Lect 5: electrons in periodic potential – Bloch theory

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r), \quad \text{where } V = \sum_i U(r-R_i), \text{ thus}$$

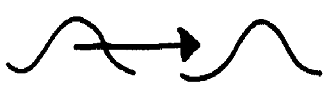
$$V(r+R_i) = V(r)$$

Bloch's theorem: the eigenstate can be expressed as $\psi_{n,k}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_{n,k}(\vec{r})$, where

$u_{n,k}(\vec{r}+\vec{R}_i) = u_{n,k}(\vec{r})$, and $\vec{k}$ is well-defined modula reciprocal lattice vectors.

We can confine $\vec{k}$ is the first BZ. $\Rightarrow$ $\boxed{\psi(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi(\vec{r}) \text{ for every } \vec{R} \text{ in the lattice.}}$

Proof: define translation operation $T(R)$ as $T(R)f(r) = f(r-R)$



$f(r)$ $\quad$ $f(r-R)$.

$$\Rightarrow T(R)\, H\, \psi(r) = H(\partial_r, r-R)\psi(r-R)$$
$$= H(\partial_r, r)\, T(R)\psi(r)$$
$$\Rightarrow \boxed{T(R)H = HT(R)}$$

$T(R)$ satisfies $T(R)T(R') = T(R+R')$, Abelian group.

$$\text{if } H\psi(r) = \varepsilon\psi(r) \Rightarrow H\underbrace{T\psi(r)} = TH\psi = \varepsilon\underbrace{T\psi(r)}$$

I can choose $\psi(r)$ as eigenstates of $\{H, T(R)\}$ for all $\vec{R}$.

$$T_R\psi(r) = C(R)\psi(r) \Rightarrow T(R)T(R')\psi(r) = C(R)C(R')\psi(r)$$
$$T(R+R')\psi(r) = C(R+R')\psi(r)$$

$\Rightarrow$ $C(R+R') = C(R)C(R')$. Imposing periodical BC: $\vec{R} + N_1\vec{a}_1 = \vec{R}$

Characters

$$\vec{R} + N_2\vec{a}_2 = \vec{R}$$
$$\vec{R} + N_3\vec{a}_3 = R$$

②

$$\Rightarrow \quad C^{N_1}(a_1)=1,\quad C^{N_2}(a_2)=1,\quad C^{N_3}(a_3)=1 \quad \Rightarrow \quad \begin{aligned} C_1(a_1) &= e^{i\vec{k}_1\vec{a}_1} \\ C_2(a_2) &= e^{i\vec{k}_2\vec{a}_2} \\ C(a_3) &= e^{i\vec{k}_3\vec{a}_3} \end{aligned}$$

and $\boxed{\vec{k}_1 = \frac{l_1}{N_1}\vec{b}_1,\ \vec{k}_2 = \frac{l_2}{N_2}\vec{b}_2,\ \vec{k}_3 = \frac{l_3}{N_3}\vec{b}_3.}$

$$\Rightarrow \quad T_{\vec{R}}\,\psi = \psi(r+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\,\psi(r),\quad \text{where } \vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3.$$

allowed k-grid in reciprocal space $\Rightarrow$ Volume for one state

$$\Omega = \frac{\vec{b}_1}{N_1}\cdot\left(\frac{\vec{b}_2}{N_2}\times\frac{\vec{b}_3}{N_3}\right) = \frac{\vec{b}_1\cdot(\vec{b}_2\times\vec{b}_3)}{N} = \frac{(2\pi)^3}{V}.$$

remark: ① Bloch wave states are not momentum eigenstate

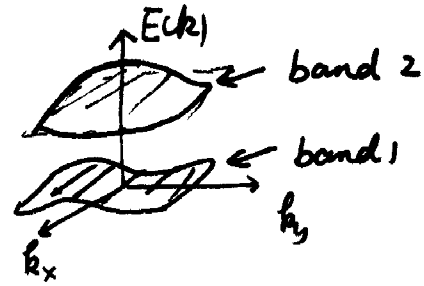
$$\psi_{\vec{k}}(r) = e^{i\vec{k}\cdot\vec{R}}\,u(r)$$

$$u(r) = \sum_{G} e^{i\vec{G}\cdot\vec{r}}\,C_{\vec{G}}\ ,\quad \text{where } \vec{G} \text{ is the receiprocal lattice vector}$$

$$\Rightarrow \quad \psi_k(r) = \sum_{\vec{G}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}}\,C_{\vec{G}} \quad \Rightarrow \quad \vec{k} \text{ is only well-define modula } \vec{G}.$$

There are many eigenfunctions share the same $\vec{k}$, which can distinguished by an nothe index $\psi_{n,k}(r)$, n — band index.

We can relate the k-space to the first BZ with band index

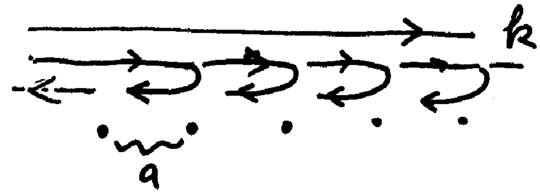


velocity $v_n(k) = \frac{1}{\hbar}\nabla_k \mathcal{E}_n(k)$

$\mathcal{E}_n(k)$ can be considered as the periodic function of k, extend to all the momentum space.

⇒ In spite of the existence of lattice, as long as it's regular, it's a eigenstate with non-vaishing velocity independent of time, as if no collisions

if $\vec{k}$ is far away the BZ boundry, the reflection waves from each collision cancels.



if $2k \cdot a \neq \pm 2\pi$ ⇒ back waves cancels.

no much effect.

if $2ka = 2\pi$ ⇒ strong back scattering,

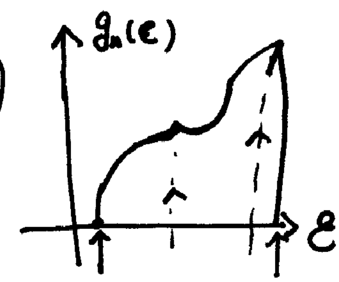
particle do not propogate ⇒ $\partial_k \mathcal{E}(k) = v_k = 0$.

§ von Hove singularities

$$g_n(\mathcal{E}) = \oint_{S(\mathcal{E})} \frac{dS}{4\pi^3} \frac{1}{|\nabla \mathcal{E}_n(k)|}$$, there're always points $\nabla \mathcal{E}_n(k) = 0$

Suppose $\mathcal{E}_n(k) = \text{const} + \frac{1}{2}\frac{\partial^2 \mathcal{E}}{\partial k_i \partial k_j}\Delta k_i \Delta k_j$ ⇒ $\nabla \mathcal{E}_n(k) \propto |k - k_0|$

⇒ $g_n(\mathcal{E}) \propto \int dk \frac{(k-k_0)}{k-k_0}$ → converge. (3D DOS)



but the derivatives $\frac{dg(\mathcal{E})}{d\mathcal{E}}$ can be divergence.

§ weak periodic potential

- Plane-wave method: $\psi_{n,k}(r) = \sum_{G} \frac{e^{i\vec{k}\cdot\vec{r} + \vec{G}\cdot\vec{r}}}{\sqrt{V}} C_{\vec{G}}$

We are using the plane wave $\frac{e^{i(\vec{k}+\vec{G})\cdot\vec{r}}}{\sqrt{V}}$ as basis, denoted as $|\vec{k}+\vec{G}\rangle$.

state vectors of different $\vec{k}'$, are not mixed with $|\vec{k}+G\rangle$, i.e $\langle\vec{k}'+G'|H|k+G\rangle = 0$.

we only need to calculated the matrix elements

$$\langle\vec{k}+\vec{G}'|H|\vec{k}+\vec{G}\rangle = \frac{\hbar^2(\vec{k}+\vec{G})^2}{2m}\delta_{\vec{G}',\vec{G}} + \langle\vec{k}+\vec{G}'|V|\vec{k}+\vec{G}\rangle$$

$$\langle k+G'|V|k+Q\rangle = \frac{1}{V}\int e^{-i(\vec{G}'-\vec{G})\cdot\vec{r}}V(\vec{r})\,d^3\vec{r} = V(\vec{G}'-\vec{G})$$

$\Rightarrow$ eigen value problem of $H_{\vec{G}',\vec{G}}(\vec{k}) = \frac{\hbar^2(\vec{k}+\vec{G})^2}{2m}\delta_{\vec{G}'\vec{G}} + V(\vec{G}'-\vec{G})$

- diagonalize this matrix $\Rightarrow$ energy level $\underline{\mathcal{E}_n(\vec{k})}$, and $\underline{\psi_{n,k}(\vec{r}) = \sum C_G|\vec{k}+}$

$$\sum_{G} H_{\vec{G}',\vec{G}}(k)\, C_{\vec{G}}(\vec{k}) = E\, C_{G'}(\vec{k})$$

$$\frac{\hbar^2(\vec{k}+\vec{G}')^2}{2m} C_{\vec{G}'}(k) + \sum_{G} V(\vec{G}'-\vec{G})\, C_{\vec{G}}(\vec{k}) = E\, C_{G'}(\vec{k})$$

or $$\boxed{\left[E - \frac{\hbar^2(\vec{k}+\vec{G}')^2}{2m}\right] C_{G'}(\vec{k}) = \sum_{G} V(\vec{G}'-\vec{G})\, C_{\vec{G}}(\vec{k})}$$

case 1: the empty lattice case $\mathcal{E}^0_{\vec{k}+\vec{G}} = \frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2$. If for $\vec{k}$ such that $\frac{(\vec{k}+\vec{G})^2}{2m}$ is far away from all other $\frac{(\vec{k}+\vec{G}')^2}{2m}$, i.e.

$$\left|\frac{(\vec{k}+\vec{G})^2}{2m} - \frac{(\vec{k}+\vec{G}')^2}{2m}\right| \gg U(\vec{G}'-\vec{G}) \quad \text{for all } G' \neq G.$$

then we can use the 2nd perturbation theory.

$$\mathcal{E}_{\vec{k}+\vec{G}} = \mathcal{E}^0_{\vec{k}+\vec{G}} + \sum_{G'} \frac{|V_{G'-G}|^2}{\mathcal{E}^0_{\vec{k}+\vec{G}} - \mathcal{E}^0_{\vec{k}+\vec{G}'}} + O(V^3)$$

$$\psi_{\vec{k}+\vec{G}} = |k+G\rangle + \sum_{G'} \frac{|k+G'\rangle\, V(G'-G)}{\mathcal{E}^0_{k+G} - \mathcal{E}^0_{k+G'}}$$

Case 2: Suppose that for the value of k, such that there are a set of reciprocal lattice vectors $G_1, \cdots, G_m$, with $\mathcal{E}^0_{k+G_1} \cdots \mathcal{E}^0_{k+G_m}$ are close to each other, but all other reciprocal lattice vectors are far in term of energy. Then we can ~~truncate~~ the eigen-equation just keeping $G_1, \cdots G_m$

$$\boxed{(\mathcal{E} - \mathcal{E}^0_{k+G_i})\, C_{k+G_i} = \sum_{j=1}^{m} V(G_i - G_j)\, C_{k+G_j}}$$

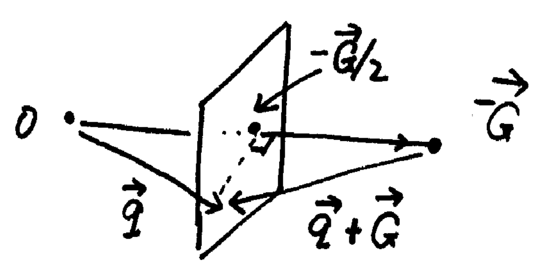
a more accurate one

$$(\mathcal{E} - \mathcal{E}^0_{k+G_i})\, C_{k+G_i} = \sum_{j=1}^{m} V(G_i - G_j)\, C_{k+G_j} + \sum_{j=1}^{m} \Big({\sum_{G}}' \frac{V(G_i-G)\,V(G-G_j)}{\mathcal{E} - \mathcal{E}^0_{k+G}} \Big) C_{k+k_j}$$

for $G \neq j = 1, \cdots m$.

§ energy levels near BZ boundary (Bragg plane)

for $\vec{q}$ close to the plane $-\frac{\vec{G}}{2}$, then $\vec{q}+\vec{G}$ is close to the plane normal to $\frac{\vec{G}}{2}$. $\Rightarrow$ $\mathcal{E}_{\vec{q}} \simeq \mathcal{E}_{\vec{q}+\vec{G}}$.



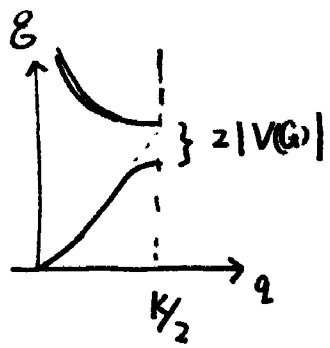
Keep the 2 terms $\Rightarrow$

$$\begin{cases} (\mathcal{E} - \mathcal{E}^0_q)\, C_q = V(\vec{G})\, C_{q+G} \\ (\mathcal{E} - \mathcal{E}^0_{q+G})\, C_{q+G} = V(-\vec{G})\, C_q \end{cases}$$

$\leftarrow$ set $V(0) = 0$

$$\begin{vmatrix} \mathcal{E} - \mathcal{E}^0_q , & -V(\vec{G}) \\ -V(\vec{G}) , & \mathcal{E} - \mathcal{E}^0_{q+G} \end{vmatrix} = 0 \Rightarrow \mathcal{E}^2 - (\mathcal{E}^0_q + \mathcal{E}^0_{q+G})\mathcal{E} + \mathcal{E}^0_q \mathcal{E}^0_{q+G} - |V(\vec{G})|^2 = 0$$

$$\mathcal{E} = \frac{\mathcal{E}^0_q + \mathcal{E}^0_{q+G}}{2} \pm \sqrt{\left(\frac{\mathcal{E}^0_q - \mathcal{E}^0_{q+G}}{2}\right)^2 + |V(G)|^2}$$



$$\underset{1,2}{\psi}\left(\frac{K}{2}\right) \propto \cos\frac{1}{2}\vec{K}\cdot\vec{r} , \quad \mathcal{E} = \mathcal{E}^0_q - |V(G)|$$

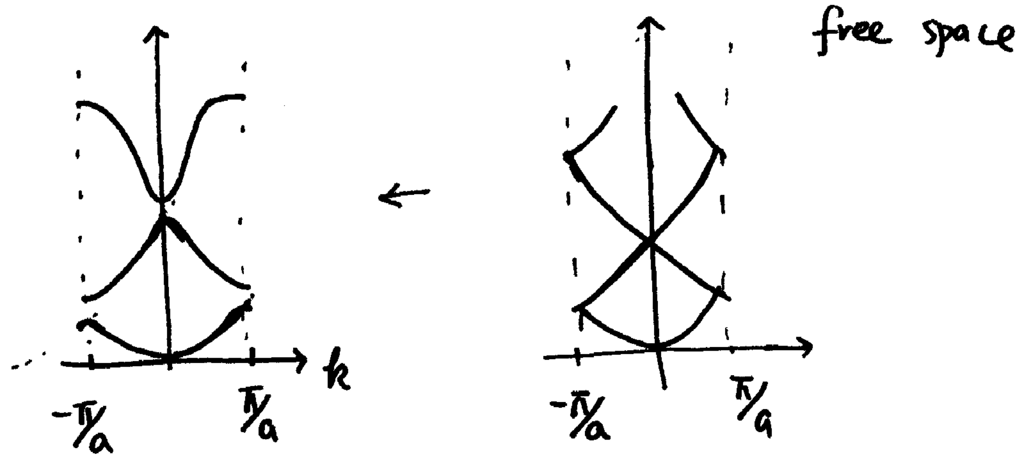
$$\sin\frac{1}{2}\vec{K}\cdot\vec{r} , \quad \mathcal{E} = \mathcal{E}^0_q + |V(G)|$$

$\boxed{\text{if } U_K < 0}$

$$\frac{\partial \mathcal{E}}{\partial \vec{q}} = \frac{\hbar^2 \vec{q}}{2m} + \frac{\hbar^2(\vec{q}+\vec{G})}{2m} + \frac{(\mathcal{E}^0_q - \mathcal{E}^0_{q+G})}{\sqrt{\cdots}}\Bigg|_{\vec{q} = -\vec{G}/2} = \frac{\hbar^2}{2m}(\vec{G} + 2\vec{q}) = 0$$

↗ group velocity at BZ boundary is zero.

Example: 1D:



2D