

Lecture 4

Electrons in a periodic potential - Band structure

Reciprocal lattice

In a crystal the electron density (as well as many other quantities) is a periodic function of \vec{r}

$$\rho(\vec{r} + \vec{R}_n) = \rho(\vec{r})$$

$$\text{with } \vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \quad (1)$$

Let us make a Fourier transform of $\rho(r)$

$$\rho(\vec{q}) = \int \rho(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d^3 r$$

shifting $\vec{r} \rightarrow \vec{r} + \vec{R}_n$ we obtain

$$\begin{aligned} \rho(\vec{q}) &= \int \rho(\vec{r} + \vec{R}_n) e^{i\vec{q} \cdot (\vec{r} + \vec{R}_n)} d^3 r = \\ &= e^{i\vec{q} \cdot \vec{R}_n} \int \rho(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d^3 r = e^{i\vec{q} \cdot \vec{R}_n} \rho(\vec{q}) \end{aligned}$$

Thus for \vec{q} : $\vec{q} \cdot \vec{R}_n \neq 2\pi \times \text{integer}$ Fourier component is zero.

Thus we have a Fourier series

$$g(\mathbf{r}) = \sum_{\vec{G}} g_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}, \quad g_{\vec{G}} = \frac{1}{V_{uc}} \int_{uc} d^3r g(\mathbf{r}) e^{-i\vec{G}\cdot\vec{r}}$$

uc - unit cell

where \vec{G} is obtained from the condition

$$\vec{G}_m \cdot \vec{R}_n = 2\pi N$$

With R_n given by Eq. (1) reciprocal lattice vectors

$$\vec{G}_m = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3 \quad \text{with}$$

$$\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}, \quad i, j = 1, 2, 3$$

This gives

$$\vec{b}_1 = \frac{2\pi(\vec{a}_2 \times \vec{a}_3)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad \vec{b}_2 = \frac{2\pi(\vec{a}_3 \times \vec{a}_1)}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)}, \quad \vec{b}_3 = \frac{2\pi(\vec{a}_1 \times \vec{a}_2)}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)}$$

The reciprocal lattice of a simple cubic lattice is simple cubic. But a body centered cubic (bcc) has a fcc reciprocal lattice and vice versa.

The volume of a unit cell of the reciprocal lattice is $(2\pi)^3 / V_{uc}$. The reciprocal of the reciprocal is the original lattice. One defines the (first) Brillouin zone as the Wigner-Seitz cell in the reciprocal lattice.

Bloch's theorem

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Consider an electron in a periodic potential $V(r)$

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

The Schrödinger equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r) \psi(r) = \epsilon \psi(r)$$

If $\psi(r)$ is a solution then $\psi(r + R_n)$ is also a solution. Thus

$$\psi(r + R_n) = C \psi(r)$$

From the normalisation condition we obtain

$$|C|^2 = 1 \Rightarrow C = e^{i\phi(R_n)}$$

Let's make two consecutive translations R_n and R_m . Then we obtain

$$C(R_n + R_m) = C(R_n) \cdot C(R_m) \Rightarrow$$

$\phi(R_n) = \vec{k} \cdot \vec{R}_n$, where \vec{k} is some vector. Then

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

This can be rewritten as

$$\underline{\psi_{\vec{k}}(r) = e^{i\vec{k} \cdot \vec{r}} u(r)}, \text{ where } u(r + R_n) = u(r)$$

Bloch's theorem

Bloch's function

Bloch's theorem states that the wave function in a periodic potential is a plane wave modulated by the periodic function (Bloch's function).

The choice of \vec{k} is not unique. Adding any reciprocal lattice vector G does not change the wave function $\psi_{\vec{k}+G_n}(r) = \psi_{\vec{k}}(r)$.

\vec{k} is called pseudo (quasi) momentum.

Electron energy $E(\vec{k})$ is a function of \vec{k} .

Since \vec{k} and $\vec{k} + G_n$ are equivalent $E(k)$ is periodic function in reciprocal lattice.

For every k we may have different levels $\Rightarrow E_e(k)$. It is natural to restrict \vec{k} to the smallest possible nonequivalent vectors. Thus we obtain the first Brillouin zone

Because $E_e(k)$ is a periodic function it has its maximal and minimum value \Rightarrow for every l we get allowed energy bands.

They may be separated by the energy gaps but may also overlap.

Nearly free electron model

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Let us consider the weak periodic potential $V(r)$ that can be treated perturbatively

We can expand it in a Fourier series

$$V(r) = \sum_{G_n} V_{G_n} e^{i G_n \cdot r}$$

Consider for simplicity 1d case where

$$G_n = \frac{2\pi}{d} n$$

The first order perturbation theory gives constant shift of the energy level

$$\mathcal{E}^{(1)} = V_0 \text{ that we will neglect.}$$

The second order gives correction

$$\mathcal{E}(k) = \frac{\hbar^2 k^2}{2m} + \sum_{G_n} \frac{|V_{G_n}|^2}{\left(\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 (k-G_n)^2}{2m}\right)} \quad (2)$$

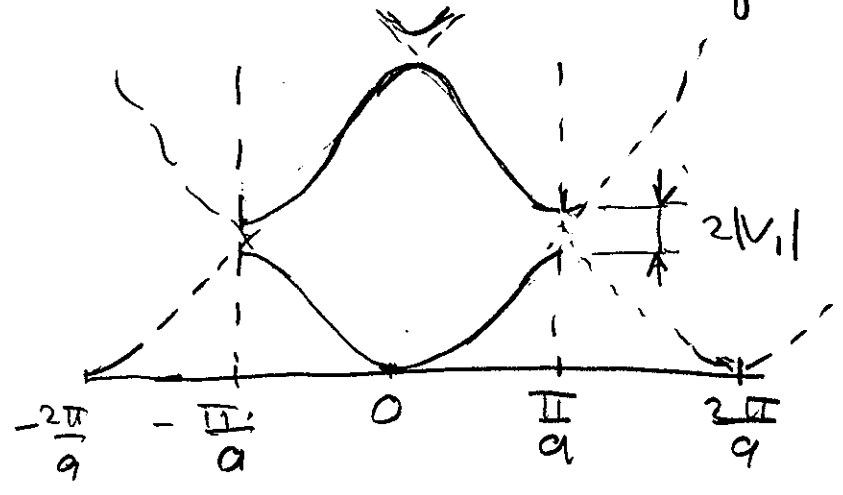
Close to the bottom of the band $k \ll G$

we can expand in k and obtain

$$\mathcal{E}(k) = E_0 + \frac{\hbar^2 k^2}{2m^*} \quad \text{with} \quad \frac{1}{m^*} = \frac{1}{m} \left(1 - 4 \sum_{G \neq 0} \frac{|V_G|^2}{(\hbar^2 G^2/2m)}\right)$$

so we have small mass renormalization $m \rightarrow m^* > m$

The perturbation theory breaks down for $k \rightarrow \frac{G}{2} = \frac{\pi}{a}$. Then two states k and $k - G$ have the same energy and the denominator in the Eq. (2) goes to zero



Then we should use perturbation theory for degenerate states. Considering linear combination $\psi = A_1 \psi_1 + A_2 \psi_2$ we get the Schrödinger Eq.

$$A_1 (\epsilon_1 - \epsilon) \psi_1 + V (A_1 \psi_1 + A_2 \psi_2) + A_2 (\epsilon_2 - \epsilon) \psi_2 = 0$$

with $\epsilon_1 = \frac{\hbar^2 k^2}{2m}$, $\epsilon_2 = \frac{\hbar^2 (k - G)^2}{2m}$

Multiplying first by ψ_1^* and integrating, and by ψ_2^* and integrating and using orthogonality of ψ_1 and ψ_2 we obtain

$$\begin{cases} A_1 (\varepsilon_1 - \varepsilon + V_0) + V_1 A_2 = 0 \\ A_2 (\varepsilon_2 - \varepsilon + V_0) + V_1^* A_1 = 0 \end{cases}$$

We get eigenvalues from the secular equation

$$\det \begin{bmatrix} \varepsilon_1 - \varepsilon + V_0 & V_1 \\ V_{-1} & \varepsilon_2 - \varepsilon + V_0 \end{bmatrix} = 0 \Rightarrow$$

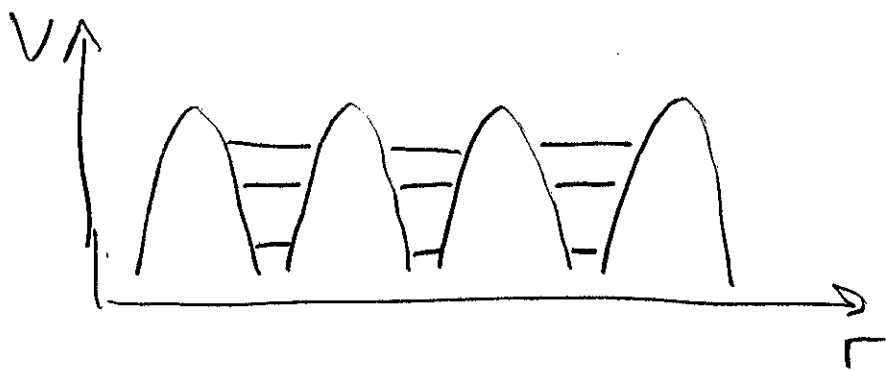
$$\varepsilon = V_0 + \frac{1}{2} (\varepsilon_1 + \varepsilon_2) \pm \sqrt{\frac{1}{4} (\varepsilon_1 - \varepsilon_2)^2 + |V_1|^2}$$

And the energy gap is $2|V_1|$

One can generalize the arguments to 3d and get energy jump at the Brillouin zone boundary

Tight binding approximation

We consider opposite case - lattice of atoms which are well separated such that their orbitals have small overlap. The lowest order approximation is the localized atomic orbitals



Consider 1d case

Schrödinger Equation is

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi(x) = \epsilon \psi(x)$$

with
$$V(x) = \sum_n \psi(x - na)$$

$\psi(x)$ is potential of a single atom

Instead of the Bloch's waves we can introduce their superposition - Wannier functions $W_n(x)$ (9)

$$W_n(x) = N^{-1/2} \sum_k e^{-ikna} \psi_p(x), \quad -\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$$

$$\psi_p(x) = N^{-1/2} \sum_k e^{ikna} W_n(x)$$

Here N is the number of atoms in 1d chain

Wannier functions with different n are orthogonal.

Using property of the Bloch's function

$$\psi_p(x-a) = e^{-ik a} \psi_p(x) \quad \text{one can show that}$$

$$W_n(x) = W_0(x-na)$$

$W_n(x)$ decays fast away from na .

We can rewrite the Schrödinger equation as

$$\sum_n \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x-na) + \underbrace{V(x) - U(x-na)}_{h(x)} \right] e^{ikna} W_n(x) =$$

$$= \epsilon(p) \sum_n e^{ikna} W_n(x)$$

$$\sum_n \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \mathcal{U}(x-na) \right) e^{ikna} \psi_n(x) +$$

$$+ \sum_n h(x) e^{ikna} \psi_n(x) = \mathcal{E}(k) \sum_n e^{ikna} \psi_n(x)$$

The term with $h(x)$ is small because it contains only product $\mathcal{U}(x-na) \psi_m(x-na)$ with $n \neq m$. In lowest order neglecting it we obtain $\psi^{(0)} = \psi(x)$ - atomic orbital

Then $\mathcal{E}^{(0)}(k) = \mathcal{E}_0$ - corresponding level of the isolated atom. In next order $\psi = \psi^{(0)} + \psi^{(1)}$

$$\sum_n \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \mathcal{U}(x-na) - \mathcal{E}(k) \right] \psi^{(1)} e^{ikna} =$$

$$= (\mathcal{E}(k) - \mathcal{E}_0) \sum_n e^{ikna} \psi_n^{(0)}(x) - \sum_n h(x) e^{ikna} \psi_n^{(0)}(x)$$

Multiplying by $\psi^{(0)}$ and integrating L.H.S would be $\sim \int (\mathcal{E}_0 - \mathcal{E}(k)) \psi^{(0)} \psi^{(1)} d^3r$ which is higher order correction. Thus R.H.S should be orthogonal to $\psi^{(0)}$

Then we obtain

$$\varepsilon(p) - \varepsilon_0 = \frac{\sum_n h(n) e^{iKn a}}{\sum_n I(n) e^{iKn a}}$$

$$\text{with } h(n) = \int \varphi^*(x) h(x) \varphi(x-na) dx$$

$$I(n) = \int \varphi^*(x) \varphi(x-na) dx$$

$h(n)$ and $I(n)$ are decaying with n

Then one can keep only terms with $n=0, 1$ and we obtain

$$\varepsilon - \varepsilon_0 = h(0) + 2 \left[\underbrace{h(1) - h(0) I(1)}_{\sim U(a) \frac{\varphi(a)}{\varphi(0)}} \right] \cos ka$$

Then every atomic orbital is transformed to the narrow band.