

Boltzmann Transport with Band Structure and Quantum Mechanical Scattering

Semiclassical Equations of Motion

The last essential upgrade to the Boltzmann transport formalism is to account for the ever-present interaction between the transport particles and the background atoms, or lattice in the case of a crystalline solid. We have previously dealt specifically with electrons in the crystalline case and invoked Bloch’s theorem as a means of classifying the wavefunctions and categorizing the possible electronic energy states into bands. In the process, we learned that the good quantum mechanical independent variable in the particle dynamics was the crystal wave vector, \vec{k} . The classical momentum became the crystal momentum $\hbar\vec{k}$, and the mechanical velocity became the “group” velocity $\vec{v}_g = (1/\hbar)\vec{\nabla}U_n(\vec{k})$ where $U(\vec{k})$ is the nth band and the subscript on the gradient operator reminds us that the operation is made in k space. In terms of these quantities, the particle position is given by

$$\frac{d\vec{r}}{dt} = \vec{v}_g = \hbar^{-1}\vec{\nabla}U_n(\vec{k}) \tag{1}$$

And the reaction of an electron to an external force can then be written

$$\hbar\frac{d\vec{k}}{dt} = \vec{F} \tag{2}$$

In electronic solids, the two most common external forces are the electric and magnetic:

$$\vec{F}_e = q\vec{E} \qquad \vec{F}_m = \frac{q}{\hbar}\vec{\nabla}_k U \times \vec{B} \tag{3}$$

These are the same as the classical forces except that the velocity in (3) is replaced by the quantum-mechanical group velocity. In the general case of nonzero electric and magnetic fields, the combination of (1), (2) and (3) lead to the “semiclassical” single-particle equations of motion with (2) expressible in cartesian coordinates as

$$\begin{aligned} \hbar dk_x / dt &= q \left[E_x + \frac{1}{\hbar} \left((\vec{\nabla}U)_y B_z - (\vec{\nabla}U)_z B_y \right) \right] \\ \hbar dk_y / dt &= q \left[E_y + \frac{1}{\hbar} \left((\vec{\nabla}U)_z B_x - (\vec{\nabla}U)_x B_z \right) \right] \end{aligned} \tag{4}$$

$$\hbar dk_z / dt = q \left[E_z + \frac{1}{\hbar} \left((\vec{\nabla} U)_x B_y - (\vec{\nabla} U)_y B_x \right) \right]$$

The combination of (1) and (2) form a coupled pair, similar to Newton’s equations but in terms of \vec{r} and \vec{k} instead of \vec{r} and \vec{p} . Another difference is that \vec{r} in (1) can not be a point in space, as in Newton’s law, but rather the *expectation* value for the position value of the particle. We will see below more precisely how to define this expectation value. Yet another difference is that (1) is linked intimately to the band structure of the particle if it is moving within a crystal lattice. More specifically, (1) couples the motion in real space to the “motion” in k space through a map – the $U_n(\vec{k})$ function for a given band, indexed by n.

Semiclassical Equations of Motion: Behavior of particles in real space

Before embarking on the development of semiclassical Boltzmann transport formalism, it is helpful to better understand what the position vector \vec{r} really means in the semiclassical model. This can be accomplished by transforming from \vec{k} space to \vec{r} space using Fourier techniques. We start with a truly “free” particle in vacuum for which the solution to the Schrodinger equation has the mathematical form of a *plane wave*

$$\psi(\vec{r}, t) = \psi_0 e^{j(\vec{k} \cdot \vec{r} - \omega t)} = \psi_0 e^{j(\vec{k} \cdot \vec{r} - U t / \hbar)} \tag{5}$$

As in electromagnetics, the plane wave is a physically inadmissible solution when allowed to extend to infinity along any direction. To fix this problem, we formulate a wavepacket

$$\psi_n(\vec{r}, t) = \sum_{\vec{k}'} \underbrace{g(\vec{k}')}_{\text{Fourier amplitude}} \underbrace{\exp[j(\vec{k}' \cdot \vec{r}) - jU(\vec{k}')t / \hbar]}_{\text{basis function}}$$

In the presence of a crystal lattice, we must generalize (5) to include a cell-periodic portion, which is just the Bloch function:

$$\psi_{n,\vec{k}}(\vec{r}) = e^{j\vec{k} \cdot \vec{r}} u_{n,\vec{k}}(\vec{r}) \tag{6}$$

To make this physically admissible, we again form a wave packet, confined to band n,

$$\psi_n(\vec{r}, t) = \sum_{\vec{k}'}^{\vec{k}_N} \underbrace{\psi_{n\vec{k}'}(\vec{r})}_{\text{basis function}} e^{-j[U_n(\vec{k}')t/\hbar]}$$

where $g(\vec{k})$ is the Fourier amplitude function and the sum extends only up to \vec{k}_N , the Nyquist wave vector, within the 1st Brillouin zone (BZ).

The meaning of \vec{r} in the semi-classical theory is now addressed by considering the size of the wave packet using the translation property of Bloch functions:

$$\psi(\vec{r} + \vec{r}') = e^{j\vec{k} \cdot \vec{r}'} \psi(\vec{r})$$

This should apply to the wavepacket as well, meaning that for a particular $\vec{r} = \vec{r}_0$,

$$\psi(\vec{r}_0 + \vec{r}', t) = \sum_{\vec{k}'} g(\vec{k}') \psi_{n,\vec{k}'}(\vec{r}_0) \exp\left[j(\vec{k}' \cdot \vec{r}' - U_n(\vec{k}')t/\hbar)\right] \quad (7)$$

We can think of this as a function of \vec{r}' for fixed \vec{r}_0 . And because the entire sum extends only over the 1st BZ, we expect that the product $g(\vec{k}') \cdot \psi_{n,\vec{k}'}(\vec{r}_0)$ extends over a Δk much narrower than the Brillouin zone, i.e.,

$$\Delta k \ll k_N = \pi/a.. \quad (8)$$

By Fourier-transform theory, the extent of the wavepacket, $\Delta r'$, in (7) should abide by the mutual uncertainty relation,

$$\Delta r' \cdot \Delta k \approx 1 \quad (9)$$

Substitution of (8) into (9) leads to

$$\Delta r' \gg \frac{a}{\pi} \quad (10)$$

In other words, the spatial extent of the Bloch wave packet (in real space) must be significantly greater than a lattice constant, which means even greater than the interatomic separation.

The analysis of the Bloch wave packet also guides us to better understand the time evolution associated with (1). We should think of \vec{r} as the position of the center of the Bloch wave packet, moving with velocity \vec{v}_g . Through (1) and (2), any external force thereby changes the location of the particle in real space and \vec{k} space as well. External forces are treated

classically but, consistent with (10), must vary even move slowly in space than the wavepackets. For example, the wavelength of an ac electric field must satisfy $\lambda \gg \Delta r$.

The only remaining subtlety of the semiclassical equations is the implicit requirement that the motion be confined to one band. This is much more difficult to analyze, but can be tested with respect to the external forces by the following general conditions:

- (a) For dc electric fields: $eEa \ll [U_G]^2 / U_F$, where $U_G \rightarrow$ gap to nearest other band and $eEa \rightarrow$ electrostatic potential energy shift over a unit cell
- (b) For dc and ac magnetic fields: $\hbar\omega_c \ll [U_G]^2 / U_F$, where $\omega_c = \frac{qB}{m}$ is the cyclotron frequency and $\hbar\omega_c$ is the kinetic energy shift due to magnetic quantization.
- (c) For ac electric fields: $\hbar\omega \ll U_G$, $\omega = 2\pi c/\lambda$ for ac field $E_0 e^{j\omega t}$

Example of semiclassical theory: Bloch oscillations

We recall from the analysis of band structure that the first-order effect of the background lattice in crystals is the strong Bragg scattering at the Nyquist wave vector, $k_N = \pi/a$. The other key result was quadratic behavior around local-minimum points (free-electron-like behavior). So for a band having a minimum at $k = 0$, a good approximate one-dimensional model of band structure (along z direction) would be

$$U(k_x) = (1/2)U_B [1 - \cos(k_x a)]. \tag{11}$$

where U_B is the band width, a is the lattice constant, and the absolute minimum energy of the band is set arbitrarily to zero. The group velocity is then given by

$$v_g = \frac{U_B a}{2\hbar} \sin k_z a$$

$$\frac{dz}{dt} = v_g \equiv \frac{1}{\hbar} \frac{\partial U}{\partial k} = \frac{U_B a}{2\hbar} \sin(k_z a) \tag{12}$$

The second semiclassical equation is

$$\hbar \frac{dk_z}{dt} = F \equiv -qE_0 = +eE_0$$

for which the solution is simply $k_z = \frac{eE_0 t}{\hbar} + k_0$ (13)

The initial value of k_0 can be set to zero with no loss of generality for the present argument.

Substitution of (13) back into (12) then yields

$$\frac{dz}{dt} = v_g \equiv \frac{1}{\hbar} \frac{\partial U}{\partial k_z} = \frac{U_B a}{2\hbar} \sin(eE_0 a t / \hbar)$$

for which the solution (by inspection) has the oscillating form

$$z = -\frac{U_B}{2eE_0} \cos(eE_0 a t / \hbar) \equiv -\Delta z \cos(\omega_B t) \quad (14)$$

where the last step defines the amplitude Δz and circular frequency ω_B of the oscillation, and again, the initial value has been set arbitrarily to zero. This is arguably one of the most interesting yet simple predictions of the semiclassical theory, predicted first by F. Bloch, and hence called the *Bloch oscillation*.

Clearly, the solution for k (13) is progressive in k space, meaning that k changes linearly with time across the 1st Brillouin zone until it reaches k_N , after which it suddenly re-appears at $k_x = -k_N$ and continues the linear progression once again. But the solution for the wave-packet center (14) is more interesting, displaying oscillations of frequency ω_B and amplitude Δx .

Example of Bloch oscillations in a direct band-gap semiconductor. Suppose the semiconductor is crystalline and has a conduction band centered at $k_x = 0$ with a bandwidth $U_B = 3.0$ eV and a lattice constant $a = 5$ Ang. The resulting model band function of (11) and the associated group velocity are shown in Figs. 1(a) and (b), respectively. The applied dc electric field is assumed to be 5×10^4 V/cm (5×10^6 V/m), a rather large value, but easily sustained in high-purity, high-resistivity semiconductors. Under these conditions, the linear Bloch frequency will be

$$f_B = \omega_B / 2\pi = eE_0 a / h = 6.04 \times 10^{11} \text{ Hz} = 604 \text{ GHz}.$$

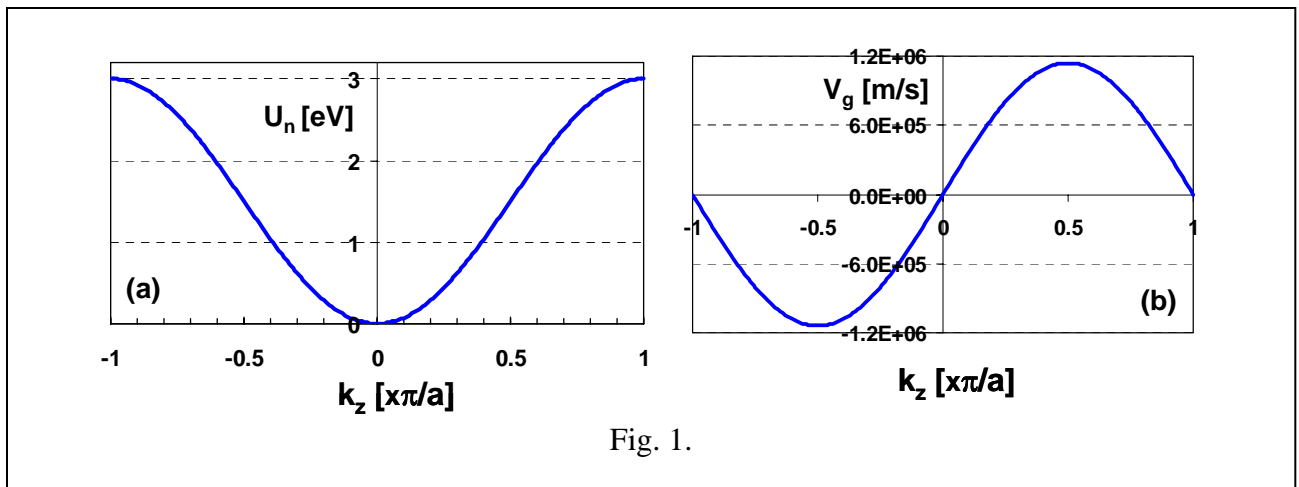


Fig. 1.

And the amplitude will be $\Delta z = U_B/2eE_0 = 3 \times 10^{-7} \text{ m} = 0.3 \text{ } \mu\text{m}$

In many ways, the Bloch oscillation predicted above has been a “holy grail” of solid-state and semiconductor physics since it was predicted. And as of the time of composition, the author has not heard of such oscillations being observed in any bulk semiconductor *at any temperature of operation*. The reasons for this is rather simple, but frustrating, to solid-state engineers trying to develop Bloch oscillators. They can be seen through the following two requirements. In order for the oscillation to occur, the crystal wavevector must be progressive over the 1st Brillouin zone, meaning that transport must be ballistic (i.e., collision-free), or nearly ballistic. Stated differently, the oscillation of the wave packet in real space must be sustained over a distance of typically 100-to-1000 lattice constants.

It turns out that these requirements are very difficult (if not impossible) to achieve in a bulk semiconductor for one fundamental reason that is clear from Fig. 1(a) and (b). Typically bulk semiconductors have conduction band widths in excess of $U_B = 1 \text{ eV}$. As the electron wave packet moves in k space within such a band, it will necessarily have to experience a very high group velocity, such as the peak values in excess of 10^6 m/s as shown in Fig. 1(b). Although still far below the speed of light and thus nonrelativistic, such velocities create a very strong interaction with lattice waves or phonons via acoustic or optical phonon absorption in all semiconductors around room temperature, or optical phonon emission in polar semiconductors at low temperatures.

Semiclassical Generalization of Boltzmann Equation

The importance of particle collisions and scattering in all solids, even in very pure semiconductors, forces us to generalize the semiclassical equations in the same fashion as done previously for the classical Newton equation. Not surprisingly, the first and most common way to generalize (2) is through a phenomenological relaxation term

$$\hbar \frac{d\vec{k}}{dt} = q \left(\vec{E} + \frac{1}{\hbar} \vec{\nabla}_k U_n(\vec{k}) \times \vec{B} \right) + \hbar \vec{k} / \tau(\vec{k}) \tag{15}$$

where $\tau(\vec{k})$ is written explicitly as a function of \vec{k} to account for energy-dependent scattering. No such relaxation term is added to the real-space semiclassical Eqn (1) since τ is assumed *not to depend on spatial location of the wavepacket*.

Just as in the classical case, we expect that certain types of particle scattering will have a strong dependence on kinetic energy and, therefore, even a stronger dependence on \vec{k} . This compels us to immediately consider a statistical approach to the semi-classical transport

A key issue in the development of a statistical semi-classical approach is that the Boltzmannian concept of a “phase space” in which to place each and every particle and to define a distribution function is still valid. We just have to replace of \vec{r} and \vec{p} by \vec{r} and \vec{k} , and stay cognizant of the fact that the location of particles in this space is made “fuzzy” by the inherently probabilistic nature of the quantum mechanics. To remind ourselves of this fact, we replace the variable \vec{r} by \vec{r}_{wp} where “wp” stands for wave packet. Fortunately, the space is still six dimensional, so that we can define the distribution function in the same way mathematically as in the classical Boltzmann case, and expand it by the chain rule of (partial) differential calculus as

$$\frac{df}{dt} = - \frac{\partial f}{\partial \vec{r}_{wp}} \frac{d\vec{r}_{wp}}{dt} - \frac{\partial f}{\partial \vec{k}} \frac{d\vec{k}}{dt} - \frac{\partial f}{\partial t} \Big|_{scattering} \tag{16}$$

And guided also by the classical case, we approximate the scattering term by the (small-perturbation) semiclassical relaxation-time approximation:

$$\frac{\partial f}{\partial t} \Big|_{scattering} = \frac{f - f_0}{\tau(\vec{k})}$$

so that (16) becomes

$$\frac{df}{dt} = -\frac{\partial f}{\partial \vec{r}_{wp}} \frac{d\vec{r}_{wp}}{dt} - \frac{\partial f}{\partial \vec{k}} \frac{d\vec{k}}{dt} - \frac{f - f_0}{\tau(\vec{k})} \quad (17)$$

Given this semi-classical Boltzmann equation, if f is independent of \vec{r} , we can write the electrical current formally as

$$\vec{J}_q = qn\vec{v}_g = \frac{qn \int_{band} \vec{v}_g(\vec{k}) f[U_n(\vec{k})] d\vec{k} \cdot 2 \cdot (L/2\pi)^3}{\int_{band} f[U_n(\vec{k})] d\vec{k} \cdot 2(L/2\pi)^3} \quad (18)$$

where the factor $(L/2\pi)$ is the volume per state in k space. So (18) becomes

$$\vec{J}_q = q \frac{N}{V} \frac{\int_{band} \vec{v}_g(\vec{k}) f[U_n(\vec{k})] d\vec{k} \cdot 2 \cdot (L/2\pi)^3}{N} = q \frac{\int_{band} \vec{v}_g(\vec{k}) f[U_n(\vec{k})] d\vec{k}}{4\pi^3}$$

Similarly, the thermal current can be written

$$\vec{J}_K = \int_{band} \vec{v}_g(\vec{k}) U(\vec{k}) f[U_n(\vec{k})] d\vec{k} / 4\pi^3 \quad (19)$$

As in the classical case, the non-equilibrium distribution function $f[U_n(\vec{k})]$ is found as the solution to Boltzmann's equation. If we assume f is uniform in real space so that $\partial f / \partial r_{wp} = 0$ and analyze the steady-state, (17) becomes

$$0 = -\frac{\partial f}{\partial \vec{k}} \frac{d\vec{k}}{dt} - \frac{f - f_0}{\tau}$$

or
$$f \cong f_0 - \tau \frac{\partial f}{\partial \vec{k}} \cdot \frac{d\vec{k}}{dt} \cong f_0 - \tau \frac{\partial f}{\partial U} \frac{\partial U}{\partial \vec{k}} \cdot \frac{d\vec{k}}{dt}.$$

Where we show a dot product in the last step between two intrinsically vector derivatives. But from the semiclassical equations (1) and (2), we have

$$\frac{d\vec{k}}{dt} = \frac{\vec{F}}{\hbar} \quad \text{and} \quad \frac{\partial U}{\partial \vec{k}} = \hbar \vec{v}_g.$$

Furthermore, if the perturbation created by F is small, then as in the classical analysis

$$\frac{\partial f}{\partial U} \approx \frac{\partial f_0}{\partial U} = \frac{-f_0(1-f_0)}{k_B T}$$

Thus the solution to (17) becomes

$$f \cong f_0 + \frac{\tau f_0(1-f_0)}{k_B T} \vec{F} \cdot \vec{v}_g \equiv f_0 + f'$$

In the special and very useful case of a uniform electric field, this becomes

$$f = f_0 + \frac{\tau f_0(1-f_0) q \vec{E} \cdot \vec{v}_g}{k_B T} \quad (20)$$

Example of semiclassical Boltzmann equation: uniform electric field in a solid having a single filled band. The general solution for the electrical current is

$$\langle \vec{J}_q \rangle = \frac{q}{4\pi^3} \int_{band} \vec{v}_g f_0 d\vec{k} + \frac{q}{4\pi^3} \int_{band} \frac{\vec{v}_g \tau f_0 (1 - f_0) q \vec{E} \cdot \vec{v}_g d\vec{k}}{k_B T}$$

But for a filled band, the second integral has no available states within band ($f_0 = 1$ for all values of k), so this term is approximately zero. Hence

$$\langle \vec{J}_q \rangle \approx \frac{q}{4\pi^3} \int_{band} \vec{v}_g f_0 d\vec{k} = \frac{q}{4\pi^3 \hbar} \int_{band} \frac{\partial U_n}{\partial \vec{k}} f_0 [U_n(\vec{k})] d\vec{k} \quad (21)$$

To evaluate this integral, we utilize yet another important consequence of band structure - its symmetry in k space. Specifically, we recall that for a given band index,

$$U_n(\vec{k}) = U_n(-\vec{k}), \quad (22)$$

which in mathematics is called an “even” function. And since $U_n(k)$ is even, so is $f_0[U_n(k)]$. Eqn

(22) also implies that $\frac{\partial U_n(\vec{k})}{\partial \vec{k}} = -\frac{\partial U_n(-\vec{k})}{\partial \vec{k}}$, which in mathematics is called an “odd” function.

So in total, (21)

is an integral over the product of an “odd” function times an “even” function. But such a product is also an “odd” function. And from calculus, we know that the integral of an odd function over any zero-centered domain of the independent variable must be zero. So in the end we get for the electrical current from a full band,

$$\langle \vec{J}_q \rangle = 0$$

Similarly for the heat flux, we can derive a solution to (17) analogous to (20) and use the non-equilibrium function to formulate the thermal current via (19):

$$\langle \vec{J}_Q \rangle = \frac{1}{4\pi^3} \int_{band} \vec{v}_g U_n f_0 d\vec{k} + \frac{1}{4\pi^3} \int_{band} \vec{v}_g(\vec{k}) U_n(\vec{k}) f' d\vec{k}$$

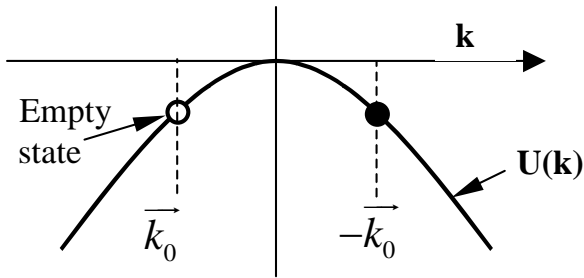
Without even going through the work, we can immediately derive the solution for free carriers in a filled band based on the same symmetry arguments as above. As with the electrical current, the non-equilibrium term f' in the second integral will be proportional to $f_0(1-f_0)$ so will go to zero for a filled band since there are no available states. Furthermore, the 1st integral also vanishes since the integrand is now a product of two even functions (U_n and f_0) and an odd function (\vec{v}_g). And from mathematics, the product of two “evens” and one “odd” is “odd”. This leads to the following profound theorem of semiclassical transport:

A filled band cannot conduct electrical or thermal current.

Corollary: Partially filled bands make good conductors. In other words, it is not the availability of electrons that makes a solid a conductor or insulator. Rather, it is how the electrons are distributed in bands. We came to this same conclusion when covering band structure.

Hole Theorem

Yet another profound consequence of the semi-classical theory is the transport behavior of a band in which most of the states are occupied with electrons and just a few are empty. We start with the band picture shown below with just one missing electron at wave vector \vec{k}_0 , and we analyze the effect of this on the crystal momentum and energy of the carriers:

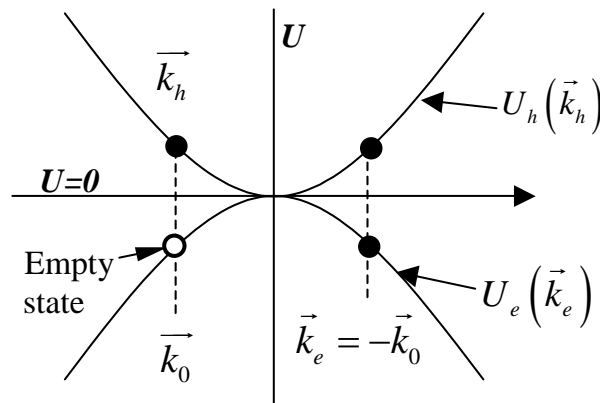


In terms of crystal momentum, the missing electron at \vec{k}_0 means that the net wave crystal momentum of the sample is $-\hbar\vec{k}_0$ since all other electrons (occupied states) cancel in pairs.

In terms of energy, we can write from the (assumed known) electronic band structure and symmetry properties:

$$U_e(\vec{k}_0) = U_e(-\vec{k}_0) = -U_h(-\vec{k}_0) \equiv -U_h(\vec{k}_h) \tag{23}$$

where U_h is a fictitious “hole” band that is a mirror-image of the real electronic band about the $U = 0$ axis. This mirror imaging is shown in the sketch below



To complete the hole theorem we need to analyze the semiclassical equations of motion, starting with evaluation of the group velocity. Since, the momentum of all electrons cancel in

pairs except for the state $\vec{k}_e = -\vec{k}_0$ then from (2) we can write one semiclassical equation for the entire band

$$\hbar \frac{d\vec{k}_e}{dt} = -\hbar \frac{d\vec{k}_0}{dt} = -e \left[\vec{E} + \frac{1}{\hbar} \vec{\nabla}_k U_e(\vec{k}_e) \times \vec{B} \right] \equiv -\hbar \frac{d\vec{k}_h}{dt} \quad (24)$$

Then using (23) along with symmetrical properties of the gradient operator, we can write

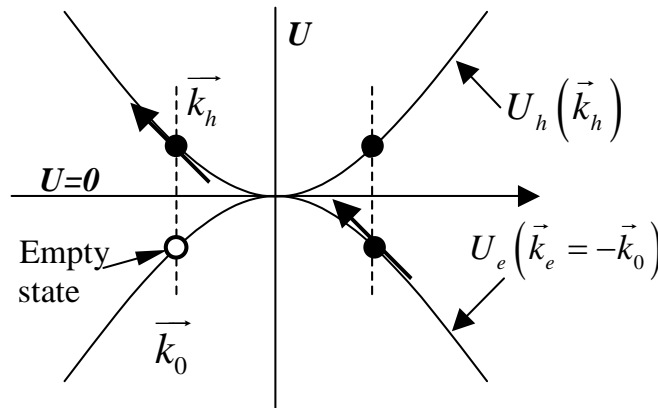
$$\vec{\nabla} U_k(\vec{k}_e) = \vec{\nabla} U_k(-\vec{k}_0) = -\vec{\nabla} U_h(-\vec{k}_0) = \vec{\nabla} U_h(\vec{k}_h) \quad (25)$$

where the last equality is justified graphically in the sketch below. Substitution of the outside equality of (25) into (24) leads to the

$$-\hbar \frac{d\vec{k}_h}{dt} = -e \left[\vec{E} + \frac{1}{\hbar} \vec{\nabla}_k U_h(\vec{k}_h) \times \vec{B} \right]$$

or by negation,

$$+\hbar \frac{d\vec{k}_h}{dt} = +e \left[\vec{E} + \frac{1}{\hbar} \vec{\nabla}_k U_h(\vec{k}_h) \times \vec{B} \right]$$



Given this clarification, we can treat the transport of empty states in an otherwise full band simply by the following two tricks which constitute the hole theorem:

With respect to transport in a uniform electric field by the semiclassical model, the effect of an empty (hole) state in an otherwise-full band can be accounted for by:

- (1) changing the sign of the charge from $q = -e$ to $q = +e$,
- (2) inverting the energy band about a mirror plane of $U = 0$ - the highest energy point in the band.

This is a remarkably simple result, and profoundly important for bipolar semiconductors, i.e., semiconductors with some occupied electronics states in the highest (conduction) band band, and an equal number of unoccupied electronic (hole) states in the next lowest (valence) energy band. We will be examining those shortly.

The hole theorem can be added to the embodiment of the semiclassical Boltzmann transport equation by adding a counterpart to (15) for “holes”

$$\hbar \frac{d\vec{k}_e}{dt} = -e \left[\vec{E} + \frac{1}{\hbar} \vec{\nabla}_k U_e(\vec{k}_e) \times \vec{B} \right] + \frac{\hbar \vec{k}_e}{\tau_e(\vec{k}_e)} \quad (26)$$

$$\hbar \frac{d\vec{k}_h}{dt} = +e \left[\vec{E} + \frac{1}{\hbar} \vec{\nabla}_k U_h(\vec{k}_h) \times \vec{B} \right] + \frac{\hbar \vec{k}_h}{\tau_h(\vec{k}_h)} \quad (27)$$

where τ_h is the hole scattering or relaxation time

Magnetic-Field Conservation Theorem

Yet another profound consequence of semi-classical transport comes about when there is a large magnetic field applied to a solid with an insignificant electric field. In the special case of $\vec{B} \gg 0$ and $\vec{E} = 0$, we can write the semiclassical equation (1) as

$$\frac{d\vec{r}_e}{dt} = \frac{1}{\hbar} \vec{\nabla}_k U_e(\vec{k}_e) \qquad \frac{d\vec{r}_h}{dt} = \frac{1}{\hbar} \vec{\nabla}_k U_h(\vec{k}_h)$$

When coupled to (26) and (27) above, we see the following two important facts:

- (1) the component of \vec{k}_e or \vec{k}_h along the \vec{B} field is conserved in motion \Rightarrow k-space motion is entirely in the perpendicular plane \Rightarrow cyclic motion in many crystals
- (2) the total energy $U_e(\vec{k}_e)$ or $U_h(\vec{k}_h)$ is conserved.

The proof of the energy conservation is a simple but elegant exercise in semiclassical transport. We assume the band structure is known at all points in k space and can be expanded as

$$\delta U = \frac{\partial U}{\partial \vec{k}_{e,h}} \cdot \delta \vec{k}_{e,h} = \hbar \vec{v}_g \cdot \delta \vec{k}_{e,h} \quad (28)$$

where the subscript e,h mean either electron or hole. But from the semiclassical equation (26) and (27), we can expand $\delta k_{e,h}$ as a function of time

$$\delta \vec{k}_{e,h} = \frac{d\vec{k}_{e,h}}{dt} \delta t = \frac{q}{\hbar} (\vec{v}_g \times \vec{B}) \delta t \quad (29)$$

Combining (28) and (29) we get

$$\delta U = q \vec{v}_g \cdot (\vec{v}_g \times \vec{B}) \delta t = 0 \quad (30)$$

for any uniform \vec{B} since $\vec{v}_g \times \vec{B}$ is always perpendicular to \vec{v}_g .

The practical implications of the magnetic conservation theorem are very important in materials science and for semiconductors, metals, and semi-metals. The cyclic motion and its

associated frequency are known as cyclotron resonance. The motion in k space becomes particularly simple – circular or elliptical - in spherical or spheroidal bands as usually occurs in the conduction band of semiconductors.¹ This means that the band curvature or, equivalently, the reciprocal effective-mass tensor components can be determined through measurement of the cyclotron frequency (see HW Problem) as a function of crystal orientation.

Even when the solid does not have a simple constant-energy (i.e., Fermi) surface, the magnetic field theorem is still very useful in understanding the band structure. This is because the cyclic motion in k space creates oscillatory behavior in other transport parameters, which in turn can be related to the Fermi energy, effective mass, etc. Oscillations created in the electrical resistivity (or conductivity) are called the Shubnikov-de Haas effect, and oscillations in the macroscopic magnetic susceptibility χ_m are called the de Haas-van Alphen effect.

Conductivity Effective Mass

We have seen that in the presence of a crystal lattice we must use the semi-classical picture of transport to properly account for energy band structure. For example, for individual electrons, we have

$$\hbar \frac{d\vec{k}_e}{dt} = -e \left(\vec{E} + \frac{1}{\hbar} \vec{\nabla}U(\vec{k}_e) \times \vec{B} \right) - \frac{\hbar \vec{k}_e}{\tau_e}$$

Now suppose we have an E field only and a steady state situation such that

$$\vec{k}_e = -(e\tau_e / \hbar) \vec{E} \tag{31}$$

We suppose further that the electrons are confined to a conduction band consisting of N_s “valleys” having spheroidal constant-energy surfaces. In the limit of low carrier concentration, we can thus write for the electrical current density

$$\langle \vec{J}_q \rangle = -e \sum_s \int \vec{v}_g f_s d\vec{k} = \frac{-e}{\hbar} \sum_s \int \vec{\nabla}U(\vec{k}_e) f_s d\vec{k}$$

where the sum is carried out over all spheroidal valleys indexed by the integer s , the integral is over a single spheroid, and f_s is the non-equilibrium distribution function for each spheroid. We assume further that the E field is small enough in magnitude that the carriers remain approximately equally distributed over all the valleys, as in the equilibrium state, so that $f_s \approx f/N_s$. Then we can write

¹ The effective mass parameters of the conduction-bands in both silicon and germanium were first figured out using cyclotron resonance measurements in the mid 1950s by competing groups from UC Berkeley (led by C. Kittel) and MIT (led by B. Lax). These experiments also led to the realization that the constant- energy surface of the conduction bands was *spheroidal*, rather than *ellipsoidal*, as was earlier believed.

$$\langle \vec{J}_q \rangle = \frac{-e}{N_s \hbar} \sum_s \int \vec{\nabla} U(\vec{k}_e) f \cdot d\vec{k} \quad (32)$$

Example of conduction through spheroidal-valley semiconductor. To make further progress on analyzing (32) is helpful to look at conduction in a specific example, n-type silicon. In this case the constant-energy spheroids have six different forms when expressed in cartesian coordinates

$$\text{in k space: } U(\vec{k}) = \frac{\hbar^2}{2} \left(\frac{(k_x \pm k_{x0})^2}{m_l} + \frac{k_y^2}{m_t} + \frac{k_z^2}{m_t} \right) \quad \frac{\hbar^2}{2} \left(\frac{k_x^2}{m_t} + \frac{(k_y \pm k_{y0})^2}{m_l} + \frac{k_z^2}{m_t} \right) \text{ or}$$

$$\frac{\hbar^2}{2} \left(\frac{k_x^2}{m_t} + \frac{k_y^2}{m_t} + \frac{(k_z \pm k_{0z})^2}{m_l} \right) \quad (33)$$

Without loss of generality we can restrict our analysis to transport with a uniform E field (magnitude E_0) along an arbitrary axis, say x. Then we need calculate only the x component of (32) which requires calculating the x component of the group velocity of all six ellipsoids in (33)

$$\sum_s \vec{\nabla}_x U(\vec{k}_e) = \frac{2\hbar^2 k_x}{m_l} + \frac{2\hbar^2 k_x}{m_t} + \frac{2\hbar^2 k_x}{m_t} = \frac{2\hbar^2 k_x}{m_l} + \frac{4\hbar^2 k_x}{m_t}$$

But from (31) $k_x = -(e\tau / \hbar) E_0$, so that

$$\begin{aligned} \langle J_{q,x} \rangle &= \frac{-eE_0}{6\hbar} \int \frac{-e\tau_e}{\hbar} \left[\frac{2\hbar^2}{m_l} + \frac{4\hbar^2}{m_t} \right] f(\vec{k}) d\vec{k} = \frac{e^2 E_0}{6} \left(\frac{2}{m_l} + \frac{4}{m_t} \right) \int \tau_e f(\vec{k}) d\vec{k} \\ &= ne^2 \langle \tau \rangle \left[\frac{1}{6} \left(\frac{2}{m_l} + \frac{4}{m_t} \right) \right] E_0 \equiv \frac{ne^2 \langle \tau \rangle}{m_c^*} E_0 \end{aligned}$$

where the last step defines the conductivity effective mass, m_c^* .

$$\frac{1}{m_c^*} = \frac{1}{6} \left(\frac{2}{m_l} + \frac{4}{m_t} \right) = \frac{1}{3} \left(\frac{1}{m_l} + \frac{1}{m_t} + \frac{1}{m_t} \right) \quad (34)$$

Numerically, we know for silicon that $m_l = 0.98 m_0$ and $m_t = 0.19 m_0$, so that $m_c^* = 0.26 m_0$

It is important to note that the conductivity mass is a fundamentally different quantity than the density-of-states mass m_d^* defined earlier in the statistical mechanics of semiconductors. Eqn (34) is an arithmetic average over the ellipsoids, whereas the density-of-states mass was a geometric average. We recall for silicon that $m_d^* = \sqrt[3]{m_t^2 m_l}$ which when evaluated yields $m_d^* = 0.33 m_0$.

It is not hard to see that the evaluation for silicon above is independent of the direction of the applied electric field, provided it is uniform. In other words $m_c^* = 0.26 m_0$ is a fundamental electrical transport property of silicon. It is a bit more difficult to prove that the last step of (34) is valid for all spheroidal-valley conduction bands provided that the semiconductor has cubic symmetry. We can think of it as a peculiar *arithmetic sum* that is independent of where the

ellipsoids are located or how they are oriented in k space. In contrast, the density-of-states mass is a *geometric sum*.

In conclusion it is important to be clear on when the conductivity mass is used and when the density-of-states mass is used. As a rule-of-thumb, *the conductivity mass is used whenever the physical effect involves transport via classical or quantum mechanics in response to electric fields*. An interesting example, besides electrical conduction, is electron or hole binding to hydrogenic donors or acceptors with binding energy derived earlier, $U_B = 13.6 \text{ eV } m_c^* / (\epsilon_r)^2$, where ϵ_r is the relative permittivity. To understand why this should depend on the conductivity mass rather than the density-of-states mass, we recall that in the hydrogenic model the bound electron (or hole) generally has a Bohr radius that extends over many unit cells of the crystal. So roughly speaking, the bound electron or hole can be thought of as a particle in orbit over many unit cells and under the influence of the electric field of the donor or acceptor nucleus. As such, it satisfies the criterion given above for application of the conductivity effective mass.