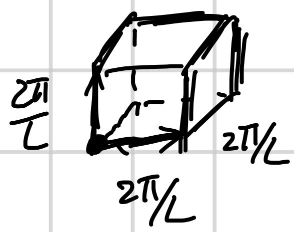
(1) Schrödinger Equation.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t)=\varepsilon\,\psi(\vec{r},t)$$

(2) 

$$\left(\frac{2\pi}{L}\right)^3=\frac{8\pi^3}{V}\qquad \varepsilon=\frac{\hbar^2k^2}{2m}.\qquad k=\frac{\sqrt{2m\varepsilon}}{\hbar}\qquad dk=\frac{\sqrt{2m}}{2\hbar}\frac{1}{\sqrt{\varepsilon}}$$

$$\begin{cases} dN=\dfrac{V}{4\pi^3}\cdot 4\pi k^2dk=\dfrac{V}{\pi^2}k^2dk=\dfrac{V}{\pi^2}\cdot\dfrac{2m\varepsilon}{\hbar^2}. \\ dN=V\cdot\rho(\varepsilon)\cdot d\varepsilon \end{cases}$$

(3) $\dfrac{V}{3\pi^2}k_F^3=N \Rightarrow k_F=(3\pi^2n)^{1/3}$

(4) $$\bar{\varepsilon}=\frac{\int\varepsilon\rho(\varepsilon)d\varepsilon}{\int\rho(\varepsilon)d\varepsilon}=\frac{\int_0^{\varepsilon_F}\varepsilon\cdot\sqrt{\varepsilon}\cdot d\varepsilon}{\int_0^{\varepsilon_F}\sqrt{\varepsilon}\cdot d\varepsilon}=\frac{\int_0^{\varepsilon_F}\varepsilon^{3/2}d\varepsilon}{\int_0^{\varepsilon_F}\varepsilon^{1/2}\cdot d\varepsilon}=\frac{\frac{2}{5}\cdot\varepsilon_F^{5/2}}{\frac{2}{3}\varepsilon_F^{3/2}}=\frac{3}{5}\varepsilon_F.$$

$$\psi(r_1,r_2)=\varphi_1(r_1)\varphi_2(r_2)-\underline{\varphi_1(r_2)\varphi_2(r_1)}=\begin{vmatrix}\varphi_1(r_1) & \varphi_1(r_2)\\ \varphi_2(r_1) & \varphi_2(r_2)\end{vmatrix}$$

$\underline{r_1\leftrightarrow r_2}$: $\psi(r_1,r_2)=-\psi(r_2,r_1)$

直积态

<u>自由电子气</u>

$[\underline{\varphi_{k_1}}\ \ \underline{\varphi_{k_2}}\ \ \underline{\varphi_{k_3}}]$.

$$\underline{\begin{vmatrix}\varphi_1(r_1) & \varphi_1(r_2) & \varphi_1(r_3)\\ \varphi_2(r_1) & \varphi_2(r_2) & \varphi_2(r_3)\\ \varphi_3(r_1) & \varphi_3(r_2) & \varphi_3(r_3)\end{vmatrix}}$$

☆ Bloch定理

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

条件 $V(\vec{r}+\vec{R})=V(\vec{r})$ 晶格周期势 (周期边界条件/无穷长)

k

(i) 引入平移算子 $T_{\vec{R}}$ ($\vec{R}$ 正格矢)

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

$$T_{\vec{R}}V(\vec{r})=V(\vec{r}+\vec{R})=V(\vec{r})$$

$$T_{\vec{R}}\cdot\psi(\vec{r})=\lambda_{\vec{R}}\psi(\vec{r})\ ?$$

(ii) $[T_{\vec{R}},H]=0$. ($T_{\vec{R}}$ 使系统不变)

$$T_R H\psi(\vec{r})=T_R\cdot\varepsilon\psi(\vec{r})=\varepsilon T_R\psi(\vec{r})$$

$$H T_R\psi(\vec{r})=H(r)\psi(\vec{r}+\vec{R})\cancel{=}H(r+R)\psi(r+R)=\varepsilon\psi(\vec{r}+\vec{R})$$

$$=\varepsilon\cdot T_R\psi(\vec{r})$$

$$\left[-\frac{\hbar^2}{2m}\nabla_r^2+V(\vec{r})\right]\psi(\vec{r}+\vec{R})=\left[-\frac{\hbar^2}{2m}\nabla_{\vec{r}+\vec{R}}^2+V(\vec{r}+\vec{R})\right]\psi(\vec{r}+\vec{R})$$

$$=\left[-\frac{\hbar^2}{2m}\nabla_{\vec{r}'}^2+V(\vec{r}')\right]\psi(\vec{r}')$$

$$=\varepsilon\psi(\vec{r}')$$

$\Rightarrow$ $T_R\cdot H=HT_R$ 对易.

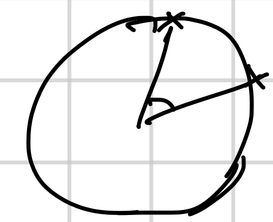
(iii) 要求 $\psi_k(\vec{r})$ 同时为 $\hat{H}$, $\hat{T}_K$ 的本征态

$$T_R\psi_k(\vec{r})=\lambda(k,R)\psi_k(\vec{r})$$

(a) $\int |\psi(\vec{r})|^2 d\vec{r} = 1$

$\int |T_R \cdot \psi(\vec{r})|^2 d\vec{r} = 1$ (物理要求)

$\Rightarrow |\lambda(k,R)|^2 = 1$ 模1圆上.



(b) $T_{R_1} T_{R_2} \psi_k(r) = \lambda(k,R_1)\lambda(k,R_2)\psi_k(r)$

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

$T_{R_2} T_{R_1} \psi_k(r) = \lambda(k,R_2)\lambda(k,R_1)\psi_k(r)$

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

$T_{R_1+R_2} \psi_k(r) = \lambda(k,R_1+R_2)\psi_k(r)$

$\{T_R\}$群 $\lambda(\vec{k},\vec{R}) = e^{i\vec{k}\cdot\vec{R}}$

$|\lambda(\vec{k},\vec{R})|^2 = 1$, $\lambda(\vec{k},\vec{R}_1)\cdot\lambda(\vec{k},\vec{R}_2) = \lambda(\vec{k},\vec{R}_1+\vec{R}_2)$

(iv) $T_{\vec{R}}\cdot\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{R}}\psi_k(\vec{r})$ 布洛赫定理.

$\rightarrow \psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_k(\vec{r})$ ← 周期函数

平面波

$T_R\psi_k(\vec{r}) = e^{ik(\vec{r}+\vec{R})} u_k(\vec{r}+\vec{R})$

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

$= e^{i\vec{k}\cdot\vec{R}}\psi_k(\vec{r})$ (✓)

(v) 周期边条件

$T_{Na}\psi(x) = \psi(x)$

$||$

$e^{ikNa}\psi(x)$

$k\cdot Na = 2\pi\cdot n$

$\Rightarrow k = \frac{2\pi}{Na}\cdot n$ 分立取值

☆ Schrödinger Eq. of Bloch electron

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

$$\psi_k(r) = e^{ikr}u_k(r)$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\cdot e^{ikr}u_k(r) = \varepsilon\cdot e^{ikr}u_k(r)$$

$$-\frac{\hbar^2}{2m}\nabla\cdot\left[i\vec{k}\cdot e^{i\vec{k}\cdot\vec{r}}u_k(r) + e^{ik\cdot r}\nabla u_k(r)\right] + V(r)e^{ikr}u_k(r) = \varepsilon e^{ikr}u_k(r)$$

$$-\frac{\hbar^2}{2m}\left[i\vec{k}\cdot i\vec{k}e^{ikr}u_k(r) + i\vec{k}e^{ikr}\nabla u_k(r) \cdots\right.$$

$$\left.\cdots i\vec{k}\cdot e^{ikr}\nabla u_k(r) + e^{ik\cdot r}\nabla^2 u_k(r)\right] + \cdots = \cdots$$

$$-\frac{\hbar^2}{2m}\left[(i\vec{k})^2 + 2(i\vec{k})\cdot \cancel{e^{i\vec{k}\cdot\vec{r}}}\vec{\nabla}u_k(r) + \cancel{e^{ik\cdot r}}\nabla^2 u_k(r)\right] + V(r)\cancel{e^{ikr}}u_k(r)$$

$$= \varepsilon\cancel{e^{ikr}}u_k(r)$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left[(i\vec{k})^2 + 2(i\vec{k})\vec{\nabla}u_k(r) + \nabla^2 u_k(r)\right] + V(r)u_k(r)$$

$$= \varepsilon u_k(r)$$

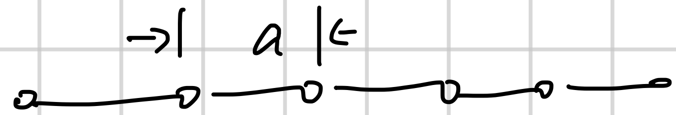
$$\|$$

$$\boxed{-\frac{\hbar^2}{2m}(\nabla + i\vec{k})^2 u_k(r) + V(r)u_k(r) = \varepsilon u_k(r)}$$

#

$$\psi_k(r) \to u_k(r)$$

☆ 近自由电子近似



(I) $\left[-\underbrace{\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{\text{动能}}+\underbrace{V(x)}_{\text{周期势}}\right]\psi(x)=\underbrace{\varepsilon}_{\text{能量}}\psi(x)$

$$V(x)=\sum_n V_n e^{i\frac{2\pi}{a}nx}$$

$\frac{2\pi}{a}n = G_n$.

n — 不同动量.

$(\frac{2\pi}{a}n)$ — 倒格矢

$$=V_0+\sum_n{}' V_n e^{i\frac{2\pi}{a}n\cdot x}$$

$\sum'$ 表示不含 0.

$$\frac{1}{L}\int_0^L V(x)\,dx=\frac{1}{L}\int_0^L\left(V_0+\sum_n{}' V_n e^{i\frac{2\pi}{a}nx}\right)dx$$

$$=V_0+\cancel{\frac{1}{L}\int_0^L\left(\sum_n{}' V_n e^{i\frac{2\pi}{a}nx}\right)dx}=0$$

$$V_0=\bar{V}=0$$

$$V_n=\frac{1}{L}\int_0^L V(x)\,e^{-i\frac{2\pi}{a}nx}dx,\quad V_n^*=V_{-n}.$$

微扰问题：

$$\begin{cases} H_0=\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V_0\right) \\ H'=\sum_n{}' V_n e^{i\frac{2\pi}{a}nx} \end{cases}$$

→ 平面波 zeroth order $\left(\psi_k^0=\frac{1}{\sqrt{L}}e^{ikx},\quad \varepsilon_k^0=\frac{\hbar^2k^2}{2m}.\right)$

$$\psi_k(x)=\psi_k^0(x)+\psi_k^{(1)}(x)+\psi_k^{(2)}(x)+\cdots$$ (布洛赫波)

$$\varepsilon_k=\varepsilon_k^0+\varepsilon_k^{(1)}+\varepsilon_k^{(2)}+\cdots$$ (能带结构)

(II) 微扰计算（非简并微扰）

☆ 能量计算：$\varepsilon_k^{(1)}=H'_{kk}=\int_0^L\overline{\psi_k^{(0)}}(x)\,V(x)\,\psi_k^{(0)}(x)\,dx$

$$= \frac{1}{L}\int_0^L \cancel{e^{-ikx}} V(x) \cancel{e^{ikx}} dx = V_0 = 0.$$

$$\Rightarrow \varepsilon_k^{(1)} = 0.$$

2nd-order perturbation. $\varepsilon_k^{(2)} = \sum_{k'}' \frac{|H'_{kk'}|^2}{\varepsilon_k^{(0)} - \varepsilon_{k'}^{(0)}}$

$$H'_{kk'} = \int_0^L \overline{\psi_k^{(0)}(x)} V(x) \psi_{k'}(x) dx$$

$$= \frac{1}{L}\int_0^L e^{-ikx} V(x) e^{ik'x} dx$$

$$= \frac{1}{L}\int_0^L e^{i(k'-k)x} \cdot \underline{V(x)} dx = \begin{cases} 0, & k'-k \neq \frac{2\pi}{a} n \\ V_n, & k'-k = \frac{2\pi}{a} n \end{cases}$$

✓ $|H'_{kk'}|^2 = |V_n|^2$, $\underline{(k-k' = \frac{2\pi}{a} n)}$

$(= V_n \cdot V_{-n})$

$$\varepsilon_k^{(0)} = \hbar^2 k^2 / 2m . \quad \varepsilon_{k'}^{(0)} = \frac{\hbar^2 k'^2}{2m}$$

$$\Rightarrow \varepsilon_k = \underline{\frac{\hbar^2 k^2}{2m}} + \sum_n' \frac{2m |V_n|^2}{\hbar^2 k^2 - \hbar^2 (k - 2\pi \frac{n}{a})^2} \quad (\text{非简并})$$

$k = \pi \cdot \frac{n}{a}$. 发散.

☆ 波函数微扰计算 (1st)

$$\psi_k^{(1)}(x) = \sum_{k'}' \frac{H_{kk'}}{\varepsilon_k^{(0)} - \varepsilon_{k'}^{(0)}} \psi_{k'}^{0}(x)$$

布洛赫波

$$= \frac{1}{\sqrt{L}} \sum_n' \frac{2m V_n}{\hbar^2 k^2 - \hbar^2 (k - 2\pi \frac{n}{a})^2} e^{i(k - \frac{2\pi}{a} \cdot n)x}$$

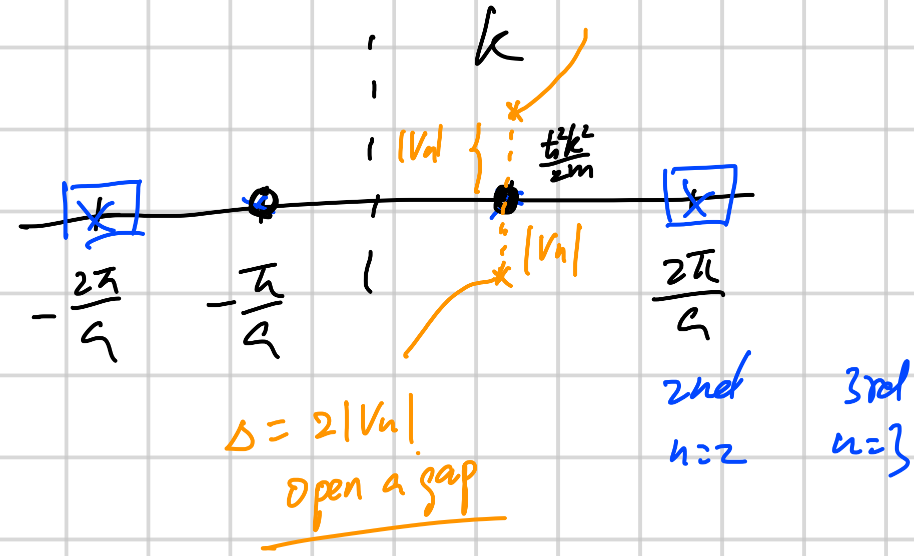
$$= \underline{\frac{1}{\sqrt{L}} e^{ikx}} \left(\sum_n' \frac{2m V_n}{\underline{\hbar^2 k^2 - \hbar^2 (k - 2\pi \frac{n}{a})^2}} \underline{e^{-i\frac{2\pi}{a} n x}} \right)$$

G_n

$$= \underline{\frac{1}{\sqrt{L}} e^{ikx}} \; \underline{u_k(x)}$$

周期函数 $e^{-i\frac{2\pi}{a} n(x+\ell a)} = e^{i\frac{2\pi}{a} nx}$.

$$\frac{\hbar^2k^2}{2m} - \frac{\hbar^2}{2m}\cdot\left(k-\frac{2\pi}{a}\cdot n\right)^2$$



if $k=\frac{\pi}{a}\cdot n$

☆ 简并微扰

$k=-\frac{\pi}{a}$ $\quad k'=\frac{\pi}{a}$ 能够简并

$\left(k=-\frac{\pi}{a}\cdot n,\ k'=\frac{\pi}{a}\cdot n\right)$ 平面波 $\frac{1}{\sqrt{L}}e^{ik^{(\prime)}\cdot x}$

$$\psi = A\psi_k^{(0)} + B\psi_{k'}^{(0)}$$

$(H_0+H')\psi(x) = \varepsilon\psi(x)$ 2-态子空间内

↳ $(H_0+H')\left[A\psi_k^{(0)}+B\psi_{k'}^{(0)}\right] = \varepsilon\left[A\psi_k^{(0)}+B\psi_{k'}^{(0)}\right]$

✓ $\int \bar{\psi}_k^{(0)}\,[\cdots]\cdot dx$

✓ $\int \bar{\psi}_{k'}^{(0)}\,[\cdots]\,dx$ $\quad \sum_n{}' V_n e^{i\frac{2\pi}{a}\cdot nx}$, $\left(k=-\frac{\pi}{a}n,\ k'=\frac{\pi}{a}n\right)$

$$\int \bar{\psi}_k^{(0)}(H_0+H')\left[A\psi_k^{(0)}+B\psi_{k'}^{(0)}\right] = \varepsilon\cdot A$$

$$\begin{cases} A\cdot\varepsilon_k^{(0)} + V_n\cdot B = \varepsilon A \\ B\,\varepsilon_{k'}^{(0)} + V_n^* A = \varepsilon\cdot B \end{cases} \Rightarrow \begin{vmatrix} \frac{\hbar^2k^2}{2m}-\varepsilon & V_n \\ V_n^* & \frac{\hbar^2k^2}{2m}-\varepsilon \end{vmatrix} = 0$$

$\left(k=-\frac{\pi n}{a},\ k'=\frac{\pi n}{a}\right)$

$$\begin{pmatrix} \varepsilon_k^{(0)} & V_n \\ V_n^* & \varepsilon_{k'}^{(0)} \end{pmatrix}\begin{pmatrix} A \\ B \end{pmatrix} = \varepsilon\begin{pmatrix} A \\ B \end{pmatrix}$$

$\Downarrow$

$$\varepsilon_\pm = \varepsilon_k^{(0)} \pm |V_n|$$

$$= \frac{\hbar^2k^2}{2m} \pm |V_n|$$

!!