3. Electrical Conduction in Solids

3A. Classical Theory
3B. Semiclassical Theory
3C. Semiconductors

3B. Semiclassical Theory

3B.1. Dynamics of Bloch State
3B.2. Semiclassical Model
3B.3. Conduction within Semiclassical Model

$$\sigma = ne\mu = ne^2\tau/m^*$$

free electron model

In the previous section, we understood the electric properties of materials using the classical picture or the modified Drude model. That is to say, the electron was regarded as a point particle, and the underlying lattice structure was almost ignored except that the lattice vibrations (phonon) scatter electrons. This classical picture explained many observations successfully but fails in some cases, most notably, the **hole carriers** in the Hall effect.

This requires the improvement in the theory. You may recall that in Chap. 2B, we learned about the band structure as a result of interactions between electrons and the periodic potential. The consideration of **band structure** should be a next step to go. Therefore, the free electron in the Drude model is replaced by the Bloch electron, and we will discuss on the **dynamics of Bloch electrons** between collisions.

$$\varepsilon_{n,k} \quad \& \quad \psi_{n,k}(r) = e^{ik\cdot r}\, u_{n,k}(r)$$

3B.1. Dynamics of Bloch States

The Bloch state is identified by the **two quantum number** – **band index *n* and Bloch vector *k***. For free electrons, $\hbar\mathbf{k}$ is the particle momentum. In crystal, $\hbar\mathbf{k}$ is called the "crystal momentum." The crystal momentum appears in the conservation law like momentum conservation. However, it is not the actual momentum (mass × velocity). In order to understand the real motion of Bloch states, one needs to construct a **wave packet** by multiplying an envelope function such as Gaussian with the **Bloch state $\psi_{n,\mathbf{k}}$**. Demonstration with simulation shows that i) a Bloch state slides through the periodic potential without any scattering, and ii) **the velocity is related to the band slope at *k***. It can be shown that the mean velocity of the Bloch state is given by (see Appendix E of A&M):

$$v_n(k) = \langle v \rangle_{nk} = \frac{\langle p \rangle}{m^*} = \frac{1}{\hbar}\frac{d\varepsilon_n(k)}{dk}$$

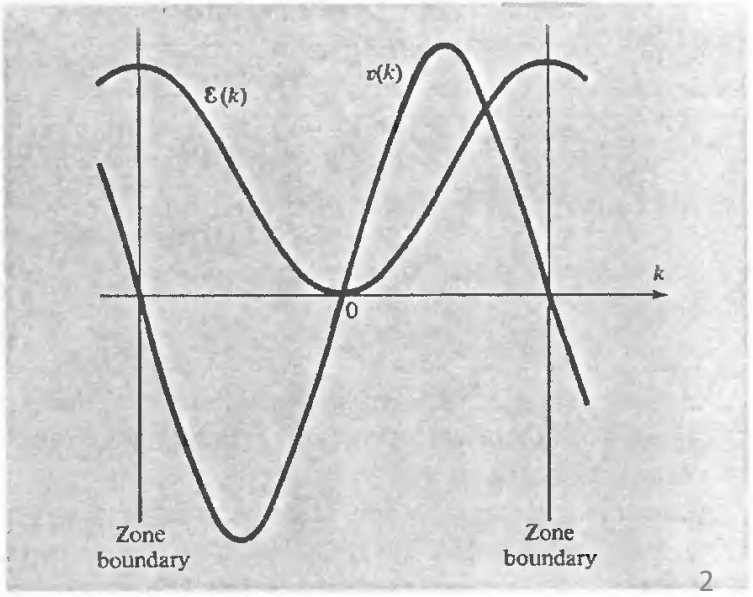
In 3D, $\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}\varepsilon_n(\mathbf{k})$

Bube Eq. (7.21)
Group Velocity

This looks similar to the velocity of free particle:

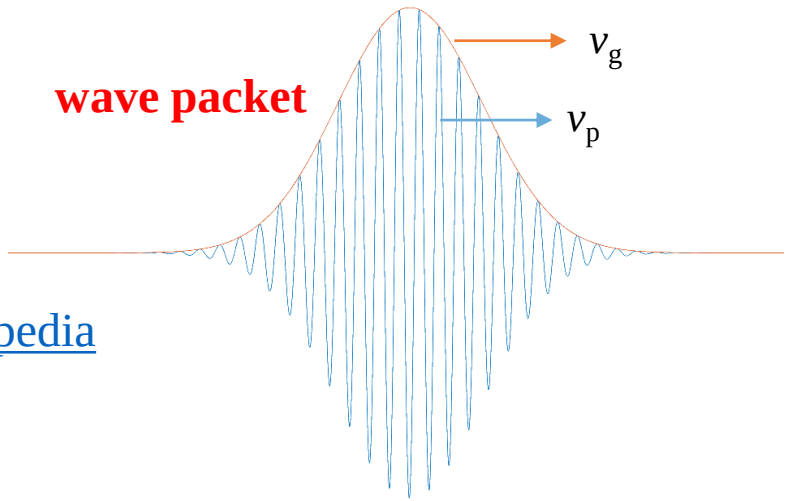
$$\langle v \rangle = v = \frac{p}{m} = \frac{\hbar k}{m} = \frac{1}{\hbar}\frac{d\varepsilon}{dk}$$

However, unlike free electron, the mean velocity is only obtained through the derivative.



PPT 1-13

The electron described by $Ae^{i(kx-\omega t)}$ is dispersed over the whole space. If there is one electron moving in free space, such a form of wave function may not be appropriate. Rather, a "**wave packet**" with the spread of ~10 nm would best represent such an electron. The figure in the below shows the wave packet with the Gaussian envelope. This state is fairly localized and has a relatively well defined wavelength although it is not the exact energy eigenstate.



Wikipedia

Suppose that the initial wave function is the Gaussian wave packet:

$$\psi(x,0) = \sqrt{\frac{2\pi}{\alpha}}\, e^{ikx} e^{-x^2/2\alpha}$$

The time evolution of the wave function can be obtained by solving the time-dependent Schrödinger equation (numerically or analytically). It is visualized by MATLAB file : wavepacket.m

You can observe that the envelope moves with a velocity that is faster than the phase velocity. The speed of such a localized wave packet is the group velocity and it is given by the following formula.

$$v_g = \frac{dw}{dk} = \frac{\hbar k}{m} = \frac{p}{m}$$

Bube (2.3)

This is exactly the same as the classical velocity! (In the case of photon, $\omega = ck$ and so $v_p = v_g = c$)

The group velocity is the speed at which energy and charge actually travels through the medium.

PPT 1-13

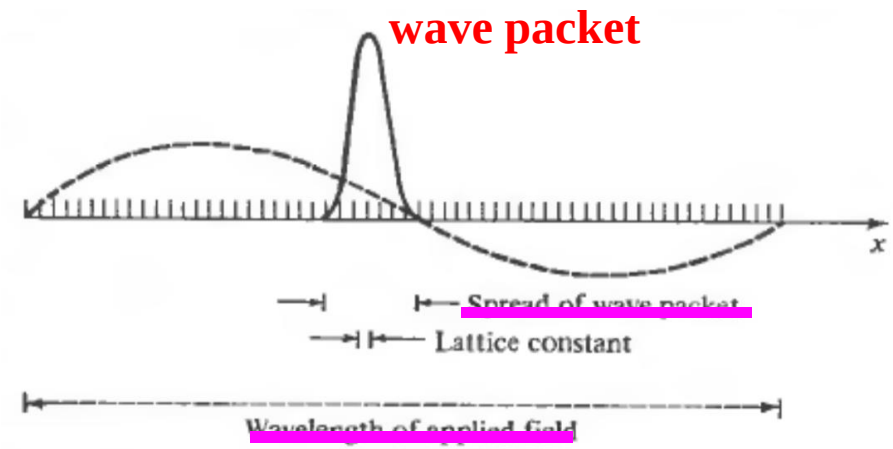
3B.2. Semiclassical Model

Next, we discuss how the Bloch states move under the external electric and/or magnetic fields when there is no scattering (or between collisions). For the Bloch electron at (n, $\mathbf{k}$) under external field that varies much longer than the lattice constant with its magnitude not too large, one can describe the motion of the corresponding wave packet within the semiclassical model.

In the semiclassical model, the slowly varying fields give rise to ordinary classical forces in an equation of motion describing the evolution of the position and wavevector of the wave packet. The difference from the free electrons is that the periodic potential varies over the lengths that are small **compared with the spread of the wave packet**, and therefore cannot be treated classically. Thus the semiclassical model is only partially classical:

- the applied fields are treated classically, but

- the periodic potential of the ions is not.



(That is to say, we ignore the **photonic nature** of EM waves.)

The semiclassical model predicts how, in the absence of collisions, **the position *r* and Bloch vector *k*** of each electron evolve in the presence of externally applied electric and magnetic fields. Theory consists of the two following statements:

1. The band index *n* is a constant of the motion. The semiclassical model **ignores the possibility of "interband transitions"**.
2. The time evolution of the position and wave vector of an electron with band index n are determined by the equation of motion:

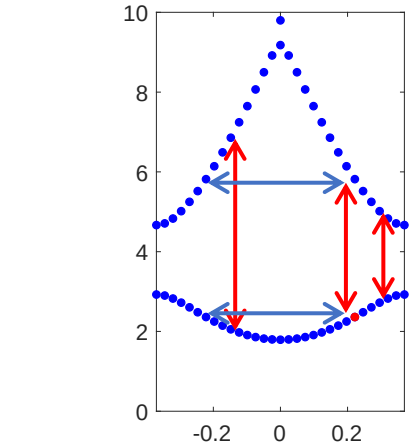
$$\frac{d\mathbf{r}}{dt} = \mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}\varepsilon_n(\mathbf{k}) \qquad \textbf{in } r \textbf{ space}$$

$$\hbar\frac{d\mathbf{k}}{dt} = -e\left[\mathbf{E}(\mathbf{r},t) + \mathbf{v}_n(\mathbf{k}) \times \mathbf{B}(\mathbf{r},t)\right] \qquad \textbf{in } k \textbf{ space}$$

[Ashcroft & Mermin]

According to the semiclassical theory, the motion of an electron is described by **considering its approximate positions in both *r* and *k* spaces simultaneously**. Note that if the electric field varies spatially, the electric field at the new position should be provided in evaluating the equation of motion in *k*-space.

This is called the semiclassical theory because
- electrons are classically treated with **momentum and effective mass**
while
- the effective mass and temporal change of **crystal momentum** are conditioned by the band structure.



Interband transition

Intraband transition

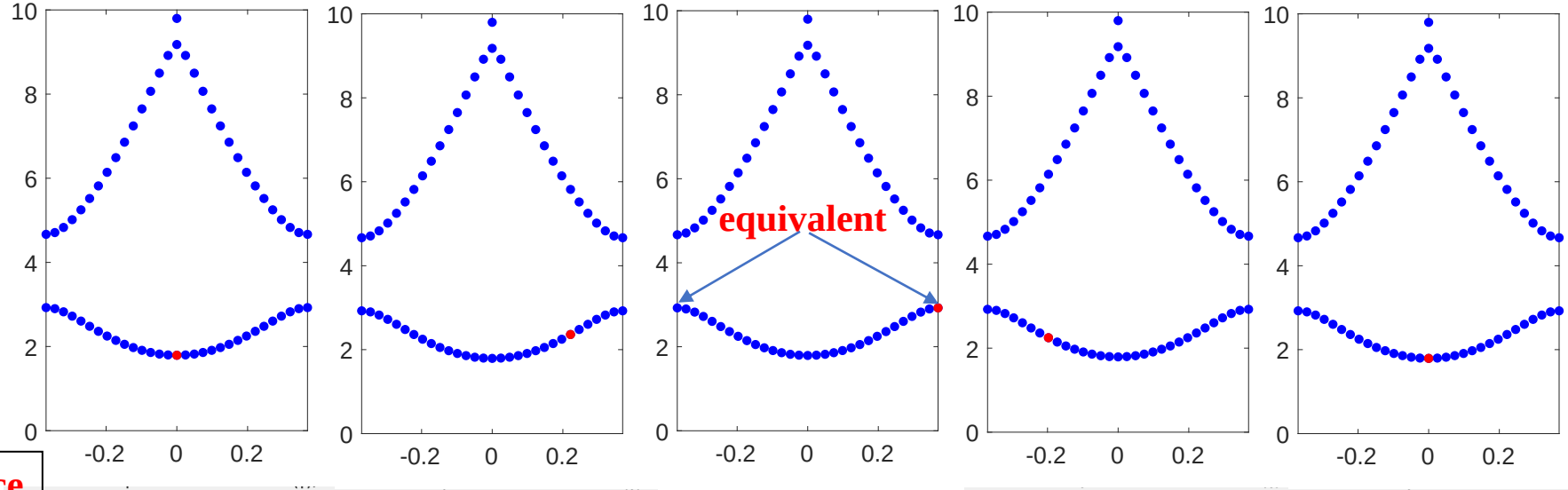
Ex) In 1D with **constant *E* field along the –*x* direction**

k-space: $\hbar \frac{dk}{dt} = eE$

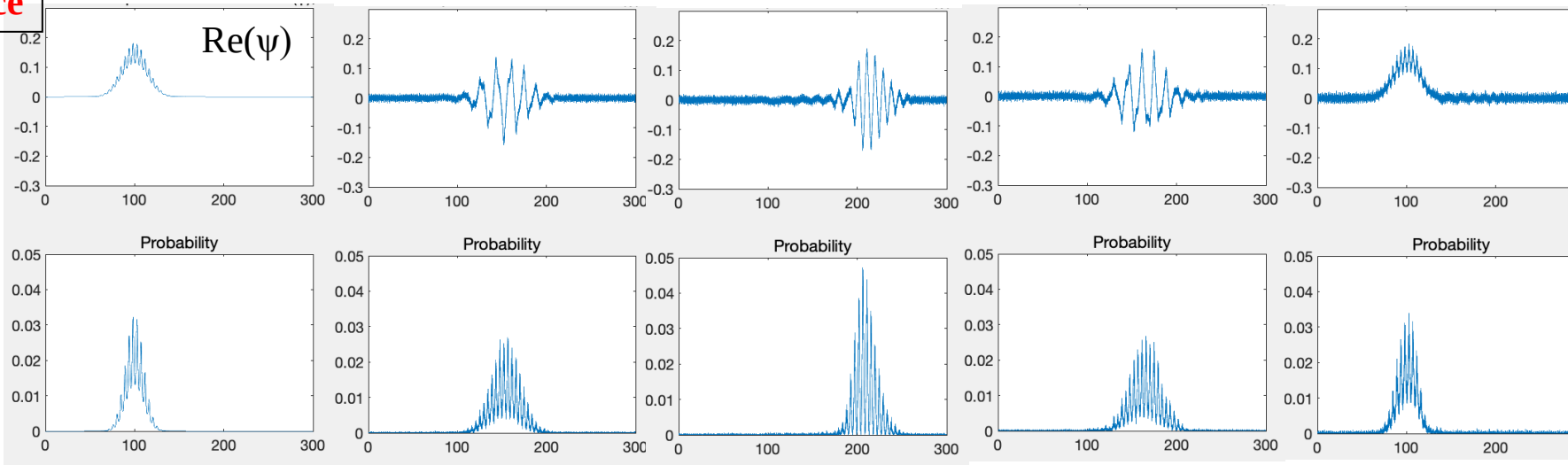
r-space: $\frac{d\langle x \rangle}{dt} = \langle v \rangle = \frac{1}{\hbar}\frac{d\varepsilon}{dk}$

***k* space**

$\leftarrow$ *E* (constant)



***r* space**



"Zener-Bloch oscillation"

Limits of Semiclassical Model

The semiclassical model **forbids interband transitions**, and therefore requires that the energy of any electron remains confined within the limits of the given band. There must be some minimum strength to a periodic potential before the semiclassical model can be applied. We here state the conditions without proof.

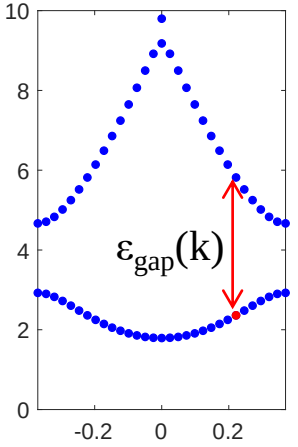
At a given point in *k*-space, the semiclassical equations will be valid for electrons in the n^{th} band provided that the amplitudes of the slowly varying external electric and magnetic fields satisfy:

$$eEa \ll \frac{\left[\varepsilon_{\text{gap}}(k)\right]^2}{E_F}$$

$$\hbar\omega_c \ll \frac{\left[\varepsilon_{\text{gap}}(k)\right]^2}{E_F}$$

a: lattice parameter and ω_c: cyclotron frequency.

If the first (second) condition is violated, it is called the electric (magnetic) breakdown.



These conditions are satisfied in most electrical devices with reasonable field strength.

For optical properties, the photon energy of visible lights is bigger than the bandgap of semiconductors.

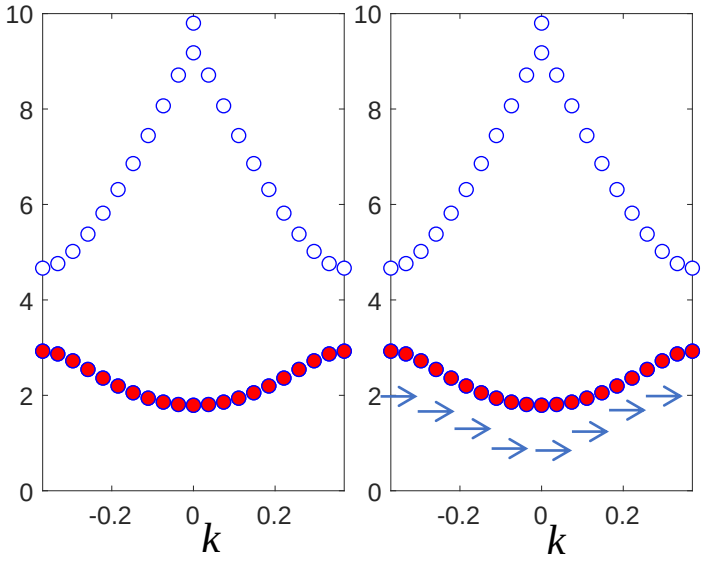
3B.3. Conduction within Semiclassical Theory

(For now, we do not consider collisions. This means that the discussion below applies to Bloch electrons between collisions.)

According to the semiclassical theory, every filled band does not carry any net current without external field. This is because the bands contain both left-moving and right-moving electrons with net velocity equal to zero. Under the external field, each Bloch state moves along the $-E$ direction. Because of periodic boundary condition, the net current is still zero. Therefore, insulators that have only filled bands are not conducting, while **partially filled metallic system can conduct electrons**. This also explains why the filled *d* electrons in Cu do not contribute to any current.

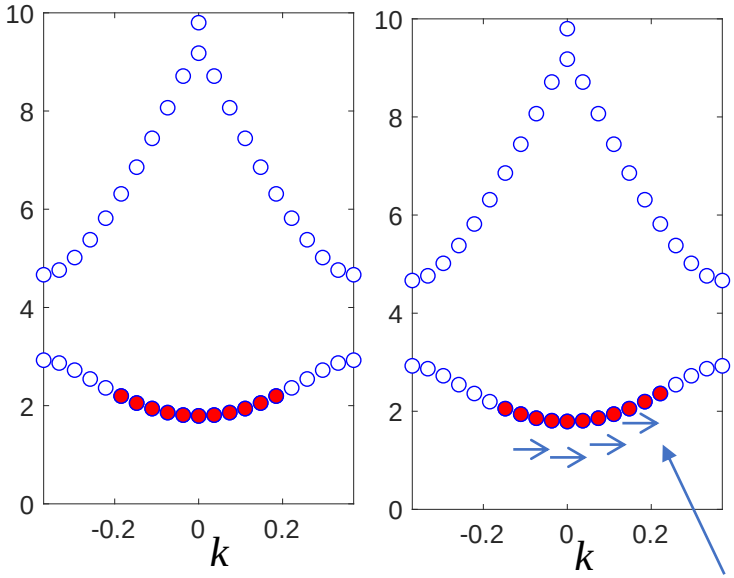
Insulator

$E = 0 \quad I_{\text{net}} = 0 \qquad E < 0 \quad I_{\text{net}} = 0$



Metal

$E = 0 \quad I_{\text{net}} = 0 \qquad E < 0 \quad I_{\text{net}} < 0$



More electrons in the right-moving states.

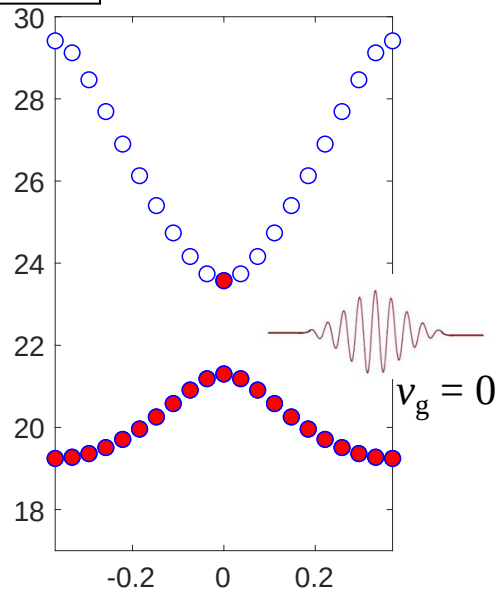
○ Empty

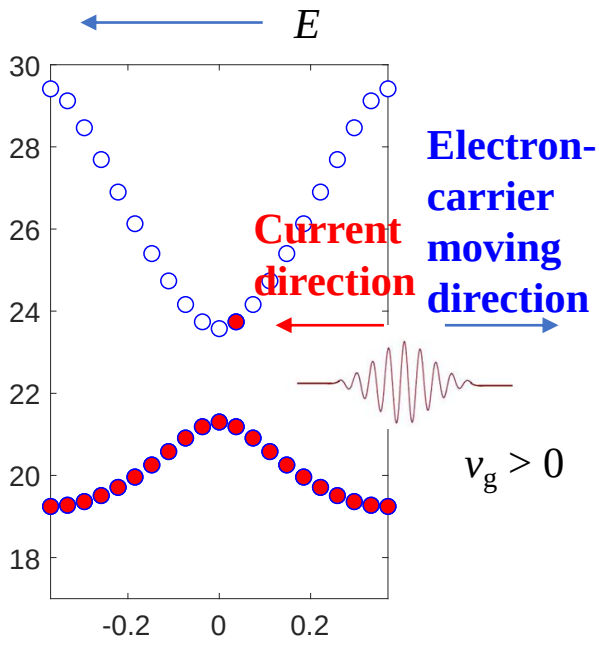
● Occupied

k-space: $\hbar \dfrac{dk}{dt} = eE$

r-space: $\dfrac{d\langle x \rangle}{dt} = \langle v \rangle = \dfrac{1}{\hbar} \dfrac{d\varepsilon}{dk}$

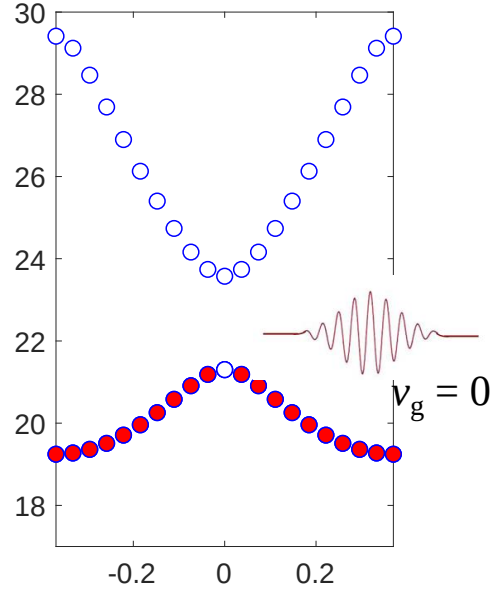
Electron

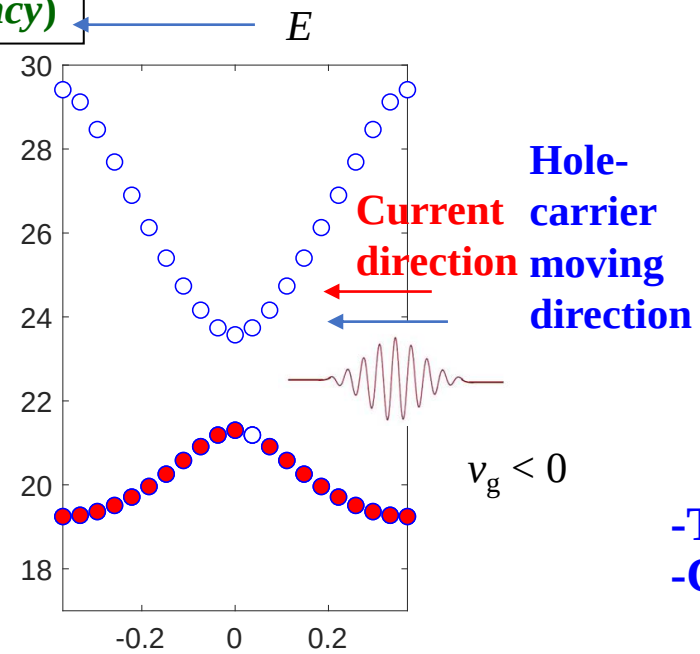




In semiconductors, small number of electrons occupy the conduction bottom or small number of empty states (holes) are present at the valence top. Since the bands are not fully occupied, these states can give rise to net currents along the electric field. However, the spatial movement is opposite in the two cases. That is to say, **hole moves spatially along the electric field (not against) like positive charge**.

Hole (= *Many Electrons with Vacancy*)





k-space: $\hbar \frac{dk}{dt} = eE$

r-space: $\frac{d\langle x \rangle}{dt} = \langle v \rangle = \frac{1}{\hbar}\frac{d\varepsilon}{dk}$

Positron (Antielectron)

Medical & Materials

-Tue/10/6/2020

-Class Exam = Tue/Oct/13/20

Chaps. 1, 2A, 2B, & 2C

Hole (= *Many Electrons with One Vacancy*)

Kittel Chap. 8

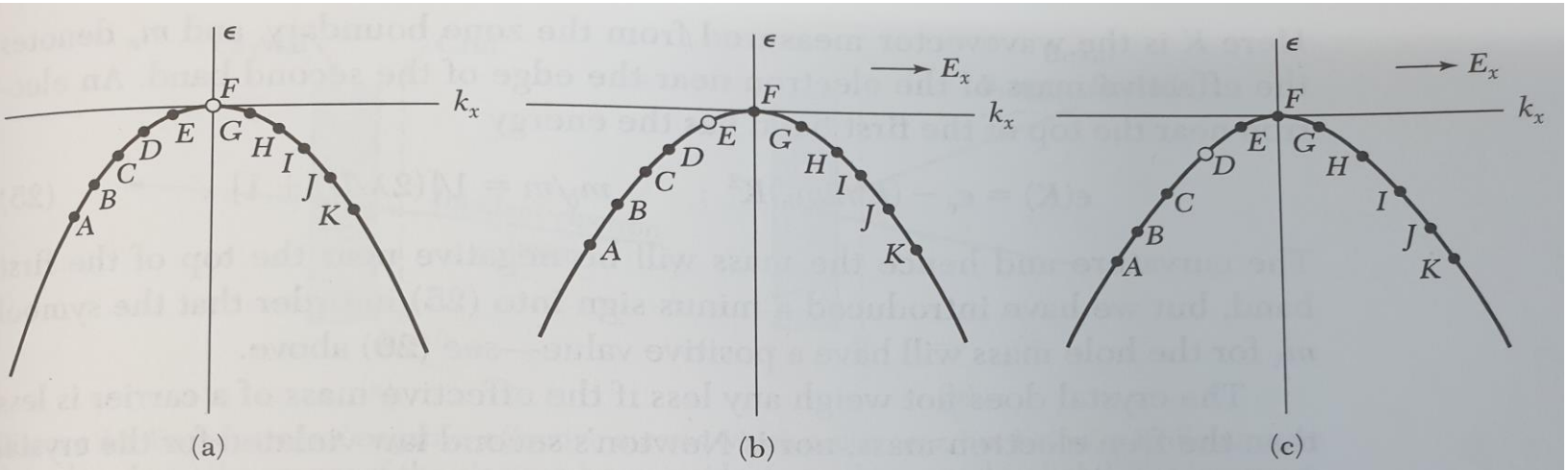
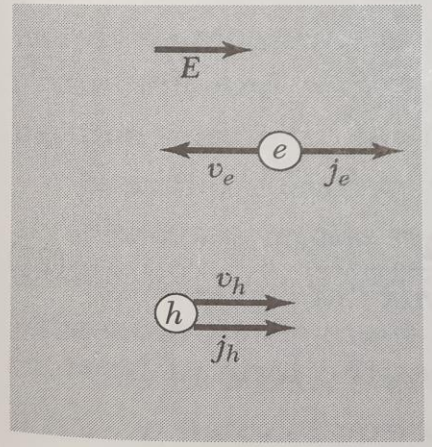


Figure 9 (a) At $t = 0$ all states are filled except F at the top of the band; the velocity v_x is zero at F because $d\epsilon/dk_x = 0$. (b) An electric field E_x is applied in the $+x$ direction. The force on the electrons is in the $-k_x$ direction and all electrons make transitions together in the $-k_x$ direction, moving the hole to the state E. (c) After a further interval the electrons move farther along in k space and the hole is now at D.



Electron vs. Hole

Figure 10 Motion of electrons in the conduction band and holes in the valence band in the electric field E. The hole and electron drift velocities are in opposite directions, but their electric currents are in the same direction, the direction of the electric field.

Effective Mass

Let's assume a constant electric field E is applied to 1D solid. **ppt 3B-5**

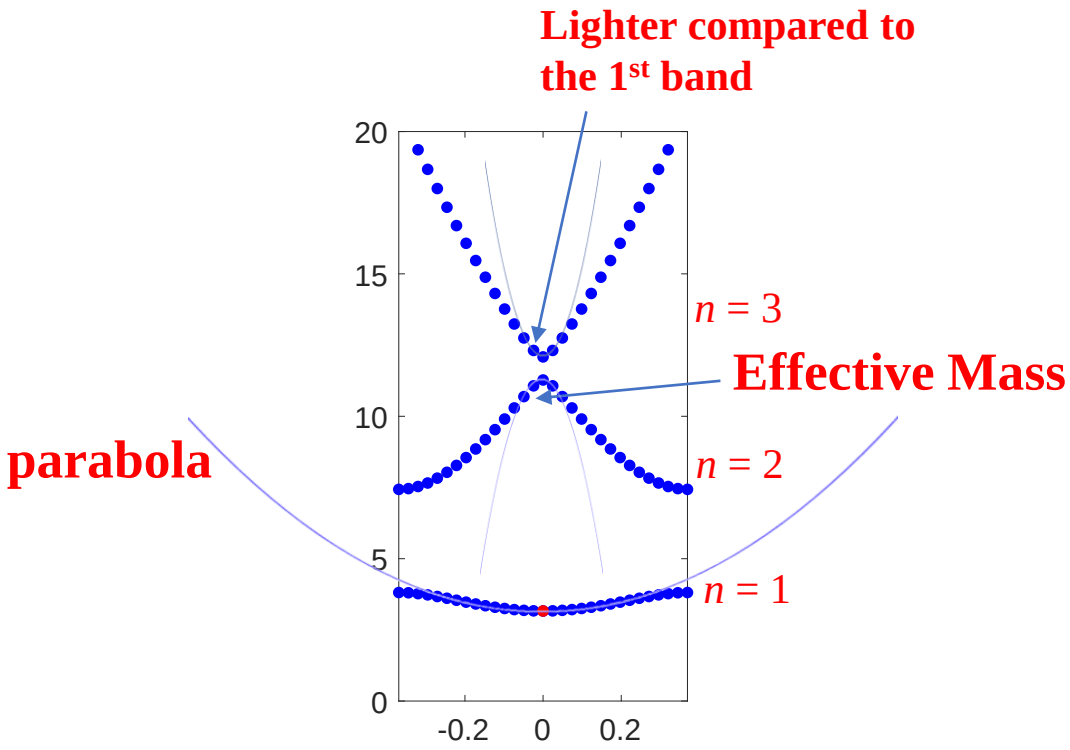
$$\begin{cases} \hbar\dfrac{dk}{dt} = -eE \\ \dfrac{d\langle x\rangle}{dt} = \langle v\rangle = \dfrac{1}{\hbar}\dfrac{d\varepsilon}{dk} \end{cases} \longrightarrow$$

$$a = \frac{d^2\langle x\rangle}{dt^2} = \frac{d\langle v\rangle}{dt} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{d\varepsilon}{dk}\right) = \frac{1}{\hbar}\frac{d^2\varepsilon}{dk^2}\frac{dk}{dt}$$

$$= \frac{1}{\hbar^2}\frac{d^2\varepsilon}{dk^2}(-eE) = \frac{F}{m^*}$$

$$m^* = \left(\frac{1}{\hbar^2}\frac{d^2\varepsilon}{dk^2}\right)^{-1}$$

Therefore, the acceleration of a Bloch state can be described classically by the effective mass. This is particularly useful for electrons **at the bandedges (top or bottom)** where the band is **parabolic** and so the effective mass is **constant over *k***. As long as the electrons (or holes) are confined in this region, they behave like classical particles. Geometrically, the effective mass is proportional to the inverse of the band curvature.



Band dispersions near the edges are well approximated by parabolas with coefficients given by the **effective mass**.

In 3D, the effective mass is a tensorial form:

$$\left[\mathbf{M}^{-1}(\mathbf{k})\right]_{ij} = \pm\frac{1}{\hbar^2}\frac{\partial^2 \varepsilon(\mathbf{k})}{\partial k_i \partial k_j}$$

$$\mathbf{a} = \frac{d\mathbf{v}}{dt} = \pm\mathbf{M}^{-1}(\mathbf{k})\hbar\frac{d\mathbf{k}}{dt}$$

Energy and (crystal) momentum conservations

In quantum mechanics, the change of states, for instance acceleration, is described by the electronic transitions between the two states. The rate of transition (transition rate) Γ between the initial state (*i*) and the final state (*f*) is calculated by the Fermi golden rule:

Density of final states

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}|\langle f|H'|i\rangle|^2 \rho$$

Transition rate per unit time from *i* to *f*. (= $1/\tau$)

Matrix element of the perturbation H' between the final and initial states (= $\int \psi_f^* H' \psi_i$)

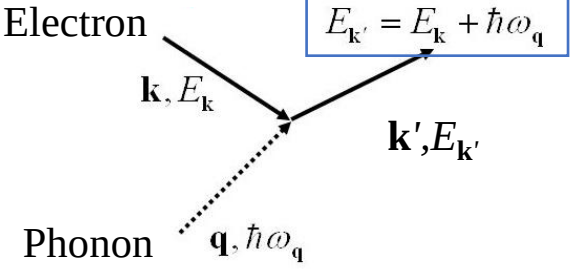
H' is related to scattering mechanism such as lattice vibration, impurity,.. etc. If it is the lattice vibration, the matrix element can be understood in terms of (inelastic) collision between electrons and phonons.

***** During the collision, energy and (crystal) momentum conservations are always satisfied.**

Phonon absorption

$\hbar\mathbf{k}' = \hbar\mathbf{k} + \hbar\mathbf{q}$

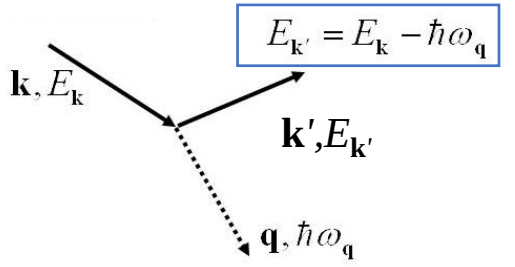
$E_{\mathbf{k}'} = E_{\mathbf{k}} + \hbar\omega_{\mathbf{q}}$



Phonon emission

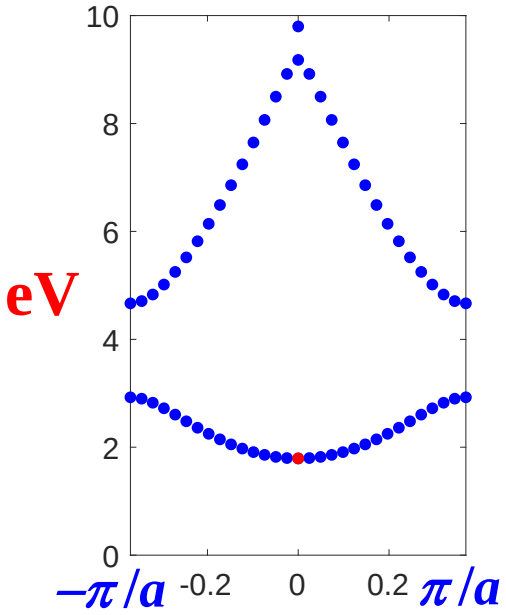
$\hbar\mathbf{k}' = \hbar\mathbf{k} - \hbar\mathbf{q}$

$E_{\mathbf{k}'} = E_{\mathbf{k}} - \hbar\omega_{\mathbf{q}}$

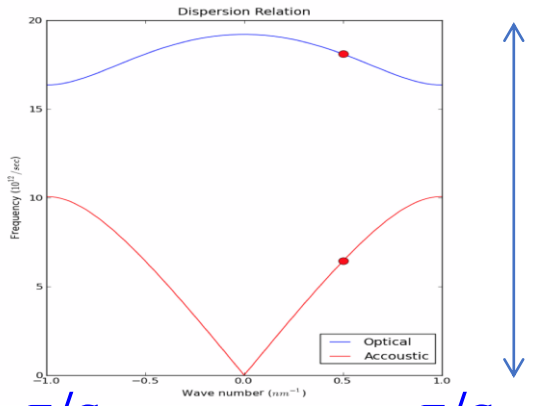


+**G**?

Electron Band structure



Phonon Band Structure



< 0.05 eV

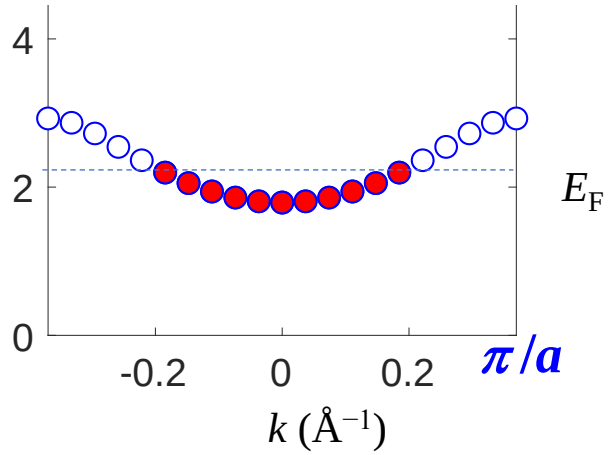
The same 1st BZ

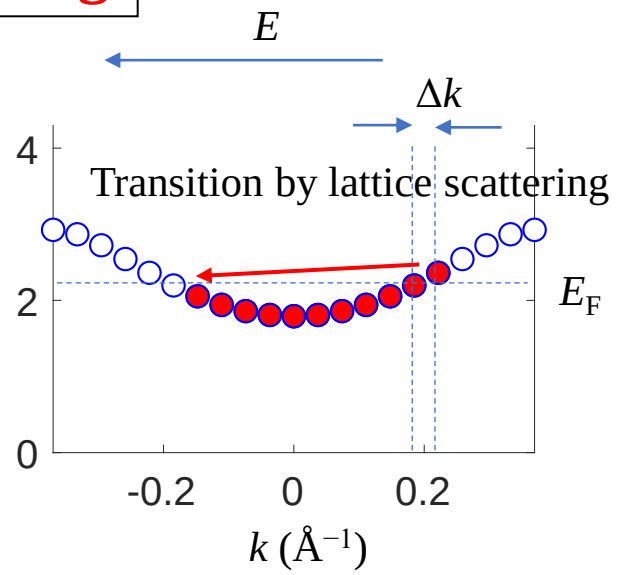
Phonon energy is negligible while **the momentum transfer is significant**.

Visible Photon λ = 400 - 600 nm

$h\nu$ = 2 - 3 eV

Electronic Transition by Scattering





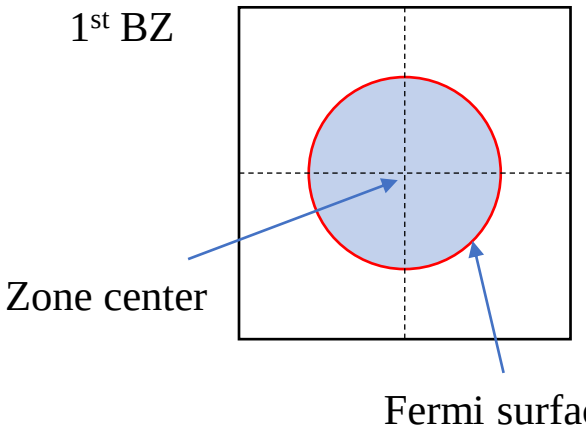
The energy-loss by the lattice scattering results in the Joule heating.

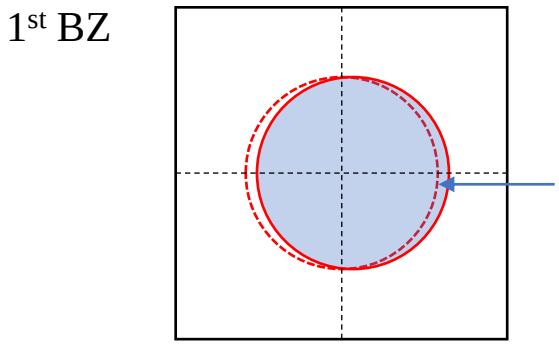
When τ is 25 fs and the external field is **100 V/cm**, the displacement in k-space (Δk) is:

ppt 3A-9
ppt 3B-5

$$\hbar\frac{dk}{dt} = -eE \rightarrow \hbar\Delta k = -eE\tau \qquad |\Delta k| = \frac{eE\tau}{\hbar} \sim 10^6 \text{ m}^{-1} = 10^{-4} \text{ Å}^{-1}$$

Therefore, **the net conduction is essentially limited to the electrons at the Fermi level**.
This is also the case in 2D or 3D.

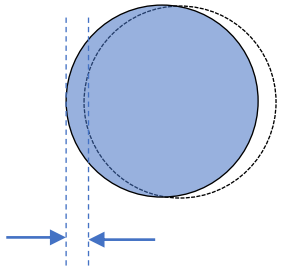




Only electrons near the Fermi surface contributes to the net current.

Conduction in Metals – Derivation of Drude Model from Quantum Theory

Homework



$$\hbar\Delta k = e\vec{E}\tau$$

$$E = \frac{\hbar^2 k^2}{2m} \rightarrow \Delta E = \frac{\hbar^2 k \Delta k}{m} = \frac{\hbar k e\vec{E}\tau}{m} = v_F e\vec{E}\tau$$

$$J = eDnv = eD(E_F)DEv_F = e^2 v_F^2 t\, D(E_F)\vec{E}$$

$$\rightarrow s = e^2 v_F^2 t\, D(E_F)$$

This is correct for 1D system. In 3D crystal, because of the spherical geometry, this is modified with a factor of 1/3:

$$s = \frac{1}{3} e^2 v_F^2 t\, D(E_F)$$

Using the previous results on the density of states, one can show that

$$s = \frac{ne^2 t}{m}$$

which is exactly the same as that of the classical model!

$$\frac{d\mathbf{r}}{dt} = \mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}\varepsilon_n(\mathbf{k})$$

$$\hbar\frac{d\mathbf{k}}{dt} = -e\left[\mathbf{E}(\mathbf{r},t) + \mathbf{v}_n(\mathbf{k}) \times \mathbf{B}(\mathbf{r},t)\right]$$

ppt-2A-8
ppt-2A-18
ppt-2A-21

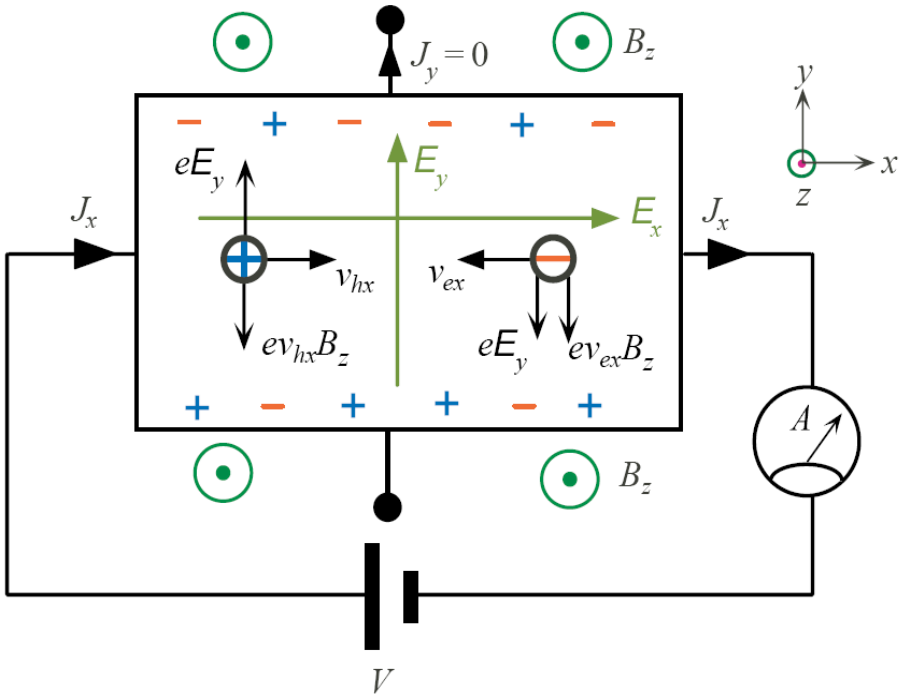
$$D(E) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E}$$

$$E_F(0) = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{\frac{2}{3}}$$

Experiments: Hall Measurements

Metal or Semiconductor

When both electrons and holes coexist like in divalent metals, the Hall coefficient is obtained by considering the dynamics of both carrier types.



Both electrons and holes experience the Lorentz force in the same direction and pile up at the bottom

$$R_H = \frac{p\mu_h^2 - n\mu_e^2}{e\left(p\mu_h + n\mu_e\right)^2} = \frac{p - nb^2}{e(p + nb)^2} \quad \left(b = \frac{\mu_e}{\mu_h}\right)$$

(See Kasap for the derivation)

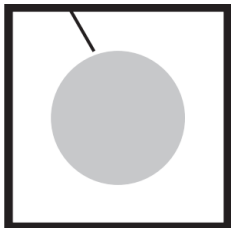
***** From the conventional Hall measurements, we cannot separate the values of *n* and *p*.**

(carrier concentrations *n* and *p*)

(skip)

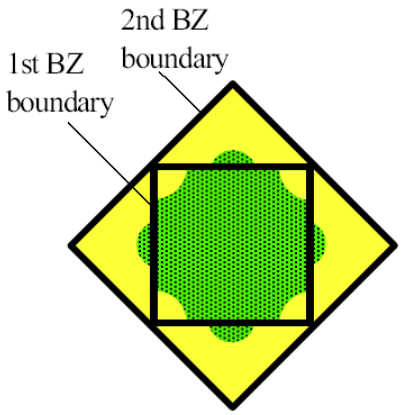
For divalent or trivalent metals, the Fermi surface extends beyond 1st BZ.

$N_e = 1$



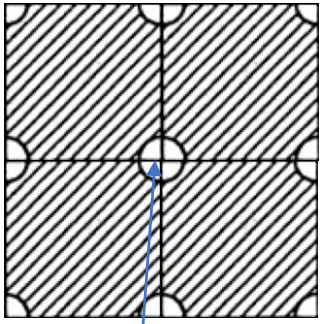
Li, Na, or K

$N_e = 2$



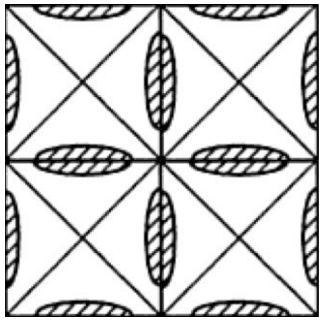
Be, Cd, Zn

The electrons in each BZ move only within the same BZ according to the semiclassical model. This means that electrons near the Fermi surface move quite differently in 1st and 2nd BZ.



Electrons in the 1st BZ

"Hole pocket"



Electrons in the 2nd BZ

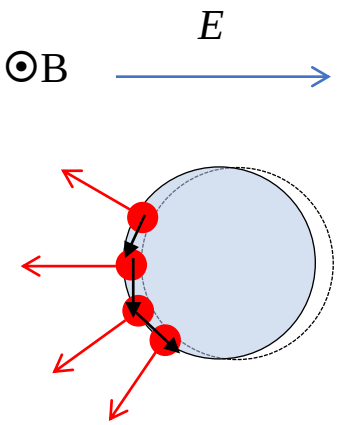
(skip)

Hall effects within the semiclassical model

N_e = 1 or 2nd BZ of divalent metals

1st BZ of divalent metals

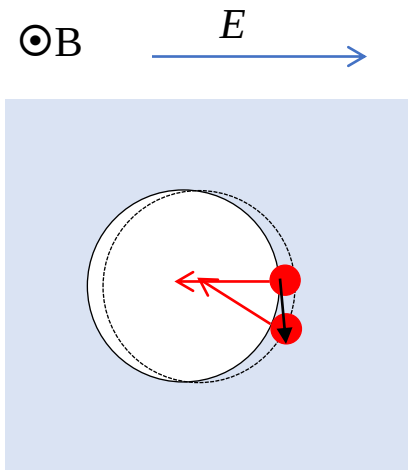
k-space



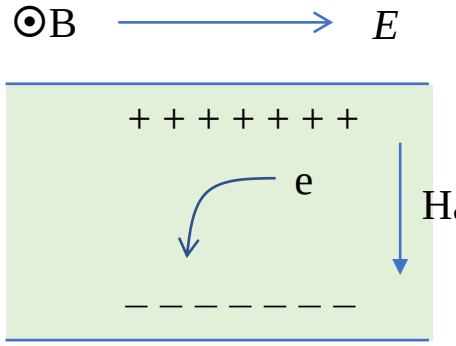
: velocity in r-space

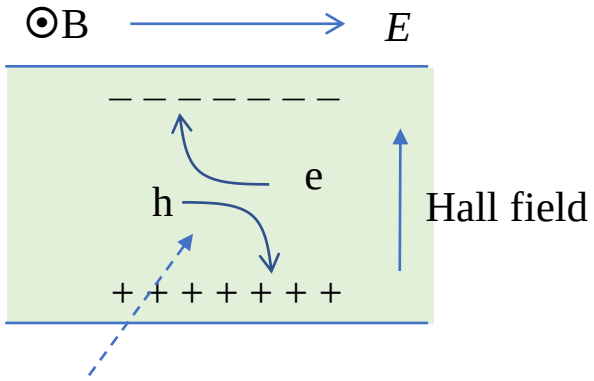
$\sim \nabla_{\mathbf{k}} e_n(\mathbf{k})$

: shift in k-space due to B



r-space





Electrons at the hole pocket effectively behaves like positive charge carriers