CALIFORNIA INSTITUTE OF TECHNOLOGY
APh 114B Solid State Physics Lecture 4
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Electron Group Velocity and Effective Mass

For *free electrons*, with plane wave eigenfunctions $e^{\pm ikz}$, and energy eigenstates $\mathcal{E} = \frac{\hbar^2 k^2}{2m}$, the **momentum**, $\hbar\mathbf{k}$, is a constant of the motion. In a periodic potential, the actual momentum is not in general translationally invariant, and is not a constant of the motion. In *periodic potentials* it is the **crystal momentum** which is a constant of the motion. If we picture an electron as a localized wavepacket, then the group velocity of the wavepacket is

$$V_g = \frac{\partial \omega_n(\mathbf{k})}{\partial k} = \frac{1}{\hbar}\frac{\partial \mathcal{E}_n(\mathbf{k})}{\partial k}$$

where $\mathcal{E} = \hbar\omega$.

Now suppose that the electron is in an applied electric field E. Its change in energy is

$$d\mathcal{E}_n = \frac{\partial \mathcal{E}_n}{\partial k} dk = -eE\,dx = -eEv_g\,dt = -\frac{eE}{\hbar}\frac{\partial \mathcal{E}_n}{\partial k} dt$$

so

$$dk = -\frac{eE}{\hbar} dt$$

and

$$\hbar \frac{dk}{dt} = -eE$$

where we now use $\mathbf{p} = \hbar\mathbf{k}$ to denote the crystal momentum.

The derivative of the group velocity with time is

$$\frac{dv_g}{dt} = \frac{1}{\hbar}\frac{\partial}{\partial t}\frac{\partial \mathcal{E}_n(\mathbf{k})}{\partial k} = \frac{1}{\hbar}\frac{\partial_n^2 \mathcal{E}(\mathbf{k})}{\partial k^2}\frac{\partial k}{\partial t}$$

$$\frac{dv_g}{dt} = -\frac{eE}{\hbar^2}\frac{\partial_n^2 \mathcal{E}_n}{\partial k^2} = -\frac{eE}{m^*}$$

where m^* is termed the **effective mass**; these can be rearranged so that

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 \mathcal{E}_n(\mathbf{k})}{k^2}$$

Notice the striking distinctions between the velocity and mass of an electron in the Drude model and the present result. According to Drude, the velocity of an electron would be zero except in the presence of an applied field. Here we see that for a state with a wavevector **k**, the electron velocity is a *time-independent* quantity!! Moreover, a Drude electron always has a mass m_e, whereas these results imply that electrons move as though possessed of an *effective* *mass* which *depends entirely on* the value $\frac{\partial^2 \mathcal{E}_n(\mathbf{k})}{k^2}$, which we will see can be *positive*, *negative* or *zero*, depending on the form of $\mathcal{E}_n(\mathbf{k})$. These relations can be formalized using time-independent perturbation theory. We expand $\mathcal{E}_n(\mathbf{k}+\mathbf{q})$ in $\mathbf{q}$

$$\mathcal{E}_n(\mathbf{k}+\mathbf{q}) = \mathcal{E}_n(\mathbf{k}) + \sum_i \frac{\partial \mathcal{E}_n}{\partial k_i} q_i + \frac{1}{2}\sum_{ij} \frac{\partial^2 \mathcal{E}_n}{k_i k_j} q_i q_j + O(q^3)$$

using a Hamilton $\mathcal{H}_{\mathbf{k+q}}\psi_n = \mathcal{E}(\mathbf{k}+\mathbf{q})\psi_n$;

$$\mathcal{H}_{\mathbf{k+q}} = \mathcal{H}_k + \frac{\hbar^2}{m}\mathbf{q}\cdot(-i\nabla + \mathbf{k}) + \frac{\hbar^2 q^2}{2m}$$

Time-independent perturbation theory for $\mathcal{H}\psi = (\mathcal{H}_0 + \mathcal{H}')\psi = \mathcal{E}_n\psi$ gives

$$\mathcal{E}_n = \mathcal{E}_n^0 + \int \psi_n^* \mathcal{H}' \psi_n \, d^3r + \sum_{n'\neq n} \frac{\left|\int \psi_n^* \mathcal{H}' \psi_n \, d^3r\right|^2}{\mathcal{E}_n^0 - \mathcal{E}_{n'}^0}$$

Ignoring quadratic and higher terms in q,

$$\sum_i \frac{\partial \mathcal{E}_n}{\partial k_i} q_i = \sum_i \int u_{n\mathbf{k}}^* \frac{\hbar^2}{m}(-i\nabla + \mathbf{k})_i q_i u_{n\mathbf{k}} \, d^3r$$

so

$$\frac{\partial \mathcal{E}_n}{\partial \mathbf{k}} = \frac{\hbar^2}{m}\int u_{n\mathbf{k}}^* (-i\nabla + \mathbf{k}) u_{n\mathbf{k}} \, d^3r$$

Since Bloch's theorem gives

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$$

$$\frac{\partial \mathcal{E}_n}{\partial \mathbf{k}} = \frac{\hbar^2}{m}\int \psi_{n\mathbf{k}}^* (-i\nabla) \psi_{n\mathbf{k}} \, d^3r$$

Since

$$\mathbf{v}_g \equiv -\frac{i\hbar}{m}\nabla$$

$$\frac{1}{\hbar}\frac{\partial \mathcal{E}_n(\mathbf{k})}{\partial \mathbf{k}} = \mathbf{v}_g$$

For the effective mass,

$$\sum_{ij} \frac{1}{2}\frac{\partial_n^2 \mathcal{E}}{\partial k_i \partial k_j} q_i q_j = \frac{\hbar^2 q^2}{2m} + \sum_{n'\neq n} \frac{\left|\int u_{n\mathbf{k}}^* \frac{\hbar^2}{m}\mathbf{q}\cdot(-i\nabla + \mathbf{k}) u_{n\mathbf{k}}' \, d^3r\right|^2}{\mathcal{E}_{n\mathbf{k}} - \mathcal{E}_{n'\mathbf{k}}}$$

See the second-order terms now:

$$\sum_{ij} \frac{1}{2}\frac{\partial_n^2 \mathcal{E}}{\partial k_i \partial k_j} q_i q_j = \frac{\hbar^2 q^2}{2m} + \sum_{n'\neq n} \frac{\left|\int u_{n\mathbf{k}}^* \left(-\frac{i\hbar^2}{m}\right)\mathbf{q}\cdot\nabla u_{n\mathbf{k}}' \, d^3r\right|^2}{\mathcal{E}_{n\mathbf{k}} - \mathcal{E}_{n'\mathbf{k}}}$$

The **Effective Mass Theorem** is thus:

$$\frac{\partial^2 \mathcal{E}_n}{\partial k_i\,\partial k_j} = \frac{\hbar^2}{m}\delta_{ij} + \left(\frac{\hbar^2}{m}\right)^2\left[\frac{\langle n\mathbf{k}|-i\nabla_i|n'\mathbf{k}\rangle\langle n\mathbf{k}|-i\nabla_j|n\mathbf{k}\rangle + \langle n\mathbf{k}|-i\nabla_j|n'\mathbf{k}\rangle\langle n\mathbf{k}|-i\nabla_i|n\mathbf{k}\rangle}{\mathcal{E}_n(\mathbf{k}) - \mathcal{E}_{n'}(\mathbf{k})}\right]$$

where

$$\langle n\mathbf{k}|-i\nabla_i|n'\mathbf{k}\rangle = \int \psi^*_{n\mathbf{k}}\,(-i\nabla)\,\psi_{n\mathbf{k}}\,d^3r$$

Thus we (?) that the **effective mass** is a **tensor quantity**, whose values depend on the form of $\mathcal{E}(k)$ in a particular direction in momentum space.

In a simple case where ϕ_i is a spherically symmetry s-orbital, we can write down the nearest neighbor tight binding band structure as

$$\mathcal{E}(k) = \mathcal{E}_i - \mathcal{E}'_{io} - \mathcal{E}'_{inn}\sum_{m=\text{nearest neighbors}} e^{i\mathbf{k}\cdot(\mathbf{r}_n-\mathbf{r}_m)}$$

where

$$\mathcal{E}'_{io} = -\int \phi_i^*(\mathbf{r}-\mathbf{R}_n)\mathcal{H}'(\mathbf{r}-\mathbf{R}_n)\phi_i(\mathbf{r}-\mathbf{R}_n)d^3r$$

$$\mathcal{E}'_{inn} = -\int \phi_i^*(\mathbf{r}-\mathbf{R}_n)\mathcal{H}'(\mathbf{r}-\mathbf{R}_n)\phi_i(\mathbf{r}-\mathbf{R}_n)d^3r$$

Note that $\mathcal{E}'_{io} > 0$ since $\mathcal{H}'(\mathbf{r}-\mathbf{R}_n) < 0$. Now let's specialize to a simple cubic lattice with

$$\begin{aligned}\mathbf{r}_n - \mathbf{r}_m &= (\pm a, 0, 0)\\ &\ (0, \pm a, 0)\\ &\ (0, 0, \pm a)\end{aligned}$$

For the simple cubic lattice, $\mathcal{E}(\mathbf{k})$ is then

$$\mathcal{E}(\mathbf{k}) \simeq \mathcal{E}_i - \mathcal{E}'_{io} - 2\mathcal{E}'_{inn}(\cos k_x a + \cos k_y a + \cos k_z a)$$