Momentum-Space Schrödinger Equation in Solids

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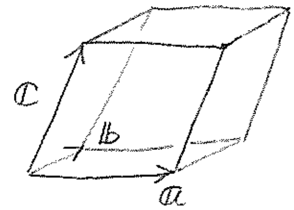
Consider a periodic solid with the unit cell, $(\mathbb{a}, \mathbb{b}, \mathbb{c})$.



The periodic potential, $V(\mathbb{r})$, can be expanded as

$$V(\mathbb{r}) = \sum_{\mathbb{G}} V_{\mathbb{G}} \exp(i\mathbb{G}\cdot\mathbb{r}) \qquad (1)$$

where

$$V_{\mathbb{G}} = \frac{1}{\Omega}\int d\mathbb{r}\, V(\mathbb{r}) \exp(-i\mathbb{G}\cdot\mathbb{r}) \qquad (2)$$

and the reciplocal vector is

$$\mathbb{G} = \frac{2\pi}{\Omega}\left[m_1(\mathbb{b}\times\mathbb{c}) + m_2(\mathbb{c}\times\mathbb{a}) + m_3(\mathbb{a}\times\mathbb{b})\right] \quad (m_1, m_2, m_3 \in \mathbb{Z}) \qquad (3)$$

and $\Omega = \mathbb{a}\cdot(\mathbb{b}\times\mathbb{c}) = \mathbb{b}\cdot(\mathbb{c}\times\mathbb{a}) = \mathbb{c}\cdot(\mathbb{a}\times\mathbb{b})$ is the unit-cell volume.

- Bloch's Theorem

Assume that the unit cell is repeated $M \times M \times M$ times, and we solved the Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{4}$$

in this "supercell".

We can expand the wave function as

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} a_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r}) \tag{5}$$

where

$$a_{\mathbf{k}} = \frac{1}{M^3\Omega}\int_{M^3\Omega} d\mathbf{r}\, \psi(\mathbf{r}) \exp(-i\mathbf{k}\cdot\mathbf{r}) \tag{6}$$

and

$$\mathbf{k} = \frac{2\pi}{M^{\cancel{3}}\Omega}\left[m_1 \cancel{M^2}(\mathbf{b}\times\mathbf{c}) + m_2 \cancel{M^2}(\mathbf{c}\times\mathbf{a}) + m_3 \cancel{M^2}(\mathbf{a}\times\mathbf{b})\right]$$

$$= \frac{2\pi}{\Omega}\left[\frac{m_1}{M}(\mathbf{b}\times\mathbf{c}) + \frac{m_2}{M}(\mathbf{c}\times\mathbf{a}) + \frac{m_3}{M}(\mathbf{a}\times\mathbf{b})\right] \tag{7}$$

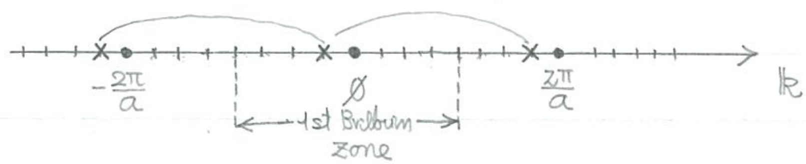
Substituting Eq.(5) in (4),

$$\sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} a_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \underbrace{\sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \sum_{\mathbf{k}} a_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}}_{\sum_{\mathbf{k}}\sum_{\mathbf{G}} V_{\mathbf{G}} a_{\mathbf{k}} e^{i\underbrace{(\mathbf{k}+\mathbf{G})}_{\mathbf{k}'}\cdot\mathbf{r}}} = E\sum_{\mathbf{k}} a_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$= \sum_{\mathbf{k}'}\sum_{\mathbf{G}} V_{\mathbf{G}} a_{\mathbf{k}'-\mathbf{G}} e^{i\mathbf{k}'\cdot\mathbf{r}}$$

$$\therefore \sum_{\mathbf{k}}\left[\frac{\hbar^2 k^2}{2m} a_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} a_{\mathbf{k}-\mathbf{G}} - E a_{\mathbf{k}}\right] e^{i\mathbf{k}\cdot\mathbf{r}} = \emptyset \tag{8}$$

Therefore $\mathbb{k}$ components that are connected by the lattice reciplocal vectors, $\mathbb{G}$, are coupled.



We can therefore label the eigenstates by $\mathbb{k}$ modulo $\mathbb{G}$, or $\mathbb{k}$ in the first Brillouin zone. An eigenstate can then be expressed as

$$\psi_{\mathbb{k}}(\mathbb{r}) = \sum_{\mathbb{G}} a_{\mathbb{G}} \exp[i(\mathbb{k}+\mathbb{G})\cdot\mathbb{r}] \qquad \mathbb{k} \in \text{1st Brillouin zone} \tag{9}$$

$$= e^{i\mathbb{k}\cdot\mathbb{r}} \sum_{\mathbb{G}} a_{\mathbb{G}} \exp(i\mathbb{G}\cdot\mathbb{r}) \tag{10}$$

$$\equiv e^{i\mathbb{k}\cdot\mathbb{r}}\, u(\mathbb{r}) \tag{11}$$

where $u(\mathbb{r})$ is periodic and $\mathbb{k}$ is in the 1st Brillouin zone.

– Schrödinger Equation in Momentum Space

$$\begin{cases} \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi_{\mathbf{k}}(\mathbf{r}) = E\,\psi_{\mathbf{k}}(\mathbf{r}) & (12) \\ \psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} a_{\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}] & (13) \end{cases}$$

Substituting Eq. (13) in (12),

$$\sum_{\mathbf{G}} \frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 a_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} + \underbrace{\sum_{\mathbf{G}'} V_{\mathbf{G}'} e^{i\mathbf{G}'\cdot\mathbf{r}} \sum_{\mathbf{G}} a_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}} = \sum_{\mathbf{G}} E a_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$\sum_{\mathbf{G}}\sum_{\mathbf{G}'} V_{\mathbf{G}'} a_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\underbrace{\mathbf{G}+\mathbf{G}'}_{\mathbf{G}''})\cdot\mathbf{r}}$$

$$= \sum_{\mathbf{G}}\sum_{\mathbf{G}''} V_{\mathbf{G}''-\mathbf{G}} a_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}'')\cdot\mathbf{r}}$$

$$= \sum_{\mathbf{G}}\sum_{\mathbf{G}'} V_{\mathbf{G}-\mathbf{G}'} a_{\mathbf{k}+\mathbf{G}'} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$\boxed{\therefore\ \frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 a_{\mathbf{k}+\mathbf{G}} + \sum_{\mathbf{G}'} V_{\mathbf{G}-\mathbf{G}'} a_{\mathbf{k}+\mathbf{G}'} = E\, a_{\mathbf{k}+\mathbf{G}}} \qquad (14)$$