Dynamics of electrons in bands

The electron velocity

In one dimension, the general form of the Schrödinger equation in a periodic system is $\psi(x) = u(x)\exp(ikx)$ where $u(x)$ is a periodic function. We know that the energy depends on k. We now consider the velocity. We first consider the momentum by calculating the expectation value of the momentum operator $-i\hbar d/dx$ in the state i.e.

$$< p >= \int_{-\infty}^{\infty} u^*(x)\exp(-ikx)(-i\hbar)\left(ik\exp(ikx)u(x) + \exp(ikx)du/dx\right)dx$$
$$= \hbar k - i\hbar \int_{-\infty}^{\infty} u^* \frac{du}{dx} dx \qquad (1)$$

since the state $\psi(x)$ is normalised. For free particles, the second term does not appear since they are simply plane waves with $u(x) = 1$. This gives us the standard momentum equation. To understand the second term (which comes from the effect of the lattice) we must consider the Schrödinger equation in more detail. We insert the wavefunction $\psi(x) = u(x)\exp(ikx)$ into the standard Schrödinger equation and obtain

$$-\frac{\hbar^2}{2m}\left(-k^2\exp(ikx)u(x) + 2ik\exp(ikx)\frac{du}{dx} + \exp(ikx)\frac{d^2u}{dx^2}\right)$$
$$+\left(V - E_k\right)\exp(ikx)u(x) = 0 \qquad (2a)$$

Differentiate this with respect to k.

$$ik\left[-\frac{\hbar^2}{2m}\left(-k^2\exp(ikx)u(x) + 2ik\exp(ikx)\frac{du}{dx} + \exp(ikx)\frac{d^2u}{dx^2}\right) + (V - E_k)\exp(ikx)u(x)\right]$$
$$-\frac{\hbar^2}{2m}\left(-2k\exp(ikx)u(x) + 2i\exp(ikx)\frac{du}{dx}\right) - \frac{dE_k}{dk}\exp(ikx)u(x) = 0 \qquad (2b)$$

The term in square brackets must vanish due to (2a) , so we are left with (after cancelling out some common factors).

$$\frac{\hbar^2}{m}\left(ik\exp(ikx)u(x) + \exp(ikx)\frac{du}{dx}\right) = iu(x)\exp(ikx)\frac{dE_k}{dk} \qquad (2c)$$

We can use this to substitute for the bracketed term for $<p>$ above to get

$$< p >= \int_{-\infty}^{\infty} \exp(-ikx)u^*(x)(-i\hbar)\frac{m}{\hbar^2}\frac{dE_k}{dk} i\exp(ikx)u(x)dx = \frac{m}{\hbar}\frac{dE_k}{dk} \qquad (3)$$

This gives the result $< p >= \hbar k$ when the expression $E_k = \hbar^2 k^2 / 2m$ for the energy of a free electron is used. If we now note the definition of the momentum as the electron mass (in the light of later discussion note that this is the *free* electron mass) multiplied by the velocity, then

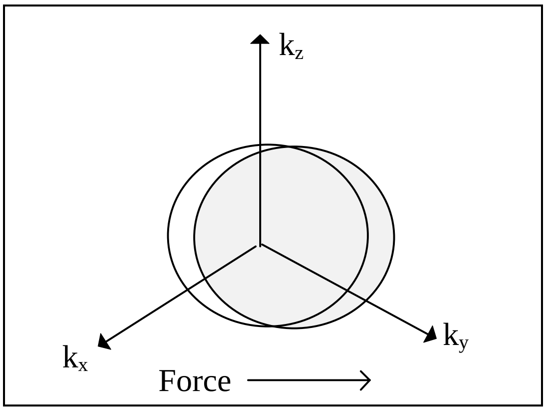
$$v_k = \frac{1}{\hbar}\frac{dE_k}{dk} \qquad (4)$$

and the effect of the lattice on the electron velocity can clearly be seen. Note the similarity of this to the velocity of phonons ($d\omega_k/dk$; recall that for phonons $E_k = \hbar\omega_k$) discussed above. As with phonons, the velocity goes to zero at the Brillouin zone boundaries (we get standing electron waves as we got standing lattice waves). A further point can be seen if we calculate the acceleration, f_k. From the equation above, this is clearly

$$f_k = \frac{dv_k}{dt} = \frac{1}{\hbar}\frac{d^2E_k}{dk^2}\frac{dk}{dt}. \qquad (5)$$

If this were a free electron, we could write that $p = \hbar k$ and so the force would be the rate of change of momentum, i.e. $F = dp/dt = \hbar dk/dt = mf$. We can continue to use these ideas within the lattice provided that we assume that the electron acts as though it had a mass, m^* given by

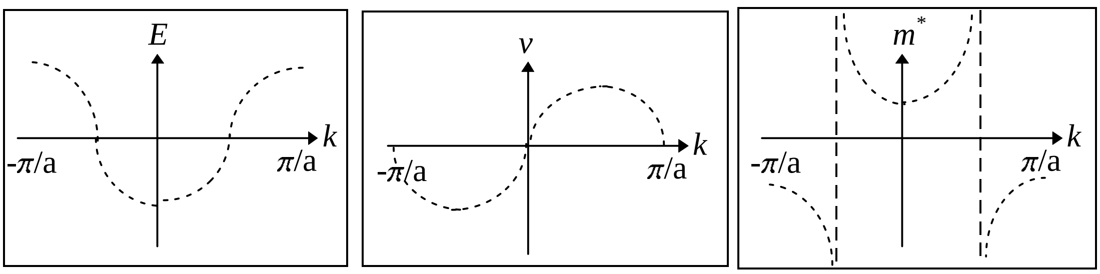
$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2E_k}{dk^2} \qquad (6)$$



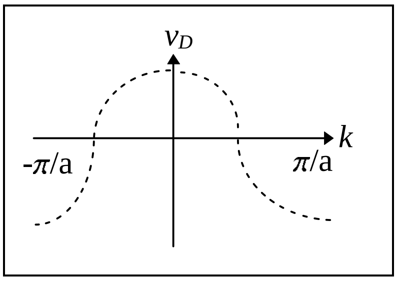
If this holds, then the standard definitions of force and momentum for free electrons still work, but with a different definition of the mass. If we are in the free electron case, the definition given above does indeed reduce to *m*. (Check it!) . Note that in a crystal, $\hbar k$ is not simply the momentum of the electron, it is the response of the *crystal* to the force *F*; there are contributions from both the electron and the lattice to the total crystal momentum that cannot be separated out. $\hbar k$ is therefore best considered as the *crystal momentum*. In the absence of a force, the filled electron states form a sphere centred on the origin $k_x = k_y = k_z = 0$ and radius k_F. The effect of applying a force is to move the sphere bodily in the direction of the force; new states are occupied in that direction and states on the other side of the sphere become vacant. This is not the only effect, otherwise the sphere would just drift off to the right. The effect of scattering (second term in the transport equation) is to slow electrons down - removing electrons from the states on the right and putting them back on the left. Thus in the steady state, the sphere is displaced from the origin at a point giving the balance between the applied force and the scattering. The replacement of *m by* m^* also applies to the transport equation for an electron discussed before. We must use

$$m^*\left(\frac{dv_D}{dt} + \frac{v_D}{\tau}\right) = F \qquad (7)$$

Note that m^* can take on all kinds of values; it is not even obliged to be positive. For example, if we take the tight-binding model for a 1-D chain, we have (from the previous section) $E_k = E_0 - 2\beta\cos(ka)$ and so the velocity is given by $v_k = (2\beta a/\hbar)\sin(ka)$ and the effective mass by $m^* = \hbar^2 / 2\beta a^2 \cos(ka)$. Near the top of the band ($k \approx \pm\pi/a$), the effective mass is negative and the electrons move in the opposite direction to the applied force.



Filled bands



The drift velocity of electrons in an external field F is

$v_D = \tau F / m^*$. (8)

We obtained above an expression for the effective mass of an electron in the tight-binding model for a linear chain. $m^* = \hbar^2 / 2\beta a^2 \cos(ka)$ and showed that the electrons move against the direction of force at the top of the band. The drift velocity will have the form shown above. Clearly at the bottom of the band (small k), m^* is positive and the electrons move in the direction of the force. At the top (large k) electrons will drift in the opposite direction. If the band is full, the symmetry of the situation implies that the net drift velocity of the electrons in the band is zero. This is, however, also true in general. We can see this for our linear model using the using the general definitions of v_D and m^* given above and remembering that in one dimension $g(k)$ is a constant. We then obtain the following expression for the average drift velocity;

$$\overline{v_D} = \frac{\int_{k=-\pi/a}^{\pi/a.} v_D g(k)dk}{\int_{k=-\pi/a}^{\pi/a} g(k)dk} = \frac{a\tau F}{2\pi\hbar^2}\int_{k=-\pi/a}^{\pi/a}\frac{d^2E_k}{dk^2}dk = \frac{a\tau F}{2\pi\hbar^2}\left[\frac{dE_k}{dk}\right]_{k=-\pi/a}^{\pi/a} = 0 \qquad (9)$$

In other words, you get insulating behaviour even though all the electrons are individually drifting.

Holes in a nearly-filled band

Let us consider a system where the band is full, except for one electron. The momentum of the full band would be zero. If the remaining empty electron state has a wavevector of **k,** (and hence a momentum of $\hbar\mathbf{k}$), then the rest of the band must have a total momentum of $-\hbar\mathbf{k}$. Similarly, the drift velocity of the band must be given by $v_D = -\tau F / m^*$ where m^* is the effective mass corresponding to the unfilled state. Since this electron is close to the top of the band (by hypothesis), it will have a negative effective mass, say $-m_h^*$. Hence the drift velocity of the band is $v_D = \tau F / m_h^*$. If we assume that the force is an electric field, $\mathbf{F} = -e\mathbf{E}$, then the current density (rate of charge movement per unit volume) would be $j = -ev_D / V = -e^2\tau E / Vm_h^*$. (Note that if we considered a single electron, we would get $j = -ev_D / V = e^2\tau E / Vm^*$). The point is that the *band* is acting as though it were a single electron, with positive charge and effective mass corresponding to the unfilled state. This is much easier to think about than a band of electrons. Hence, rather than think directly about the unfilled band, we will consider the system as a filled band, but with a hole in it.

With this idea, we can consider the *promotion* of an electron from a filled valence band into an empty conduction band as the *creation* of an electron-hole pair. Similarly, if the electron then falls back into the valence band, the pair is annihilated.

The transport equation for holes is clearly

$$m_h\left(dv_h / dt + v_h / \tau\right) = e\mathbf{E} \qquad (10a)$$

and for the promoted electron

$$m_e\left(dv_e / dt + v_e / \tau\right) = -e\mathbf{E} \qquad (10b)$$

where m_e is the effective mass of the electron - from now on we will drop the stars). If the densities of electrons in the conduction band and holes in the valence band are n_e,

n_h respectively, then the total current density $j = j_e + j_h = -en_e v_e + en_h v_h = \sigma\mathbf{E}$. Hence, we can write the conductivities in terms of the electron and hole mobilities, $\sigma = en_e\mu_e + en_h\mu_h$ and the mobilities are given by $\mu_e = e\tau / m_e$, $\mu_h = e\tau / m_h$ from the standard definitions of the velocities. If $n_e << n_h$, then the Hall coefficient $R_H = 1/n_h e$. i.e. it is greater than zero. This is the explanation (in outline) of the worst problem we found in the free-electron model.

Summary

- In the simplest free-electron models, electrons can be considered to be a gas of particles with velocities about 10^6m/sec which scatter every 10^{-14} seconds. When the lattice is considered, the velocity of the electron is a much more complex affair and depends on the electronic state
- When we consider electronic conductivity, what matters is the drift velocity. A filled band has no drift velocity although the individual electrons move.
- A nearly-filled band behaves like a positively charged particle with a **k** vector equal in magnitude but opposite in sign to that of the unfilled state.