

Start again with our second-quantized Hamiltonian for electrons in a solid:

$$H = \int d\vec{r} \sum_{\sigma} \psi_{\sigma}^{\dagger}(\vec{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) \right] \psi_{\sigma}(\vec{r})$$

Plane waves no longer diagonalize this.
To diagonalize need to solve the Schrödinger equation for electron in periodic potential:

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

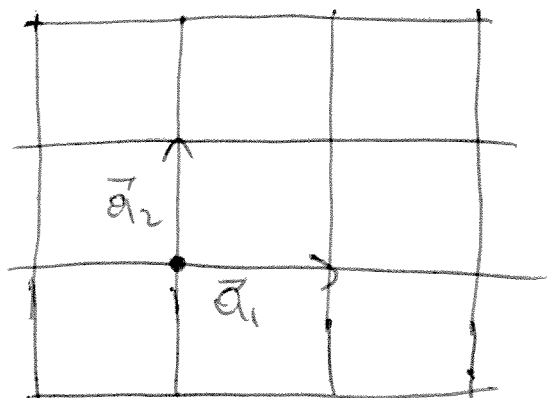
$U(\vec{r})$ is the periodic crystal potential.

Crucial property: $U(\vec{r} + \vec{R}) = U(\vec{r})$

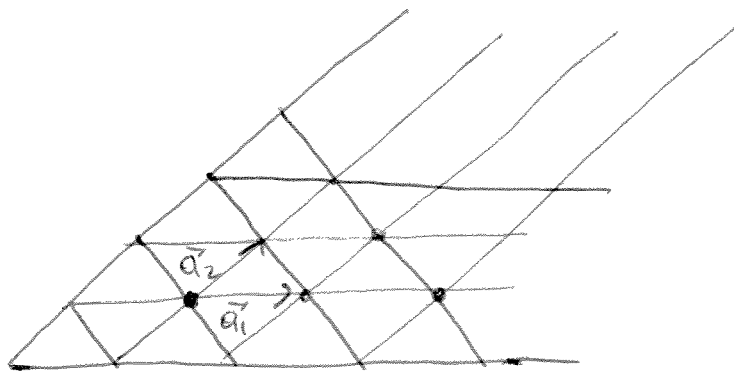
Here \vec{R} is any lattice vector:

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

n_i are integers and \vec{a}_i are basis vectors of the lattice.



$$\vec{a}_1 = a \hat{x}, \vec{a}_2 = a \hat{y}$$



$$\vec{a}_1 = a \hat{x}, \vec{a}_2 = a \left(\frac{\hat{x}}{2} + \frac{\sqrt{3}}{2} \hat{y} \right)$$

Just as in the free electron case, try to solve the Schrodinger equation by Fourier transform.

$$\psi(\vec{r}) = \sum_{\vec{k}} \psi_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} ;$$

$$U(\vec{r}) = \sum_{\vec{G}} U(\vec{G}) e^{i\vec{G} \cdot \vec{r}}$$

$$U(\vec{r} + \vec{R}) = \sum_{\vec{G}} U(\vec{G}) e^{i\vec{G} \cdot (\vec{r} + \vec{R})} = U(\vec{r}).$$

This means that $e^{i\vec{G} \cdot \vec{R}} = 1$ for any lattice vector \vec{R} .

\vec{G} are called reciprocal lattice vectors.

\vec{G} is a much smaller set of vectors than \vec{k} in the expansion of $\psi(\vec{r})$.

~~$$\vec{G} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3$$~~

~~$$\vec{G} = 2\pi m_1 \vec{b}_1 + 2\pi m_2 \vec{b}_2 + 2\pi m_3 \vec{b}_3$$~~

$$\vec{G} = 2\pi m_1 \vec{b}_1 + 2\pi m_2 \vec{b}_2 + 2\pi m_3 \vec{b}_3$$

where m_i are integers and $\vec{b}_i \cdot \vec{a}_j = \delta_{ij}$.

\vec{b}_i are basis vectors of the reciprocal lattice.

$$\vec{b}_1 = \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad \vec{b}_2 = \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)}, \quad \vec{b}_3 = \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)}$$

~~$$\psi(\vec{r}) = \sum_{\vec{k}, \vec{G}} \psi_{\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G}) \cdot \vec{r}}$$~~

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Thus we must have:

$$e^{i(\vec{k}+\vec{G}) \cdot N_i \vec{a}_i} = 1$$

$$e^{i\vec{G} \cdot \vec{a}_i N_i} = e^{2\pi i m_i N_i} = 1 \text{ automatically}$$

$$e^{i\vec{k} \cdot \vec{a}_i N_i} = 1$$

$$\vec{k} \cdot \vec{a}_i = (\vec{k}_1 \vec{b}_1 + \vec{k}_2 \vec{b}_2 + \vec{k}_3 \vec{b}_3) \cdot \vec{a}_i = k_i$$

$$k_i N_i = 2\pi m_i, \quad m_i = 0, \pm 1, \pm 2, \dots$$

$$k_i = \frac{2\pi m_i}{N_i}$$

First Brillouin zone:

$$-\frac{N_i}{2} \leq m_i < \frac{N_i}{2}$$

Could have taken $0 \leq m_i < N_i$ but convenient to shift this by $-\frac{N_i}{2}$.

Rewrite Schrodinger equation in momentum space

$$\begin{aligned}\psi(\vec{r}) &= \sum_{\vec{k}, \vec{G}} \psi_{\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G}) \cdot \vec{r}} \\ &= \sum_{\vec{k}, \vec{G}} u_{\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G}) \cdot \vec{r}}\end{aligned}$$

$$u_{\vec{k}}(\vec{G}) \equiv \psi_{\vec{k}+\vec{G}}$$

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} u_{\vec{k}}(\vec{G}) e^{i\vec{G} \cdot \vec{r}}$$

$u_{\vec{k}}(\vec{r})$ is a periodic function:

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

$$\psi(\vec{r}) = \sum_{\vec{k}} u_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$$

$$V(\vec{r}) = \sum_{\vec{G}} V(\vec{G}) e^{i\vec{G} \cdot \vec{r}}$$

$$V(\vec{G}) = \frac{1}{\Omega} \int_{\text{unit cell}} d\vec{r} e^{-i\vec{G} \cdot \vec{r}} V(\vec{r})$$

Ω - volume of the unit cell of the crystal.

$$\begin{aligned}-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) &= -\frac{\hbar^2}{2m} \nabla^2 \sum_{\vec{k}, \vec{G}} u_{\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G}) \cdot \vec{r}} \\ &= \sum_{\vec{k}, \vec{G}} \frac{\hbar^2 (\vec{k}+\vec{G})^2}{2m} u_{\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G}) \cdot \vec{r}}\end{aligned}$$

$$U(\vec{r})\psi(\vec{r}) = \sum_{\vec{k}, \vec{G}^1, \vec{G}''} U(\vec{G}'') U_{\vec{k}}(\vec{G}^1) e^{i(\vec{k} + \vec{G}^1 + \vec{G}'') \cdot \vec{r}}$$

$$E\psi(\vec{r}) = E \sum_{\vec{k}, \vec{G}} U_{\vec{k}}(\vec{G}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$$

Collecting everything, we obtain:

$$\sum_{\vec{k}, \vec{G}} \left[\frac{\hbar^2 (\vec{k} + \vec{G})^2}{2m} - E \right] U_{\vec{k}}(\vec{G}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} + \sum_{\vec{k}, \vec{G}^1, \vec{G}''} U(\vec{G}'') U_{\vec{k}}(\vec{G}^1) e^{i(\vec{k} + \vec{G}^1 + \vec{G}'') \cdot \vec{r}} = 0$$

In the second term, change momentum variables as:

$$\vec{G}^1 + \vec{G}'' = \vec{G} \Rightarrow \vec{G}'' = \vec{G} - \vec{G}^1$$

Then we obtain:

$$\sum_{\vec{k}, \vec{G}} \left[\frac{\hbar^2 (\vec{k} + \vec{G})^2}{2m} - E \right] U_{\vec{k}}(\vec{G}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} + \sum_{\vec{k}, \vec{G}, \vec{G}^1} U(\vec{G} - \vec{G}^1) U_{\vec{k}}(\vec{G}^1) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} = 0$$

For this equation to be satisfied, ~~on~~ the

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coefficient of $e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$ has to be zero.

Thus we obtain:

$$\left[\frac{\hbar^2 (\vec{k}+\vec{G})^2}{2m} - E \right] U_{\vec{k}}(\vec{G}) + \sum_{\vec{G}'} V(\vec{G}-\vec{G}') U_{\vec{k}}(\vec{G}') = 0$$

Define a matrix:

$$\begin{aligned} H_{\vec{G}\vec{G}'} &= \frac{\hbar^2 (\vec{k}+\vec{G})^2}{2m} \delta_{\vec{G},\vec{G}'} + V(\vec{G}-\vec{G}') \\ &= \sum_{\vec{k}+\vec{G}} \delta_{\vec{G},\vec{G}'} + V(\vec{G}-\vec{G}') \end{aligned}$$

Then we have:

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

This is the Schrodinger equation for an electron in periodic potential, written in momentum space.

To find the eigenstates we have to diagonalize

the matrix $H_{\vec{G}\vec{G}'}(\vec{k})$. Clearly \vec{k} is a conserved quantum number, since the matrix H simply depends on \vec{k} as a parameter.

This means that the eigenstates will be labelled by \vec{k} .

Thus the eigenstates will have the following general form:

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

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} u_{n\vec{k}}(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

Here n is the index, labelling the eigenvalues of the matrix $H_{\vec{G}\vec{G}'}$.

$E_{n\vec{k}}$ are the energy eigenvalues.

n is called the band index, for reasons that will become clear soon.

Thus the eigenstates ~~of~~ of electrons in periodic potential have similar form to plane waves, with \vec{k} being the analog of momentum of a free electron. The important difference is that here \vec{k} is limited to the first Brillouin zone, while the free electron momentum is unbounded.

\vec{k} is often called the crystal momentum.

$\Psi_{n\vec{k}}(\vec{r})$ are called Bloch functions.

Since $\Psi_{n\vec{k}}(\vec{r})$ are very similar to plane waves electrons are (almost) not scattered by perfectly periodic potential, they are scattered only by imperfections in it.