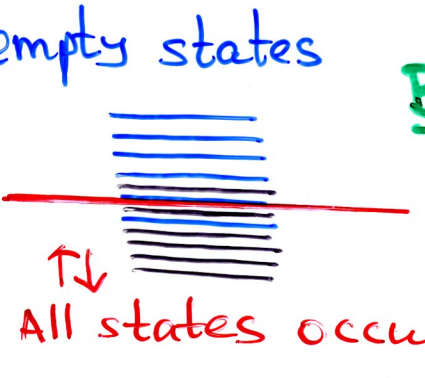
(2N)

$E_g \gg k_B T$ insulators

$E_g \sim k_B T$ intrinsic semiconductors

This may be realized when (, Z,) number of electrons per primitive cell is even.

II. **BANDS OVERLAP**



Fermi surface $\varepsilon_n(\vec{k}) = E_F$:

a surface in $\vec{k}$-space separating occupied and empty electron levels.

a constant energy surface.

$\varepsilon_n(\vec{k}+\vec{K}) = \varepsilon_n(\vec{k})$ - periodic in $\vec{k}$-space

$\Rightarrow$ Fermi surface is repeated periodically in $\vec{k}$-space

$\varepsilon_n(\vec{k}) = E_F$ is nth branch of the FS (a particular band n)

↙ we can present it in the 1st BZ

Reduced Zone Scheme

↘ we can represent it in the whole $\vec{k}$-space

Repeated Zone Scheme

Density of Levels

To perform summations

$$\sum_n \sum_{\vec{k}} Q_n(\vec{k})$$ ← some physical quantity [single-particle]

$\vec{k} \in$ 1st BZ (or any primitive cell of RL)

$$\Delta\vec{k} = \left[\frac{V}{(2\pi)^3}\right]^{-1} \quad \sum_{\vec{k}} \cdots \to \int \frac{V\,d\vec{k}}{(2\pi)^3} \cdots$$

$$q = \lim_{V\to\infty} \frac{Q}{V} = \sum_s \sum_n \int \frac{d\vec{k}}{(2\pi)^3} Q_{sn}(\vec{k})$$

s: spin index $s = \uparrow, \downarrow$

When $Q_{sn}(\vec{k})$ depends on $\vec{k}$ only through $\varepsilon_n(\vec{k})$

$$\int \frac{d^3k}{(2\pi)^3} \cdots \to \int d\varepsilon\, g_{sn}(\varepsilon) \cdots$$

$g_{sn}(\varepsilon)$: DOS corresponding to the Band n and electrons with spin s

total DOS $g(\varepsilon) = \sum_s \sum_n g_{sn}(\varepsilon)$

usually $g_{sn}(\varepsilon)$ does not depend on s.

$$q = 2\sum_n \int \frac{d^3\vec{k}}{(2\pi)^3} Q_n(\vec{k}) = 2\sum_n \int d\varepsilon\, g_n(\varepsilon) Q(\varepsilon)$$

$$\boxed{g_n(\varepsilon) = \int \frac{d\vec{k}}{(2\pi)^3} \delta(\varepsilon - \varepsilon_n(\vec{k}))}$$

$g_n(\varepsilon)d\varepsilon = \frac{1}{V} \times$ # of allowed states in the nth band in the energy range $\varepsilon \div \varepsilon + d\varepsilon$

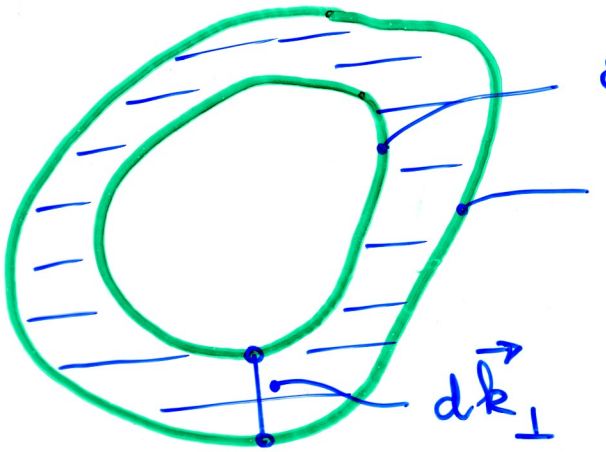
↑ here for a given spin s.

$g_n(\varepsilon) \rightarrow 2\, g_n(\varepsilon)$
2 spin states counted

$$g_n(\varepsilon)\, d\varepsilon = \int \frac{d\vec{k}}{4\pi^3} \times 1, \quad \varepsilon \le \varepsilon_n(\vec{k}) \le \varepsilon + d\varepsilon$$

$\times\, \emptyset$, otherwise

Anisotropy $\varepsilon_n(\vec{k})$



$\varepsilon_n(\vec{k}) = \varepsilon$ $\quad S_n(\vec{k})$

$\varepsilon_n(\vec{k}) = \varepsilon + d\varepsilon$

$S_n(\vec{k}+d\vec{k})$

$\varepsilon + d\varepsilon = \varepsilon_n(k) + \vec{\nabla}_k \varepsilon_n \cdot d\vec{k}$

$\vec{\nabla}_k \varepsilon_n \parallel d\vec{k}_\perp$ $\quad |\vec{\nabla}_k \varepsilon_n| \cdot |d\vec{k}_\perp|$

$$\frac{dN_n}{V} = g_n(\varepsilon)\, d\varepsilon = \int_{\varepsilon_n(\vec{k})=\varepsilon} \frac{dS_n(\vec{k})\, |d\vec{k}_\perp|}{4\pi^3}$$

$$|d\vec{k}_\perp| = \frac{d\varepsilon}{|\vec{\nabla}_{\vec{k}} \varepsilon_n(\vec{k})|}$$

$$\boxed{g_n(\varepsilon) = \int_{\varepsilon_n(\vec{k})=\varepsilon} \frac{dS_n}{4\pi^3} \cdot \frac{1}{|\vec{\nabla}_{\vec{k}} \varepsilon_n(\vec{k})|}}$$

relation between DOS and Band structure

$\varepsilon_n(\vec{k})$ ∘ continuous
∘ periodic

⇒ upper and lower bounds exist

⇒ at least one minimum
and one maximum

$\exists \vec{k}_0$ $\quad \frac{\partial \varepsilon_n(\vec{k})}{\partial \vec{k}} \Big|_{\vec{k}=\vec{k}_0} = 0$

↓

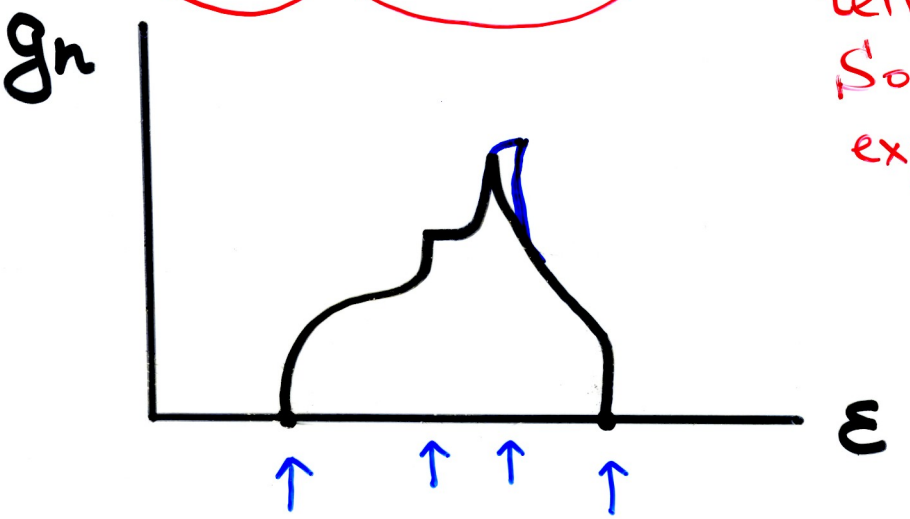
gives singularities to $g_n(\varepsilon)$

van Hove singularities

in 3D singularities are integrable:

$g_n(\varepsilon)$ is finite

$\frac{\partial g_n}{\partial \varepsilon}$ diverges → goes to low-T terms in Sommerfeld expansion



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