Charge Carriers in Semiconductors

Electron in a band state moves at the group velocity.

In 1D, \[ v_g = \frac{1}{h} \frac{dE}{dk} \]

A full band does not conduct.

Due to symmetry, the net velocity of all states of a band is zero.

These concepts extended to 3D:

\[ v_g = \frac{1}{h} \nabla_k E = \frac{1}{h} \left( \hat{x} \frac{\partial E}{\partial k_x} + \hat{y} \frac{\partial E}{\partial k_y} + \hat{z} \frac{\partial E}{\partial k_z} \right) \]

The 1st BZ is always symmetric, therefore net velocity of all states of a band is zero.
Counting electrons

Examples:
Si (group IV element, diamond structure) & GaAs (octet compound, zincblende structure)

For a crystal of $N$ primitive unit cells,
there are $N$ band states each band,
i.e., $N$ distinct $k$ in the 1$^{\text{st}}$ BZ.

The $N$ states in each band accommodate $2N$ electrons.

There are 4 bands originating from valence electron orbitals, together accommodating $4N \times 2 = 8N$ electrons.

For diamond & zincblende structures, each primitive unit cell contains 2 atoms.

Each primitive unit cell contributes $4 \times 2 = 8$ valence electrons.

$N$ primitive unit cells have $8N$ valence electrons.

Therefore the bands of valence electrons are full.
Near a band minimum, the $E$-$k$ dispersion can be written as (Taylor expansion):

$$E(k) = E(k_0) + \frac{1}{2} \left. \frac{\partial^2 E}{\partial k^2} \right|_{k=k_0} (k - k_0)^2$$

(good approx. near a minimum)

If we consider $E(k_0)$ as a potential energy $V$, and $\hbar (k - k_0)$ as a momentum $p$, then this becomes formally the same as a classical particle:

$$E = \frac{p^2}{2m} + V \iff E = \frac{\hbar^2 (k-k_0)^2}{2m^*_e} + E_c$$

The “effective mass” of the electron, $m^*_e$, can be found by:

$$\frac{1}{m^*_e} = \left. \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \right|_{k=k_0}$$

We use a 1D heuristic for simple math. In 3D, the second derivative is a tensor (the effective mass is anisotropic), and $k_0 \leftarrow k_0$ may or may not be zero.
In this semiclassical model, \( \frac{h}{d} \frac{dk}{dt} = \hbar \frac{d}{dt} (k - k_0) = F \)

The electron is pushed by the force to move in \( k \)-space.
At each \( k \), the electron’s velocity is the group velocity:

\[
\mathbf{v}_g = \frac{1}{\hbar} \frac{dE}{dk} = \frac{1}{\hbar} \frac{dE}{d(k - k_0)} \quad \mathbf{v}_g = \frac{1}{\hbar} \mathbf{V}_k E = \frac{1}{\hbar} \left( \hat{x} \frac{\partial E}{\partial k_x} + \hat{y} \frac{\partial E}{\partial k_y} + \hat{z} \frac{\partial E}{\partial k_z} \right)
\]

Notice that \( \mathbf{v}_g = 0 \) at a minimum \( k - k_0 \).

**Question**: Describe the motion of a single electron added to a perfect, static \((T = 0)\) semiconductor crystal in a constant electric field.

The **effective mass** of the electron, \( m_e^* \), is defined for the band minimum at \( k_0 \):

\[
\frac{1}{m_e^*} = \left. \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \right|_{k=k_0}
\]

Near the band minimum, the \( E-k \) dispersion is well approximated by:

\[
E = \frac{\hbar^2 (k - k_0)^2}{2m_e^*} + E_c \quad \Leftrightarrow \quad E = \frac{p^2}{2m} + V
\]

\[
p = m_e^* v_g = \hbar (k - k_0)
\]

\[
p = \hbar (k - k_0) \quad \text{in 3D}
\]
We have learned:

A full band does not conduct.

The valence bands are full and conduction bands empty for perfect, pure semiconductors at $T = 0$. No conduction.

To conduct, need charge carriers, e.g., electrons near the conduction band minimum.

The semiclassical model works well in most circumstances, because mobile electrons are near the conduction band minimum/bottom (CBM):

- in equilibrium, these mobile electrons only occupy states near CBM with non-vanishing probabilities;
- when driven by a field, these electron can not go far from equilibrium, since each is “thermalized” by collision every time interval $\tau$.

We will later discuss how these carriers distribute in the conduction band states.
The concept of the hole

Consider the topmost filled band (valence band), \[ \sum_k v(k) = 0 \]

Here \( v \) is short for \( v_g \), the velocity of each electron

(A full band of electrons do not conduct.)

Somehow one electron at \( k_e \) is removed.

\[ v_e(k_e) + \sum_{k \neq k_e} v(k) = 0 \]

\[ \Rightarrow v_e(k_e) = - \sum_{k \neq k_e} v(k) \]

The motion of all the electrons in this band can be described as the motion of this vacancy.

The effective mass of the empty state is

\[ \frac{1}{m^*} = \left. \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \right|_{k=k_0} \]

Wavevector of VBM
The effective mass of the empty state is

\[
\frac{1}{m^*_e} = \left. \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \right|_{k=k_0}
\]

Wavevector of VBM, not the empty state

We define the hole energy \( E_h = -E \), then the hole effective mass is

\[
\frac{1}{m^*_h} = - \frac{1}{m^*_e} = - \left. \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \right|_{k=k_0} = \left. \frac{1}{\hbar^2} \frac{\partial^2 E_h}{\partial k^2} \right|_{k=k_0}
\]

So, it is positive.

In equilibrium, the hole is most likely to be at \( k = k_0 \).

A positive electric field \( \mathcal{E} \) will drive the entire band of electrons towards the negative, thus the empty state moves to \( k_e = k_0 + \Delta k \), where \( \Delta k = -q\mathcal{E} \tau / \hbar \).

The corresponding momentum \( \hbar (k_e - k_0) \) and group velocity \( v_e \) are negative.

Convenient to define the hole charge to be \( +q \), thus moved towards the positive by the positive \( \mathcal{E} \). Therefore, \( k_h = k_0 - \Delta k \), so that momentum \( \hbar (k_h - k_0) \) and group velocity \( v_h \) are positive.


The hole carries charge \( +q \), and has a positive effective mass near VBM.
Carriers in semiconductors

Fermi-Dirac distribution of electrons: consequence of Pauli’s exclusion rule

Analogy: sand particles in a vessel

Fermi-Dirac distribution at $T = 0$:

$f(E)$ is the probability of a state at energy $E$ being occupied.

$E_F$ depends on total amount of sand particles and available volume of the vessel per height (non-cylindrical vessel), or total number of electrons and number of available states per energy interval (per volume).

(Recall our calculation of in the Drude-Sommerfeld model)

For semiconductors, with a gap, $E_F$ is somewhat arbitrary.
The Fermi level $E_F(T)$ is a function of $T$. 

Fermi level vs. chemical potential: difference in terminology in different fields. 

Since $E_F$ depends on number of available states per energy interval (per volume), the way $E_F(T)$ varies with $T$ depends on it.

What is this called?
Density of states (DOS) determines how $E_F(T)$ varies with $T$.

In this illustration, you may consider the electrons spinless or each small box a spin-Bloch state.

(a) 20 electrons at $T = 0$.

(b) $T > 0$, some electrons promoted to higher energies. If $E_F$ remained ~ the same, we would need 21 electrons.

(c) To keep the # of electrons unchanged, $E_F$ has to move down. The lower band is still full at low $T$.

(d) At higher $T$, $E_F$ moves further down and the distribution flattens more, so that some states in lower band vacate.