Band Structure and Bloch's Theorem

- Consider single electron in a periodic potential:

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

- $U(\vec{r}) = U(\vec{r} + \vec{R})$, for all Bravais lattice vectors $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

- Can we treat the potential semiclassically, starting from free electron gas? No!
  - Let $\lambda \sim \lambda_F$ be the characteristic wavelength of the potential. Need $\Delta x \ll \lambda \sim \lambda_F$
  - As before, $\Delta p \ll p_F$
  - So $\Delta x \Delta p \ll p_F \lambda_F \sim h$, contradicts uncertainty principle
  - Instead we will need $\Delta x \gg \lambda_F$, so the electron feels many potential wells at same time → need quantum treatment!

Quantum Treatment of Problem:

- Wavefunction $\psi(\vec{r})$ (ignore spin, it plays no role for now)

- Periodic boundary conditions: $\psi(\vec{r}) = \psi(\vec{r} + N_1 \vec{a}_1)$

$$= \psi(\vec{r} + N_2 \vec{a}_2) = \psi(\vec{r} + N_3 \vec{a}_3)$$

$\longrightarrow$ i.e. N_1 unit cells in $\vec{a}_1$-direction, etc.

$N_c = N_1 N_2 N_3$ unit cells in total.

$$\Rightarrow \psi(\vec{r}) = \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \tilde{\psi}(\vec{k}), \text{ where } \vec{k} = \frac{n_1}{N_1}\vec{b}_1 + \frac{n_2}{N_2}\vec{b}_2 + \frac{n_3}{N_3}\vec{b}_3$$

where n_1, n_2, n_3 arbitrary integers, $\vec{b}_i$ primitive RLV's.

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

Translation Symmetry: $T_{\vec{R}}\, \psi(\vec{r}) = \psi(\vec{r} + \vec{R})$

- $T_{\vec{R}}$ is unitary

$$\left.\begin{aligned} [H, T_{\vec{R}}] &= 0 \\ [T_{\vec{R}}, T_{\vec{R}'}] &= 0 \end{aligned}\right\} \Rightarrow$$

Can simultaneously diagonalize H and <u>all</u> $T_{\vec{R}}$.

- We write:

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

$$T_{\vec{R}}\psi = e^{i\phi_{\vec{R}}}\psi$$

$e^{i\phi_{\vec{R}}} = ??$

- In free space, $\psi(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \Rightarrow T_{\vec{R}}\psi = e^{i\vec{k}\cdot\vec{R}}\psi$

$$\Rightarrow \phi_{\vec{R}} = \vec{k}\cdot\vec{R}.$$

- Lattice problem: $T_{\vec{R}_1} T_{\vec{R}_2}\psi = e^{i\phi_{\vec{R}_2}} T_{\vec{R}_1}\psi = e^{i\phi_{\vec{R}_1}} e^{i\phi_{\vec{R}_2}}\psi$

$$\| $$

$$T_{\vec{R}_1+\vec{R}_2}\psi = e^{i(\phi_{\vec{R}_1}+\phi_{\vec{R}_2})}\psi$$

$$\Rightarrow \boxed{\phi_{\vec{R}_1+\vec{R}_2} = \phi_{\vec{R}_1} + \phi_{\vec{R}_2}}$$

This implies: $\boxed{\phi_{\vec{R}} = n_1\phi_{\vec{a}_1} + n_2\phi_{\vec{a}_2} + n_3\phi_{\vec{a}_3}}$,

where $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$.

- Already big simplification. We went from apparently infinite number of $\phi_{\vec{R}}$'s, to just 3 independent numbers $\phi_{\vec{a}_i}$. Can simplify more → there is a simple form for $\phi_{\vec{a}_i}$...

Try: $\phi_{\vec{a}_i} = \vec{k} \cdot \vec{a}_i$, when $\vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3$.

~~&~~ $x_i \in [0,1] \Rightarrow \vec{k}$ lies in 1 primitive cell of reciprocal lattice.

$\Rightarrow \vec{k} \cdot \vec{a}_i = \phi_{\vec{a}_i} = 2\pi x_i \Rightarrow \phi_{\vec{a}_i}$ independently lie in interval $[0, 2\pi]$. ✓

- We can just as well choose $\vec{k}$ in B.Z.

$\Rightarrow \phi_{\vec{R}} = \vec{k} \cdot \vec{R}$ for $\vec{k} \in$ B.Z.

$\Rightarrow$ $$T_{\vec{R}}\, \psi(\vec{r}) = e^{i\vec{k}\cdot\vec{R}}\, \psi(\vec{r})$$

$\vec{k}$ "crystal momentum," in B.Z.

• This implies $\psi(\vec{r})$ has the following Fourier expansion:

$$\psi(\vec{r}) = \sum_{\vec{Q}} e^{i(\vec{k}+\vec{Q})\cdot\vec{r}} \tilde{\psi}(\vec{k}+\vec{Q})$$

$\vec{Q}$ ↳ RLV's

$$= e^{i\vec{k}\cdot\vec{r}} \sum_{\vec{Q}} e^{i\vec{Q}\cdot\vec{r}} \tilde{\psi}(\vec{k}+\vec{Q})$$

$$\equiv u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}+\vec{R}) \quad \text{periodic}$$

"Bloch function"

• $\boxed{\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{\vec{k}}(\vec{r})}$ → Let's plug this form back into Schrödinger equation...

↓

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

$$\Downarrow$$

$$\left[\frac{\hbar^2}{2m}(-i\vec{\nabla})^2 + U(\vec{r})\right] e^{i\vec{k}\cdot\vec{r}}\, u_{\vec{k}}(\vec{r}) = \varepsilon\, e^{i\vec{k}\cdot\vec{r}}\, u_{\vec{k}}(\vec{r})$$

$$\Downarrow\Downarrow$$

$$e^{i\vec{k}\cdot\vec{r}}\left[\frac{\hbar^2}{2m}(-i\vec{\nabla}+\vec{k})^2 + U(\vec{r})\right] u_{\vec{k}}(\vec{r})$$

$$\equiv H(\vec{k}) \text{ "Block Hamiltonian"}$$

$$\Rightarrow \boxed{H(\vec{k})\, u_{\vec{k}}(\vec{r}) = \varepsilon_{\vec{k}}\, u_{\vec{k}}(\vec{r})} \rightarrow \text{"Block equation"}$$

- $u_{\vec{k}}(\vec{r})$ is periodic $\Rightarrow$ defined within single primitive cell. So Block equation is a kind of particle-in-a-box problem, for a small periodic box (i.e. the primitive cell).

$\Rightarrow$ Expect discrete energy spectrum for each $\vec{k}$.

Summary (Bloch's Theorem)

(1) Eigenstates labeled by $\vec{k}$ in B.Z. and discrete index n.

(2) $\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{n\vec{k}}(\vec{r})$; $u_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r}+\vec{R})$.

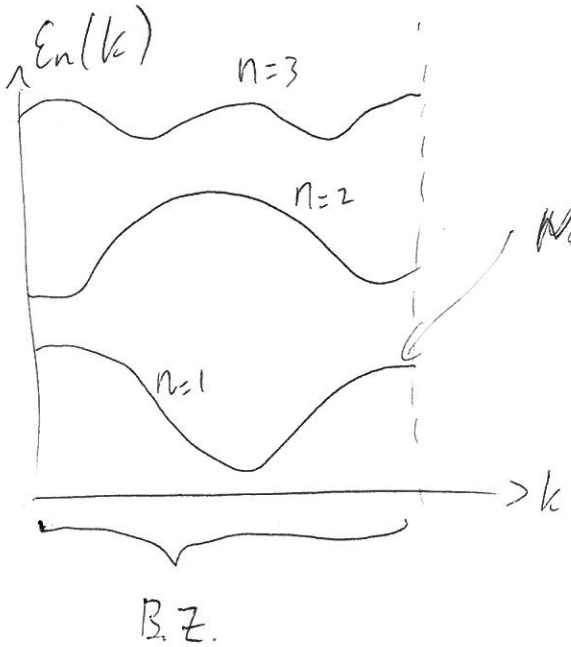
"Bloch function"

(3) $H\psi_{n\vec{k}} = \varepsilon_{n\vec{k}}\psi_{n\vec{k}}$ and $H(\vec{k})u_{n\vec{k}} = \varepsilon_{n\vec{k}}u_{n\vec{k}}$.

"Bloch Hamiltonian"

"Bloch equation"

Energy bands:



Note discrete spectrum for each $\vec{k}$, labeled by n.

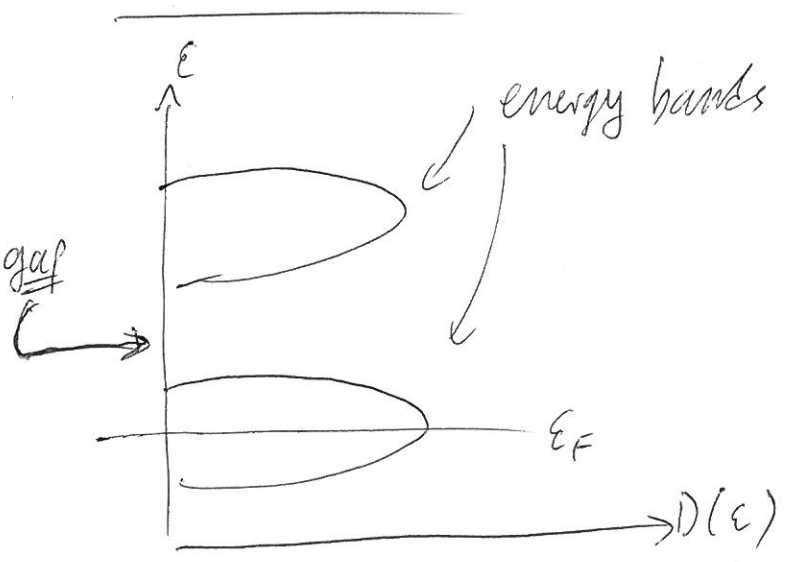
- Number of states in a band:

- Recall $N_c = N_1 N_2 N_3$ primitive cells in lattice.

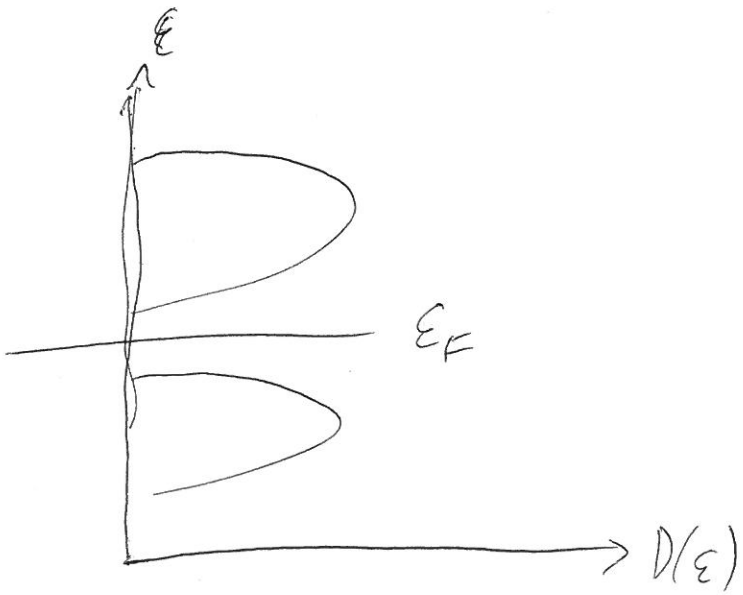
- Since $\vec{k} = \frac{n_1}{N_1}\vec{b}_1 + \frac{n_2}{N_2}\vec{b}_2 + \frac{n_3}{N_3}\vec{b}_3$, there are N_c $\vec{k}$-points in B.Z. (for any reciprocal lattice primitive cell)

$\Rightarrow$ $2N_c$ states in a band (2 is for spin)

Density of states: → might look like this



Metal: ε_F intersects some band, which is partially filled



Insulator: ε_F lies in between bands, so some bands full, others empty

- In an insulator m bands filled (m integer).

$\Rightarrow$ # electrons $= m \cdot (2N_c)$

$\Rightarrow \dfrac{\#\ \text{electrons}}{\#\ \text{primitive cells}} = \dfrac{m \cdot (2N_c)}{N_c} = 2m$ ✓

$\Rightarrow$ $\dfrac{\#\ \text{electrons}}{\text{primitive cell}}$ Must be even integer

in order to have an insulator!