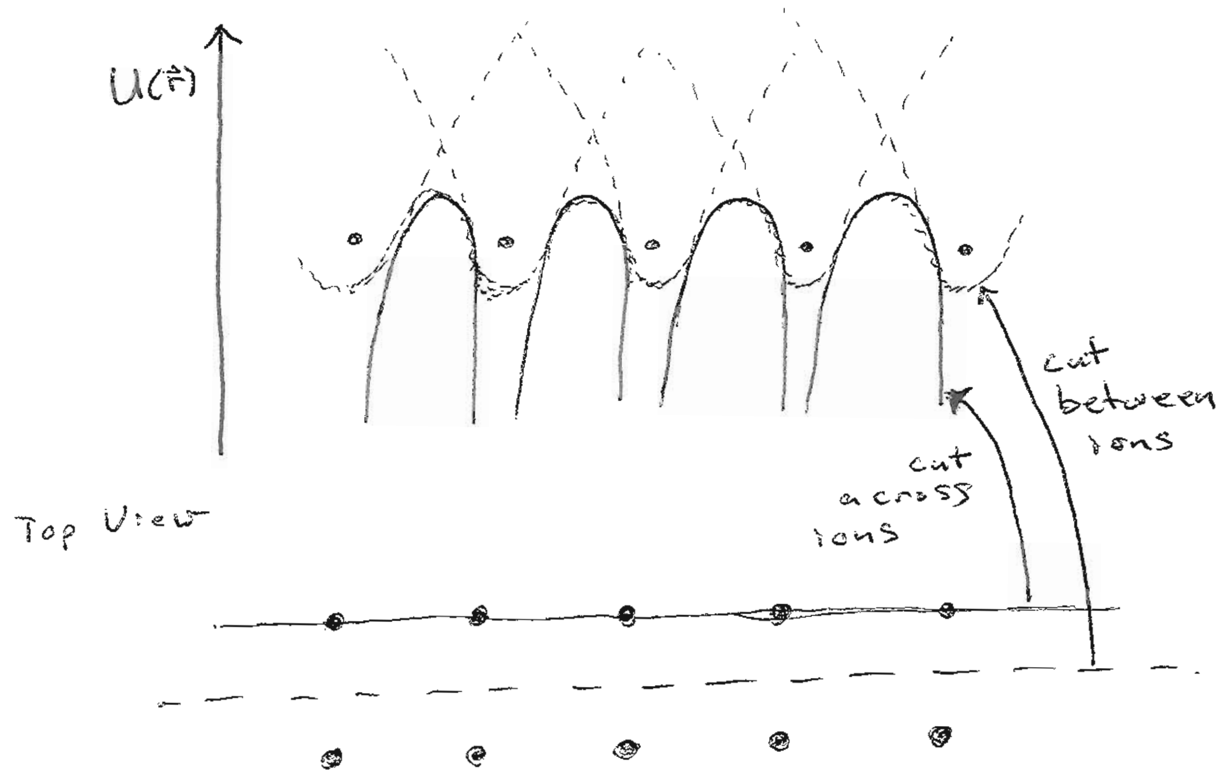
Chapter 8
Electron Levels in a Periodic Potential: General Properties

Periodic Potential



Periodic $\Rightarrow$ $U(\vec{r}) = U(\vec{r}+\vec{R})$

$\vec{R}$ = Bravais lattice vector

Quantum Mechanics

$\Rightarrow$ Schrodinger equation

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

(Recall that for free electron case, we had $U(\vec{r}) = 0$

$\Rightarrow$ free electron plane wave solutions

$$\psi_k = \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{V_\Omega}}$$

normalization)

For free electron case, we applied periodic (Born-von Karman) boundary conditions

such as $\psi(x,y,z+L) = \psi(x,y,z)$
etc.

$$\Rightarrow \quad e^{ik_xL} = e^{ik_yL} = e^{ik_zL} = 1$$

$$\Rightarrow \quad k_x = \frac{2\pi n_x}{L} \; ; \; k_y = \frac{2\pi n_y}{L} \; , \; k_z = \frac{2\pi n_z}{L}$$

$\Rightarrow$ only certain discrete values of $\vec{k}$ are allowed

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Now we add a periodic potential $U(\vec{r})$

Bloch's Theorem:

the eigenstates ψ of the 1-electron Hamiltonian
$$H = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + U(\vec{r}) \; ,$$
where $U(\vec{r}) = U(\vec{r}+\vec{R})$ ($\vec{R}$ = Bravais lattice vector)

can be chosen to have the form of a plane wave times a function with periodicity of the Bravais lattice

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

Bloch wave functions

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

for all $\vec{R}$ in the Bravais lattice periodicity of ψ in $\vec{R}$

$$\Rightarrow \quad \psi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}(\vec{r}+\vec{R})} u_{n\vec{k}}(\vec{r}+\vec{R})$$

$$\Rightarrow \quad \psi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\left[e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r})\right]$$

$$\boxed{\psi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r})}$$

alternate statement of Bloch theorem

check that Bloch wavefunction is a solution

$$\vec{\nabla}^2 \psi_{n\vec{k}}(\vec{r}) = \vec{\nabla}^2\left[e^{i\vec{k}\cdot\vec{r}} u_{nk}(\vec{r})\right]$$

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

$$\cancel{\vec{\nabla}\psi_{nk}(\vec{r})}$$

Shr. Eq.

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

$$\Rightarrow \quad \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2}{2m} \frac{\vec{\nabla}^2 u_{n\vec{k}}(\vec{r})}{u_{n\vec{k}}(\vec{r})} + U(\vec{r}) = \mathcal{E}$$

Translation Operator $T_{\vec{R}}$

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

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

$$\Rightarrow \quad T_{\vec{R}} H = H T_{\vec{R}}$$

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

$$\Rightarrow \quad T_{\vec{R}} T_{\vec{R}'} = T_{\vec{R}'} T_{R} = T_{\vec{R}+\vec{R}'}$$

$\Rightarrow$ $T_{\vec{R}}$ and H commute

$\Rightarrow$ simultaneous eigenstates

$$H\Psi = \varepsilon \Psi$$
$$T_{\vec{R}}\Psi = c(\vec{R})\Psi$$

$$T_{\vec{R}'} T_{R} \Psi = c(\vec{R}) T_{\vec{R}'} \Psi = c(\vec{R}) c(\vec{R}') \Psi$$
$$= T_{\vec{R}+\vec{R}'} \Psi = c(\vec{R}+\vec{R}')\Psi$$

$$\Rightarrow \quad c(\vec{R}+\vec{R}') = c(\vec{R})c(\vec{R}')$$

let $\vec{a}_i$ be three primitive Bravais lattice vectors

(each $\vec{a}_i$ is also belonging to the set of $\vec{R}$ vectors)

one can write

$$c(\vec{a}_i) = e^{2\pi i x_i}$$

x_i = a general complex number

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

$$= \sum n_i \vec{a}_i$$

$$\Rightarrow \quad c(\vec{R}) = c(n_1\vec{a}_1)\, c(n_2\vec{a}_2)\, c(n_3\vec{a}_3)$$

but n_i is an integer

$$\Rightarrow \quad c(n_i\vec{a}_i) = c(\underbrace{\vec{a}_i + \vec{a}_i + \dots}_{n_i \text{ times}})$$

$$= \underbrace{c(\vec{a}_i)\, c(\vec{a}_i) \dots}_{n_i \text{ factors of } \vec{a}_i}$$

$$= \prod_1^{n_i} c(\vec{a}_i)$$

$$c(n_i\vec{a}_i) = \prod_1^{n_i} e^{2\pi i x_i} = \left(e^{2\pi i x_i}\right)^{n_i}$$

Therefore,

$$c(\vec{R}) = c\left(\sum n_i \vec{a}_i\right)$$

$$= \prod_1^3 c(n_i \vec{a}_i)$$

$$= \prod_1^3 \left(e^{2\pi i x_i}\right)^{n_i} = \prod_1^3 \left[c(\vec{a}_i)\right]^{n_i}$$

$$= c(a_1)^{n_1} c(a_2)^{n_2} c(a_3)^{n_3}$$

$$= e^{2\pi i x_1 n_1 + 2\pi i n_2 x_2 + 2\pi i x_3 n_3}$$

$$= e^{2\pi i (n_1 x_1 + n_2 x_2 + n_3 x_3)}$$

$$\boxed{c(\vec{R}) = e^{i \vec{h} \cdot \vec{R}}}$$ with $\vec{h} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3$

and $b_i \cdot a_j = 2\pi \delta_{ij}$

So,

$$T_R\, \psi(\vec{r}) = c(\vec{R})\, \psi(\vec{r})$$

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

which is Bloch's Theorem