Chapter 2 Electron Levels in a Periodic Potential

Bloch Theorem :

In the presence of a periodic potential $\left(V(\vec{r}+\vec{R})=V(\vec{r})\right)$

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

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

Proof: Bloch theorem in 1 D

if $V(x+R)=V(x)$

then $\psi(x+R)=\exp(ikR)\psi(x)$

$$R = na \qquad n = 0, \pm 1, \pm 2 \ldots.$$

Define T_R (translation operation)

$$T_R[H(x)\psi(x)] = H(x+R)\psi(x+R) = H(x)\psi(x+R) = H(x)T_R\psi(x)$$

$$\therefore [T_R, H] = 0 \quad \Rightarrow \quad \begin{cases} H\psi_n = E_n\psi_n \\ T_R\psi_n = C(R)\psi_n \end{cases}$$

$$\therefore T_R\psi(x) = \psi(x+R) = C(R)\psi(x)$$

$$\int |\psi(x+R)|^2\, dx = \int |C(R)|^2 |\psi(x)|^2\, dx = \int |\psi(x)|^2 dx$$

$$|C(R)|^2 = 1 \qquad \Rightarrow C(R) = e^{i\theta(R)}$$

$$T_aT_a\psi(x) = \psi(x+2a) = T_{2a}\psi(x) \qquad \Rightarrow C(a)C(a) = C(2a)$$

$$C(a) = e^{ika}\ ; \qquad C(2a) = C(a)C(a) = e^{i2ka} \qquad C(R) = e^{ikR}$$

Proof: Bloch theorem in 3 D $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

Define $T_{\vec{R}}$ (translation operation) : $T_{\vec{R}}\psi(\vec{r}) = \psi(\vec{r} + \vec{R})$

$$T_{\vec{R}}[H(\vec{r})\psi(\vec{r})] = H(\vec{r}+\vec{R})\psi(\vec{r}+\vec{R}) = H(\vec{r})\psi(\vec{r}+\vec{R}) = H(\vec{r})T_{\vec{R}}\psi(\vec{r})$$

$$\therefore [T_{\vec{R}}, H] = 0 \quad \Longrightarrow \quad \begin{cases} H\psi_n = E_n\psi_n \\ T_{\vec{R}}\psi_n = C(\vec{R})\psi_n \end{cases}$$

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

$$\int |\psi(\vec{r}+\vec{R})|^2\, d^3r = \int |C(\vec{R})|^2 |\psi(\vec{r})|^2\, d^3r = \int |\psi(\vec{r})|^2 d^3r$$

$$|C(\vec{R})|^2 = 1 \qquad \Rightarrow C(\vec{R}) = e^{i\theta(\vec{R})}$$

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

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

$$C(\vec{R}')C(\vec{R}) = C(\vec{R})C(\vec{R}') = C(\vec{R}+\vec{R}') \quad \Longrightarrow \quad C(\vec{R}) = \exp(i\vec{k}\cdot\vec{R})$$

Another form of the Bloch function

$$\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u(\vec{r}) \qquad \textit{where} \quad u(\vec{r}+\vec{R}) = u(\vec{r})$$

Proof:

$$\begin{aligned}\psi_k(\vec{r}+\vec{R}) &= \exp[i\vec{k}\cdot(\vec{r}+\vec{R})]u(\vec{r}+\vec{R}) \\ &= \exp(i\vec{k}\cdot\vec{R})\exp(i\vec{k}\cdot\vec{r})u(\vec{r}) \\ &= \exp(i\vec{k}\cdot\vec{R})\psi(\vec{r})\end{aligned}$$

What is the physical meaning of $\vec{k}$?

For a system with spherical symmetry $V(\vec{r}) = V(r)$

$$[H, L^2] = 0 \quad ; \quad [H, L_z] = 0$$

$$\begin{cases} H\psi_{nlm} = E_{nlm}\psi_{nlm} \\ L^2\psi_{nlm} = l(l+1)\hbar\,\psi_{nlm} \\ L_z\psi_{nlm} = m\hbar\,\psi_{nlm} \end{cases} \quad ; \quad \psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

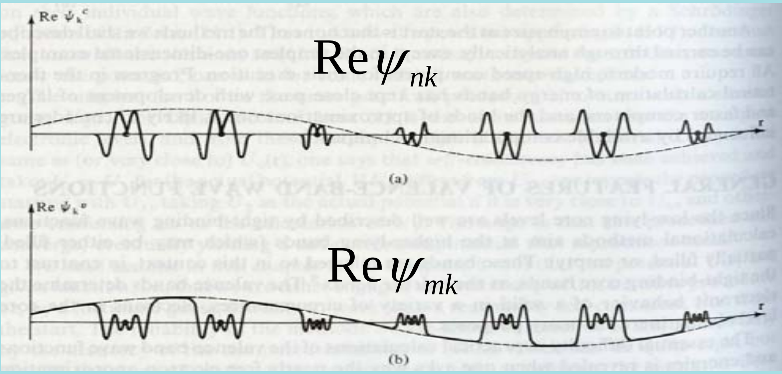
Meaning of l,m ⟹ $Y_{lm}(\theta,\phi)$

$$Y_{00} = \frac{1}{\sqrt{4\pi}}; \quad Y_{11} = -\sqrt{\frac{3}{8\pi}}e^{i\phi}\sin\theta; \quad Y_{1-1} = \sqrt{\frac{3}{8\pi}}e^{-i\phi}\sin\theta; \quad Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

For a system with translational symmetry $V(\vec{r}+\vec{R}) = V(\vec{r})$

$$[H, T] = 0$$

$$\begin{cases} H\psi_{nk} = E_{nk}\psi_{nk} \\ T(\vec{R})\psi_{nk} = e^{i\vec{k}\cdot\vec{R}}\psi_{nk} \end{cases} ; \psi_{nk} = e^{i\vec{k}\cdot\vec{r}}u_{nk}(\vec{r})$$



$\vec{k}$ is continue ⟹ energy band

General remarks about Bloch's Theorem

(1) ψ_{nk} is not a momentum eigenstate, $\hbar\vec{k}$ is crystal momentum

$$\vec{p}\psi_{nk} = \frac{\hbar}{i}\vec{\nabla}\psi_{nk} = \frac{\hbar}{i}\vec{\nabla}[e^{i\vec{k}\cdot\vec{r}}u_{nk}(\vec{r})]$$

$$= \hbar\vec{k}\psi_{nk} + e^{i\vec{k}\cdot\vec{r}}\frac{\hbar}{i}\vec{\nabla}u_{nk}(\vec{r})$$

(2) $\vec{k}$ can always be confined to the first B.Z.

let $\vec{k}' = \vec{k} + \vec{G}$

$$\because \exp(i\vec{k}'\cdot\vec{R}) = \exp[i(\vec{k}+\vec{G})\cdot\vec{R}] = \exp(i\vec{k}\cdot\vec{R})$$

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

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

$$E_{n,\vec{k}+\vec{G}} = E_{n,\vec{k}}$$

(3) It can be reduced to a hermitian eigenvalue problem which is restricted to a single primitive cell of the crystal

$$H\psi_{nk} = E_{nk}\psi_{nk} \qquad where \quad H = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + U(\vec{r})$$

$$let \quad \psi_{nk}(\vec{r}) = \exp(i\vec{k}\cdot\vec{r})u_{nk}(\vec{r})$$

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi_{nk}(\vec{r}) = -\frac{\hbar^2}{2m}\vec{\nabla}\cdot[\vec{\nabla}e^{i\vec{k}\cdot\vec{r}}u_{nk}(\vec{r})]$$

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

$$H_k u_{nk} == E_{nk}u_{nk}(\vec{r}) \qquad where \quad H_k = -\frac{\hbar^2}{2m}(i\vec{k} + \vec{\nabla})^2 + U(\vec{r})$$

$$with \quad B.C. \qquad u_{nk}(\vec{r}) = u_{nk}(\vec{r} + \vec{R})$$

It is a partial differential equation with a very complicate boundary condition.

Using variational principle, we can reduce this complicate boundary value problem to simple matrix digonalization problem

$$H_k u_{nk} == E_{nk} u_{nk}(\vec{r}) \qquad where \quad H_k = -\frac{\hbar^2}{2m}(i\vec{k}+\vec{\nabla})^2 + U(\vec{r})$$

Choose a basis function $\chi_n(\vec{r})$ where $\chi_n(\vec{r}+\vec{R}) = \chi_n(\vec{r})$

$$u_k(\vec{r}) = \sum_n C_n \chi_n(\vec{r})$$

minimize $< u_k | H_k | u_k >$ with constraint $< u_k | u_k > = 1$

$$\frac{\partial}{\partial C_l^*} < \sum_n C_n \chi_n | H_k | \sum_m C_m \chi_m > - \lambda \frac{\partial}{\partial C_l^*} < \sum_n C_n \chi_n | \sum_m C_m \chi_m > = 0$$

$$\frac{\partial}{\partial C_l^*} \sum_n \sum_m C_n^* C_m H_{nm} - \lambda \frac{\partial}{\partial C_l^*} \sum_n \sum_m C_n^* C_m S_{nm} = 0$$

$$\sum_m C_m H_{lm} - \lambda \sum_m C_m S_{lm} = 0$$

$$\Rightarrow \quad \boxed{\underset{\sim}{H}(\vec{k})\underset{\sim}{C} - \lambda \underset{\sim}{S}\underset{\sim}{C} = 0}$$

where $H_{lm} = < \chi_l | H_k | \chi_m >$; $S_{lm} = < \chi_l | \chi_m >$

$$\Rightarrow \lambda_1; \underset{\sim}{C}^{(1)} \quad , \lambda_2; \underset{\sim}{C}^{(2)} \ \lambda_3; \underset{\sim}{C}^{(3)} \ldots\ldots\ldots \lambda_n; \underset{\sim}{C}^{(N)} \qquad (\varepsilon_{nk}, \psi_{nk})$$