Lecture 13

Continue deriving electron Hamiltonian in Wannier basis:

$$\mathcal{H} = \sum_{\vec{k}\sigma} E_k C^+_{k\sigma} C_{k\sigma}$$

$|\vec{k}\rangle$ — Bloch state at momentum $\vec{k}$.

$|\vec{R}\rangle$ — Wannier state at $\vec{R}$.

$$|\vec{k}\rangle = \sum_{\vec{R}} |\vec{R}\rangle\langle\vec{R}|\vec{k}\rangle$$

This implies:

$$C^+_{k\sigma} = \sum_{\vec{R}} \langle\vec{R}|\vec{k}\rangle C^+_{\vec{R}\sigma}$$

$$\langle\vec{R}|\vec{k}\rangle = \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}}$$

$$C^+_{k\sigma} = \frac{1}{\sqrt{N}}\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} C^+_{\vec{R}\sigma}$$

Substitute this into the Hamiltonian:

$$\mathcal{H} = \sum_{\vec{k}\sigma} E_k C^+_{k\sigma} C_{k\sigma} =$$

$$= \frac{1}{N}\sum_{\vec{k}\sigma}\sum_{\vec{R}\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} E_k C^+_{R\sigma} C_{R'\sigma}$$

$$E_k = \varepsilon - t \sum_{\vec{\lambda}} \cos(\vec{k}\cdot\vec{\lambda}) =$$

$$= \varepsilon - \frac{t}{2} \sum_{\vec{\lambda}} \left(e^{i\vec{k}\cdot\vec{\lambda}} + e^{-i\vec{k}\cdot\vec{\lambda}} \right)$$

$$\mathcal{H} = \frac{1}{N} \sum_{\vec{k}\sigma} \sum_{\vec{R}\vec{R}'} e^{i\vec{k}\cdot(\vec{R}-\vec{R}')} \left[\varepsilon - \frac{t}{2} \sum_{\vec{\lambda}} \left(e^{i\vec{k}\cdot\vec{\lambda}} + e^{-i\vec{k}\cdot\vec{\lambda}} \right.\right.$$

$$C^{\dagger}_{R\sigma} C_{R'\sigma} =$$

$$= \varepsilon \sum_{\vec{R}\sigma} C^{\dagger}_{\vec{R}\sigma} C_{\vec{R}\sigma} - t \sum_{\vec{R}\vec{\lambda}\sigma} C^{\dagger}_{\vec{R}\sigma} C_{\vec{R}+\vec{\lambda}\sigma}$$

$$\mathcal{H} = \varepsilon \sum_{\vec{R}\sigma} C^{\dagger}_{\vec{R}\sigma} C_{\vec{R}\sigma} - t \sum_{\vec{R}\vec{\lambda}\sigma} C^{\dagger}_{\vec{R}\sigma} C_{\vec{R}+\vec{\lambda}\sigma}$$

The first term corresponds to energy of ~~[illegible]~~ the atomic orbital ε, while the second term ~~[illegible]~~ describes tunneling of electrons between nearest-neighbor lattice sites.

Start semiclassical electron dynamics.

Need to learn how to describe dynamics of band electrons.

As you know from quantum mechanics expectation values of operators often obey equations of motion which look exactly like the classical equations of motion. This can be interpreted in the following way: while the particle is described by a probability distribution in space $|\psi(\vec{r})|^2$, the center of this probability distribution moves according to classical equations of motion.

Derive the corresponding equations of motion for band electrons – there are both similarities and important differences from the free electron case.

First, let's find the velocity of band electrons.

$$\vec{v} = \cancel{\left\langle \frac{d\vec{r}}{dt} \right\rangle = \frac{i}{\hbar}\left\langle [H,\vec{r}] \right\rangle} \left\langle -\frac{i\hbar}{m}\vec{\nabla} \right\rangle$$

We will consider the motion in a particular band with index n and assume that transitions to other bands do not occur – this is an approximation, but a reasonable one in most cases.

Calculate the expectation values in the Bloch state $\psi_{n\vec{k}}(\vec{r})$ – we want to obtain a relation between velocity and momentum of a Bloch electron.

Drop band index from now on.

$$\vec{v}_k = \int d\vec{r}\, \psi_k^*(\vec{r}) \left(-\frac{i\hbar}{m}\vec{\nabla}\right) \psi_k(\vec{r})$$

To evaluate this recall Schrödinger equation:

$$H\psi_k = -\frac{\hbar^2}{2m}\nabla^2\psi_k + U(\vec{r})\psi_k = \varepsilon_k \psi_k$$

$$\nabla^2\psi_k = \nabla^2 u_k e^{i\vec{k}\cdot\vec{r}} = \vec{\nabla}\cdot\vec{\nabla}\left(u_k e^{i\vec{k}\cdot\vec{r}}\right) =$$

$$= \vec{\nabla}\left(\vec{\nabla} u_k e^{i\vec{k}\cdot\vec{r}} + i\vec{k} u_k e^{i\vec{k}\cdot\vec{r}}\right) =$$

$$= \left(\nabla^2 u_k\right) e^{i\vec{k}\cdot\vec{r}} + \left(i\vec{k}\cdot\vec{\nabla} u_k\right) e^{i\vec{k}\cdot\vec{r}} +$$

$$+ \left(i\vec{k}\cdot\vec{\nabla} u_k\right) e^{i\vec{k}\cdot\vec{r}} - k^2 u_k e^{i\vec{k}\cdot\vec{r}} =$$

$$= \left[\left(\vec{\nabla} + i\vec{k}\right)^2 u_k(\vec{r})\right] e^{i\vec{k}\cdot\vec{r}}$$

Thus we have:

$$-\frac{\hbar^2}{2m}\left(\vec{\nabla} + i\vec{k}\right) u_k(\vec{r}) + U(\vec{r}) u_k(\vec{r}) = \varepsilon_k u_k(\vec{r})$$

let $H_k = -\frac{\hbar^2}{2m}\left(\vec{\nabla} + i\vec{k}\right)^2 + U(\vec{r})$

$$H_k u_k = \varepsilon_k u_k$$

let's differentiate both sides with respect to $\vec{k}$:

$$\vec{\nabla}_k \left[\left(H_k - \varepsilon_k\right) u_k\right] = \vec{\nabla}_k \left(H_k - \varepsilon_k\right) u_k +$$

$$+ \left(H_k - \varepsilon_k\right) \vec{\nabla}_k u_k = 0$$

$$\vec{\nabla}_k \left(H_k - \varepsilon_k \right) = -\frac{i\hbar^2}{m}\left(\vec{\nabla} + i\vec{k}\right) - \vec{\nabla}_k \varepsilon_k$$

Now come back to the expression for $\vec{v}_k$:

$$\vec{v}_k = \int d\vec{r}\; \psi_k^*(\vec{r}) \left(-i\frac{\hbar}{m}\vec{\nabla}\right) \psi_k(\vec{r}) =$$

$$= \int d\vec{r}\; \psi_k^*(\vec{r}) \left(-\frac{i\hbar}{m}\vec{\nabla}\right) u_k(\vec{r}) e^{i\vec{k}\cdot\vec{r}} =$$

$$= \int d\vec{r}\; \psi_k^*(\vec{r}) \left(-\frac{i\hbar}{m}\vec{\nabla} u_k\right) e^{i\vec{k}\cdot\vec{r}} +$$

$$+ \int d\vec{r}\; \psi_k^*(\vec{r}) \frac{\hbar\vec{k}}{m} \psi_k(\vec{r}) =$$

$$= -\frac{i\hbar}{m}\int d\vec{r}\; u_k^*(\vec{r}) \cdot \left(\vec{\nabla} + i\vec{k}\right) u_k(\vec{r})$$

$$\vec{\nabla}_k \left(H_k - \varepsilon_k\right) u_k(\vec{r}) = \left[-\frac{i\hbar^2}{2m}\left(\vec{\nabla} + ik\right) - \vec{\nabla}_k \varepsilon_k\right] u_k(\vec{r}) =$$

$$= -\left(H_k - \varepsilon_k\right) \vec{\nabla}_k u_k(\vec{r})$$

$$-\frac{i\hbar}{m}\left(\vec{\nabla}+i\vec{k}\right)u_k(\vec{r}) = \frac{1}{\hbar}\vec{\nabla}_k\,\varepsilon_k\,u_k(\vec{r}) +$$

$$+\frac{1}{\hbar}\left(H_k-\varepsilon_k\right)\vec{\nabla}_k\,u_k(\vec{r})$$

Thus we obtain:

$$\vec{v}_k = -\frac{i\hbar}{m}\int d\vec{r}\;u_k^*(\vec{r})\left(\vec{\nabla}+i\vec{k}\right)u_k(\vec{r}) =$$

$$= \frac{1}{\hbar}\vec{\nabla}_k\,\varepsilon_k\int d\vec{r}\;u_k^*(\vec{r})\,u_k(\vec{r}) +$$

$$+\frac{1}{\hbar}\int d\vec{r}\;u_k^*(\vec{r})\left(H_k-\varepsilon_k\right)\vec{\nabla}_k\,u_k(\vec{r}) =$$

$$\cancel{= \frac{1}{\hbar}\vec{\nabla}_k\,\varepsilon_k - \frac{1}{\hbar}\int d\vec{r}\;\vec{\nabla}_k\,u_k^*(\vec{r})\left(H_k-\varepsilon_k\right)u_k(\vec{r}) -}$$

$$\cancel{-\frac{1}{\hbar}\int d\vec{r}\;u_k^*(\vec{r})\,\vec{\nabla}_k\left(H_k-\varepsilon_k\right)}$$

$$= \frac{1}{\hbar}\vec{\nabla}_k\,\varepsilon_k - \frac{1}{\hbar}\int d\vec{r}\;\left(H_k-\varepsilon_k\right)u_k^*(\vec{r})\,\vec{\nabla}_k\,u_k(\vec{r}) =$$

$$= \frac{1}{\hbar}\vec{\nabla}_k\,\varepsilon_k$$

Thus we have $\vec{v}_k = \frac{1}{\hbar}\vec{\nabla}_k\,\varepsilon_k$

Compare with free electrons:

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m}$$

$$\vec{v}_k = \frac{1}{\hbar} \vec{\nabla}_k \varepsilon_k = \frac{\hbar \vec{k}}{m} = \frac{\vec{p}}{m}$$

Relation for Bloch electrons is similar, but $\vec{v}_k \neq \frac{\hbar \vec{k}}{m}$ any more.

Now let's derive analog of Newton's second law:

$$\frac{d\vec{p}}{dt} = \vec{F}$$

Introduce translation operator:

$$T_{\vec{R}} \psi_k(\vec{r}) = \psi_k(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi_k(\vec{r})$$

Here $\vec{R}$ is any lattice vector.

$$[H, T_{\vec{R}}] = 0.$$

Add external force:

$$H \to H - \vec{F}\cdot\vec{r}$$

Equation of motion for $T_{\vec{R}}$:

$$\frac{dT_{\vec{R}}}{dt} = \frac{i}{\hbar}[H, T_{\vec{R}}]$$

Only the $-\vec{F}\cdot\vec{r}$ part doesn't commute with $T_{\vec{R}}$.

$$\left[-\vec{F}\cdot\vec{r}, T_{\vec{R}}\right]\psi_k(\vec{r}) =$$

$$= -\vec{F}\cdot\vec{r}\, T_{\vec{R}}\,\psi_k(\vec{r}) + T_{\vec{R}}\,\vec{F}\cdot\vec{r}\,\psi_k(\vec{r}) =$$

$$= -\vec{F}\cdot\vec{r}\,\psi_k(\vec{r})e^{i\vec{k}\cdot\vec{R}} + \vec{F}\cdot(\vec{r}+\vec{R})\,\psi_k(\vec{r})e^{i\vec{k}\cdot\vec{R}} =$$

$$= \vec{F}\cdot\vec{R}\,\psi_k(\vec{r})\,e^{i\vec{k}\cdot\vec{R}} = \vec{F}\cdot\vec{R}\,T_{\vec{R}}\,\psi_k(\vec{r})$$

Thus we have:

$$\frac{dT_{\vec{R}}}{dt} = \frac{i}{\hbar}\vec{F}\cdot\vec{R}\,T_{\vec{R}}$$

Take expectation value of both sides in the Bloch state $\psi_k(\vec{r})$:

$$\cancel{\langle T_{\vec{R}}\rangle = \int d\vec{r}\,\psi_k}$$

$$\langle\vec{k}|T_{\vec{R}}|\vec{k}\rangle = \int d\vec{r}\,\psi_k^*(\vec{r})\,T_{\vec{R}}\,\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{R}}$$

Thus we obtain:

$$\frac{d}{dt}e^{i\vec{k}\cdot\vec{R}} = i\frac{d\vec{k}}{dt}\cdot\vec{R}\,e^{i\vec{k}\cdot\vec{R}}$$

$$i\frac{d\vec{k}}{dt}\cdot\vec{R}\,e^{i\vec{k}\cdot\vec{R}} = \frac{i}{\hbar}\vec{F}\cdot\vec{R}\,e^{i\vec{k}\cdot\vec{R}}$$

If this is true for any $\vec{k}$ and $\vec{R}$, we must have:

$\hbar\frac{d\vec{k}}{dt} = \vec{F}$ - this is similar to Newton's second law but note that $\vec{F}$ only includes external forces, not forces on electron due to crystal lattice -

~~proof that electrons are not scattered~~

another way to see that electrons are not scattered by the perfectly periodic crystal.

The equations of motion for electron in a crystal are

$$\vec{v}_k = \frac{1}{\hbar}\vec{\nabla}_k \mathcal{E}_k$$

$$\hbar\frac{d\vec{k}}{dt} = -e\left(\vec{E} + \frac{1}{c}\vec{v}_k\times\vec{B}\right)$$