Chapter 3
Band Structure and Carriers in Semiconductors

SUMMARY

Chapter 3
What make semiconductors so useful?

Macroscopic properties

- How do semiconductors have such a wide range of conductivity? Even for the same semiconductor compound, e. g. Si?

- How do some have positive Hall effects (p-type), and some have negative Hall effects (n-type)?

- How does the conductivity vary so much vs. temperature, the type and concentration level of impurities?

- Why does the carrier concentration exhibit exp(-E/kT) behavior?

- How do charge carriers have such a wide range of mobility? Which varies vs. temperature, carrier concentration, carrier types, and semiconductor composition?

Microscopic theory

- The nature of electronic bonding and its energy structure in SC crystal

- The effects of dopant

- The quantum mechanical behavior of electrons

- The statistical mechanics behavior of the carriers

Basic electrical transport concepts

Conductivity: σ; resistivity: ρ=1/σ

length l

Cross section A

q (charge)

v (velocity)
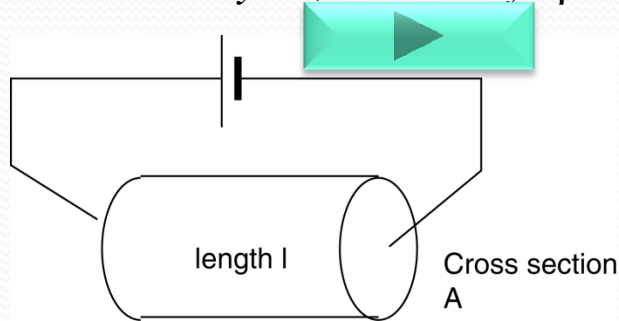
Macroscopically: the resistance of a piece of material is linearly proportional to its length and inversely proportional to its cross section: $R \propto \dfrac{l}{A}$

so a "specific resistance", called <u>resistivity</u>, can be defined: $R = \rho \dfrac{l}{A}$ or $\rho = \dfrac{RA}{l}$ unit: $\dfrac{\Omega \text{cm}^2}{\text{cm}} = \Omega \text{cm}$

Microscopically: Current density J= carrier/unit volume x charge x average carrier velocity: $J = qnv$

Steady state average carrier velocity is call <u>drift velocity</u>. $v = \mu E$

Drift velocity

where μ is <u>defined</u> as <u>carrier mobility</u>, its unit is : (cm/s)/(V/cm) = cm²/V sec

So: $I = AJ = Aqn\mu E = Aqn\mu \dfrac{V}{l};$ $R = \dfrac{V}{I} = \dfrac{l}{Aqn\mu};$ $\rho = \dfrac{RA}{l} = \dfrac{1}{qn\mu}$ or $\sigma = qn\mu$

Why does conductivity vary so much for semiconductor?

This is how (#1) →

σ=q n μ

vary a lot ⟶ ⟵ vary a lot too!

What is "drift velocity"?

Classically, a freely moving charge has a velocity:

$$v = \frac{Force}{mass} t = \frac{qE}{m} t$$

which increases with time indefinitely. But it can't, because of scattering as shown. There is a terminal "time-averaged" velocity. If you measure the net traveled distance for a long time, the particle will have an average velocity called drift velocity. We can <u>define</u> a <u>relaxation time</u> τ as the time for which:

$$v_d = \frac{qE}{m} \tau$$

So, mobility can be expressed as:

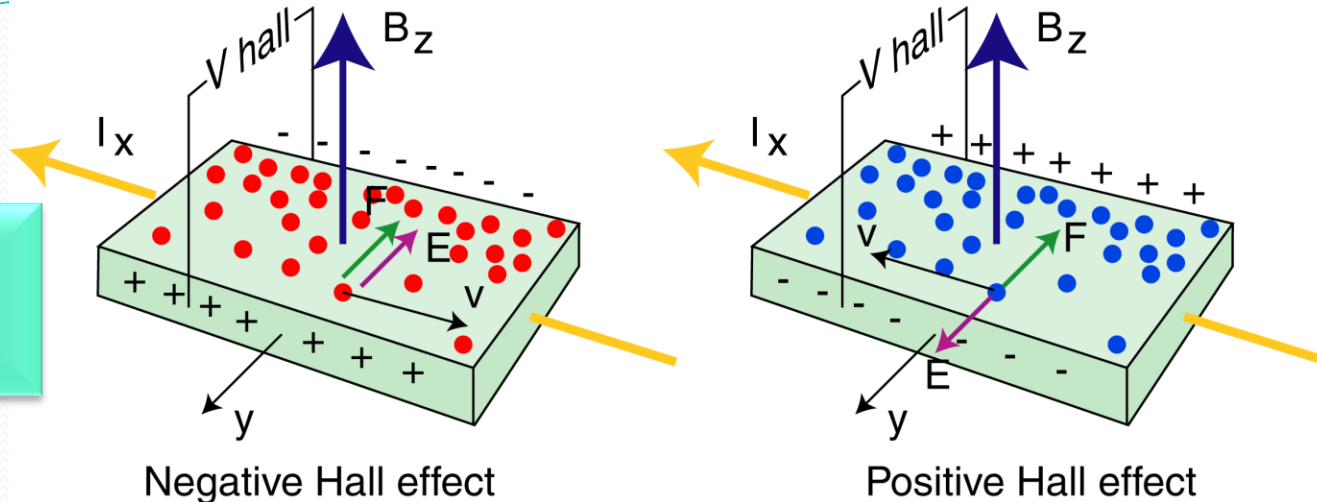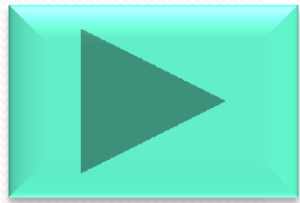$$v_d = \frac{qE}{m} \tau = \mu E \quad \Rightarrow \quad \mu = \frac{q}{m} \tau$$

How does mobility vary vs. temperature, crystal quality (impurities & defects), carrier types, and semiconductor compositions? →

Electric field

drift vel= $\frac{length\ CE}{t}$

time

E   C   Vc

Vbias
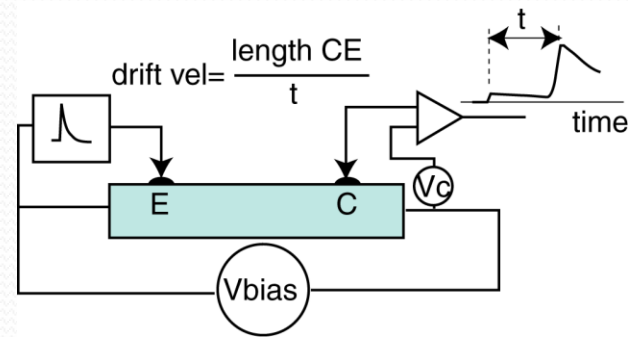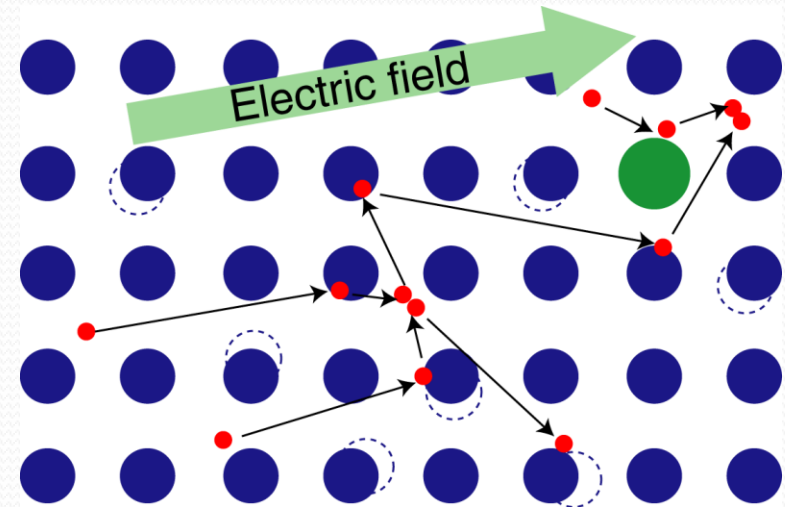
$\mu = \frac{q\tau}{m}$

Relaxation time (scattering) varies with temp., crystal quality, carriers and SC compositions

Different SC compositions, carriers (n, p) have different masses

Hall effects

Negative Hall effect   Positive Hall effect

Electromotive (Lorentz) force: $\mathbf{F} = q\mathbf{v} \times \mathbf{B}$ **or:** $F_y = -qv_x B_z$ **(In material B→H)**

At equilibrium, <u>there must be a force</u> that counters this Lorentz force: an electric field formed by the gradient of the carrier distribution: $qE_y = qv_x B_z$ $E_y = v_x B_z$

For electrodes width w, the <u>Hall voltage</u> is: $V_H = wE_y$. Define Hall coefficient R_H:

$$E_y = R_H J_x H_z \Rightarrow R_H = E_y / J_x H_z$$

- Measured Hall voltage→ Sign indicates <u>carrier types</u> (n or p)
- Measured Hall voltage→ Hall field→(Hall) drift velocity:

$$v_x = \mu E_x = \mu \frac{J_x}{\sigma} \Rightarrow \mu = v_x \frac{\sigma}{J_x} = \frac{V_H \sigma}{w H_z J_x} = R_H \sigma$$

- Drift velocity→<u>carrier concentration</u>:

$$J_x = qnv_x \Rightarrow n = J_x / qv_x = \frac{J_x w H_z}{q V_H}$$

- Drift velocity→<u>Hall mobility</u>:

$$\frac{V_H}{w} = E_y = v_x H_z \Rightarrow v_x = \frac{V_H}{w H_z}$$

Key concepts

	Carrier transport properties	Semicond structural properties
Macroscopic	-conductivity/ resistivity -mobility -relaxation time -drift velocity -Hall effects	-n-type, p-type -doped, doping,... -donor/acceptor -intrinsic/extrinsic -ambipolar -degenerate
Microscopic	-electron and hole -lattice momentum -effective mass -density of state -generation/recom-bination -Fermi-Dirac statistics -Fermi level	-covalent/ionic bond -energy bands: conduction/valence -band gap, direct indirect -band energy dispersion relation

How to solve the semiconductor puzzle
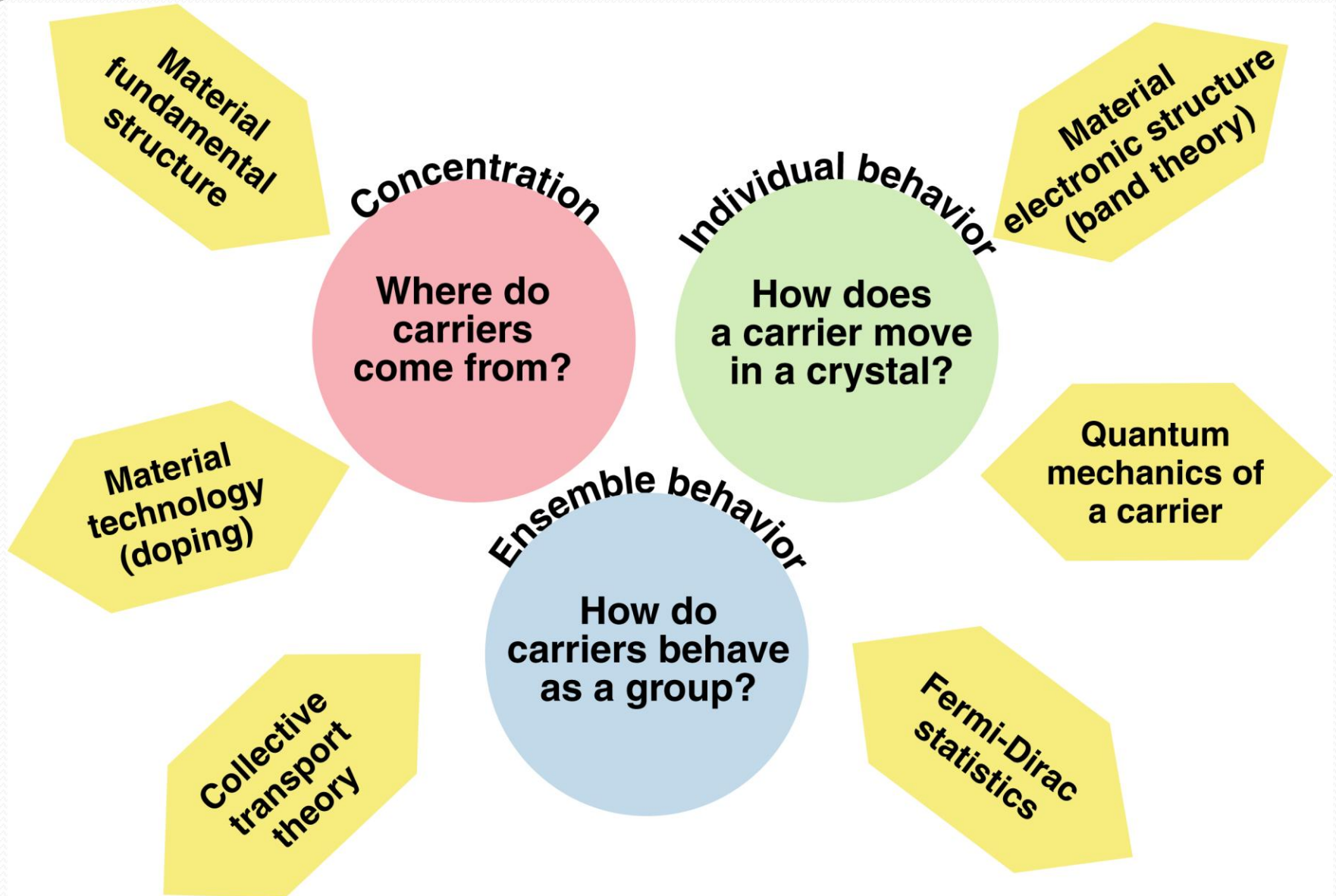
Band formation
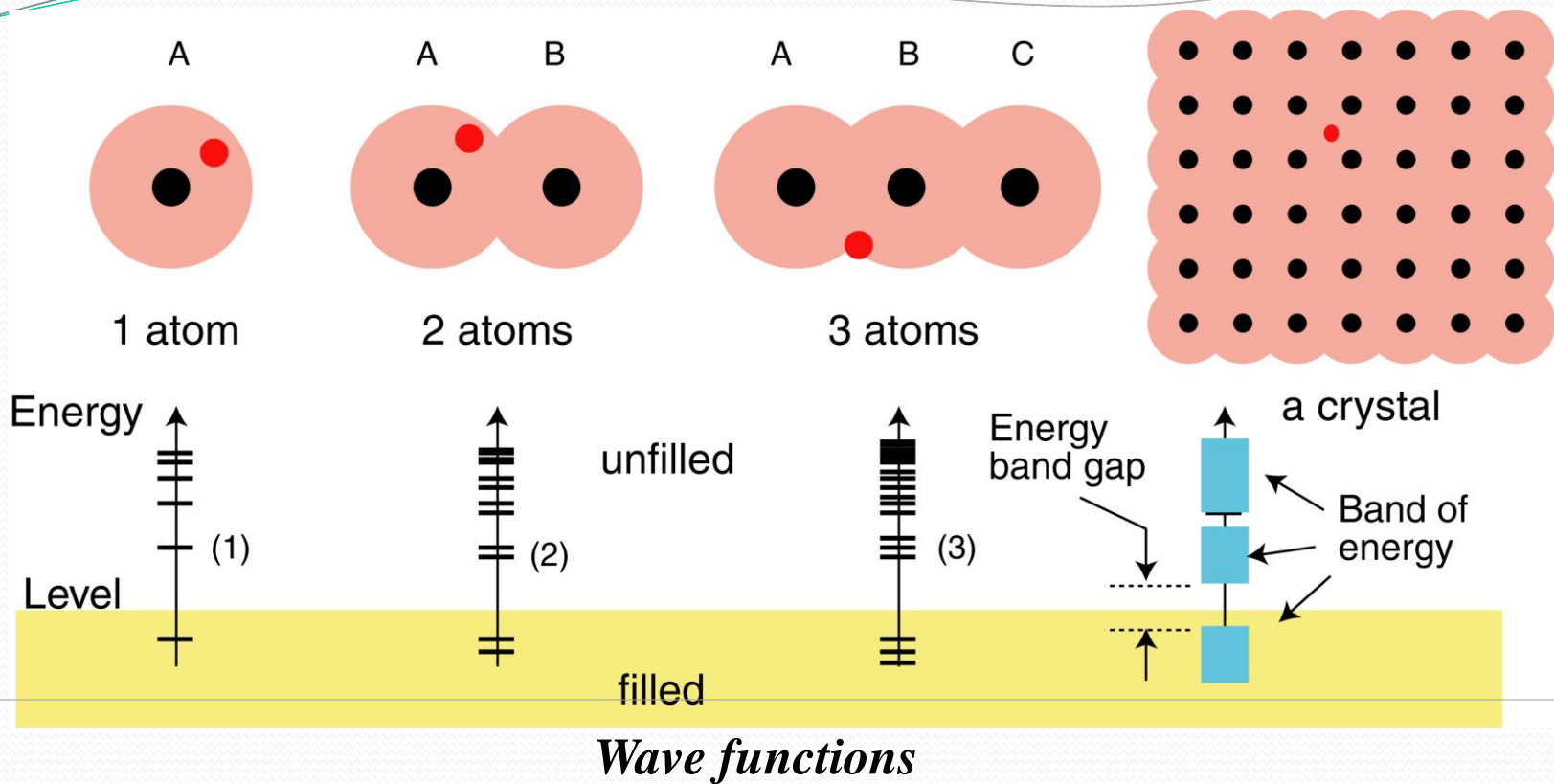
Wave functions

$$\psi_A$$

$$\sim \quad \psi_A + \psi_B$$
$$\sim \quad \psi_A - \psi_B$$

$$\sim \quad b\psi_A - \psi_B + b\psi_C$$
$$\sim \quad a\psi_A + \psi_B + a\psi_C$$
$$\sim \quad \psi_A - \psi_C$$

$$\psi_{b;\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{b;\mathbf{k}}(\mathbf{r})$$

b: band (cond., val., …)
r: coordinates *x, y, z*
$u_{b;\mathbf{k}}$: Bloch wavefunction
k: <u>lattice momentum</u>

Band formation (cont.)

- Each state in an atom yields an infinite number of states in an infinite crystal or condensed matter
- A discrete level of energy usually (but not necessarily) becomes an infinitely dense <u>energy band.</u> (if the atoms are infinitely apart, all the states are still degenerate into one energy level)
- <u>A memory refresher</u>: each quantum state has a definite energy level. But many states can have the same energy level, a situation called degeneracy. The states are said to be degenerate-usually a consequence of some geometry. Example: atomic angular momentum l has $2l+1$ degenerate states. So, the number of energy levels is always smaller or equal to the number of states.

- A periodic crystal has the <u>translational symmetry</u>: it means that you can shift the crystal by an integral number of its lattice dimension and you can not tell the difference. The <u>lattice momentum</u> is the <u>quantum number of this symmetry</u>. All values of form a 3-D zone called <u>Brillouin zone.</u>

Comparison of quantum description

Electron in an atom	Electron in a crystal or large condensed matter (macromolecule)
Radial quantum number (QN)	Band (conduction, valence, spin-orbit, …) radial QN
Angular momentum QN	Band angular momentum QN (s-like, p-like, d-like,…)
Magnetic QN	Magnetic QN
	Lattice momentum QN

Look at the Bloch wavefunction: $\psi_{b;\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{b;\mathbf{k}}(\mathbf{r})$

The part $e^{i\mathbf{k}\cdot\mathbf{r}}$ **is a plane wave. What does it do to the periodic Bloch function?**
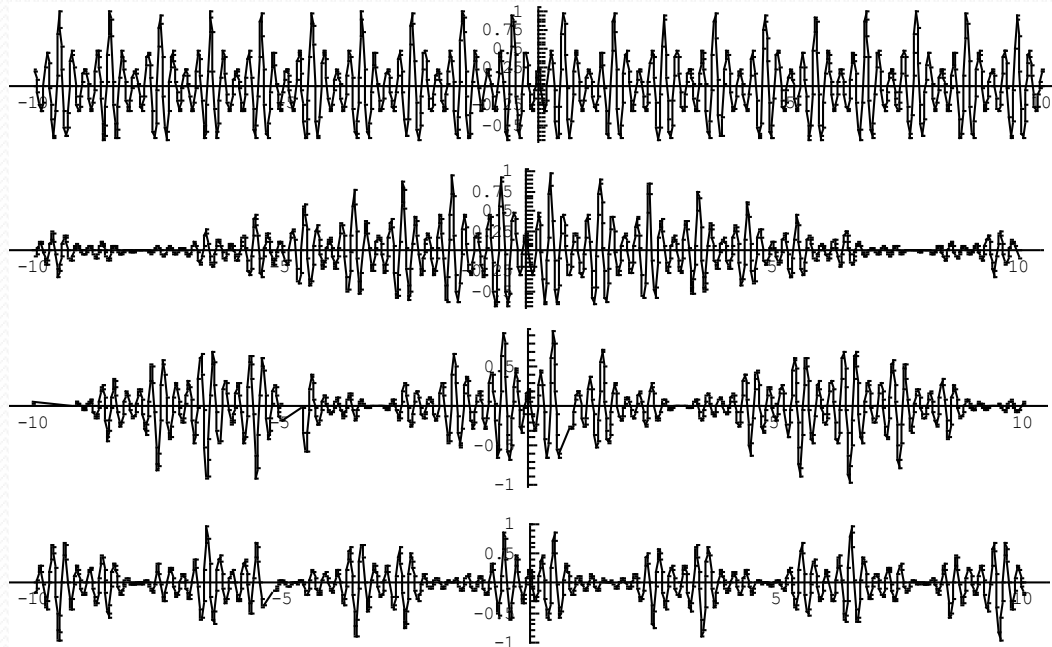
Top: k=0; 2$^{\text{nd}}$: k=0.2; 3$^{\text{rd}}$: k=0.5; bottom: k=1 (arb. unit)

It modulates the "local" Bloch function. Analogy: Christmas light string: each light bulb is a Bloch function, $e^{i\mathbf{k}\cdot\mathbf{r}}$ modulation is to turn bulbs on-off in sequence. The light appears to move: this is how electron moves in a crystal lattice.

Comparison of momentum of a free particle with that in a crystal

Free particle	Particle in crystal

Wavefunction: $\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}$

$$\psi_{b;\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{b;\mathbf{k}}(\mathbf{r})$$

Momentum:

$$\hat{\mathbf{p}} e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{\hbar}{i} \nabla e^{i\mathbf{k}\cdot\mathbf{r}} = \hbar\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$= \hbar\mathbf{k}$$

$$\hat{\mathbf{p}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{b;\mathbf{k}} = \frac{\hbar}{i} u_{b;\mathbf{k}} \nabla e^{i\mathbf{k}\cdot\mathbf{r}} + \frac{\hbar}{i} e^{i\mathbf{k}\cdot\mathbf{r}} \nabla u_{b;\mathbf{k}}$$

$$= \hbar\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} u_{b;\mathbf{k}} + \frac{\hbar}{i} e^{i\mathbf{k}\cdot\mathbf{r}} \nabla u_{b;\mathbf{k}}$$

$$\langle \hat{\mathbf{p}} \rangle = \hbar\mathbf{k} + \frac{\hbar}{i} \langle u_{b;\mathbf{k}} | \nabla u_{b;\mathbf{k}} \rangle = \hbar\mathbf{k}$$

(the 2nd term usually vanishes because of parity-mirror image symmetry)

Conclusion: the <u>expected</u> value of momentum of a particle with lattice momentum vector $\vec{\mathbf{k}}$ is $\hbar\mathbf{k}$, which is the same as that of a free particle with the same momentum vector. <u>But: it is not a quantum state of the momentum operator.</u>

Energy and Lattice Momentum

- **Each quantum state in a crystal with a lattice momentum has an energy**

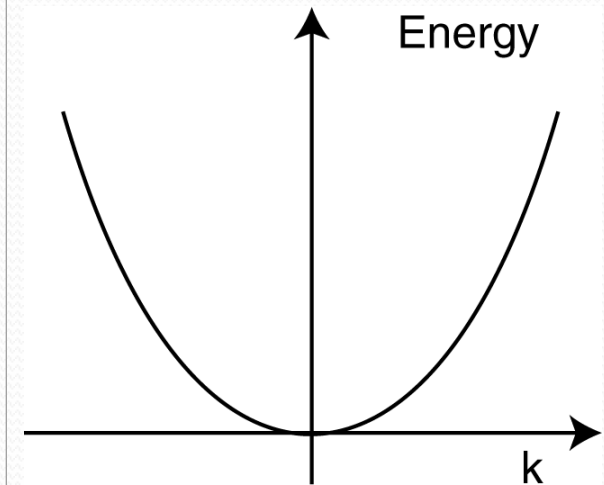- **This energy is a function of $\vec{k}$, also called as energy or E-k dispersion relation**

- **Example for a free particle:**

$$\hat{E} = \frac{\mathbf{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$$

$$\hat{E}e^{i\mathbf{k}\bullet\mathbf{r}} = -\frac{\hbar^2}{2m}\nabla^2 e^{i\mathbf{k}\bullet\mathbf{r}} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)e^{i\left(k_x x + k_y y + k_z z\right)}$$

$$= \frac{\hbar^2 k^2}{2m}e^{i\mathbf{k}\bullet\mathbf{r}}$$

$$\hbar^2 k^2 / 2m$$

$\vec{k}$

Energy

k

- **In a real crystal, the energy function of has a more complicated shape:**
- **The energy function shape (or structure) is unique for each band (conduction, valence, split-off, higher bands, …)**
- **The only way to know for sure is by <u>measurements</u>**
- **Large computation programs have been used to obtain the energy band structure**

Properties near Band Extrema

Energy

Conduction band

k

Valence band
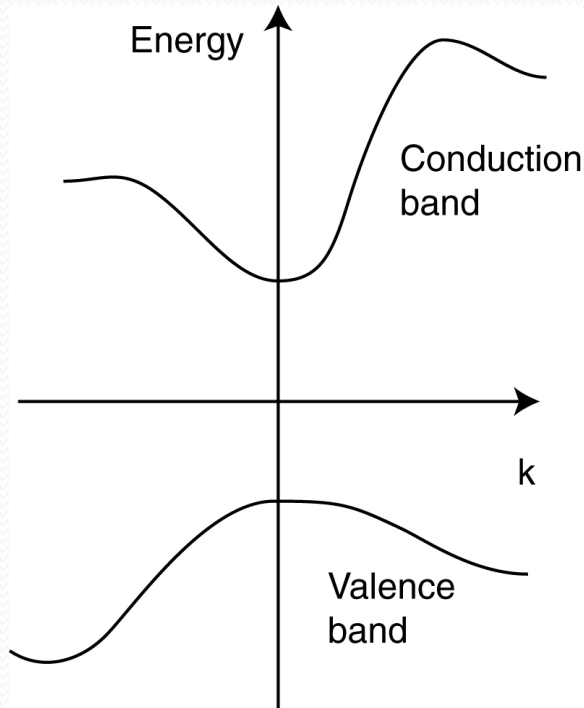
Electrons or absence of electrons are usually concentrated at energy band extrema

Energy at band extrema can be extrapolated

$$E_b(\mathbf{k}) = E_b + \vec{\nabla}_{\mathbf{k}} E \bullet \mathbf{k} + \frac{1}{2!} \frac{\partial^2 E}{\partial k_i \partial k_j} k_i k_j + \cdots$$
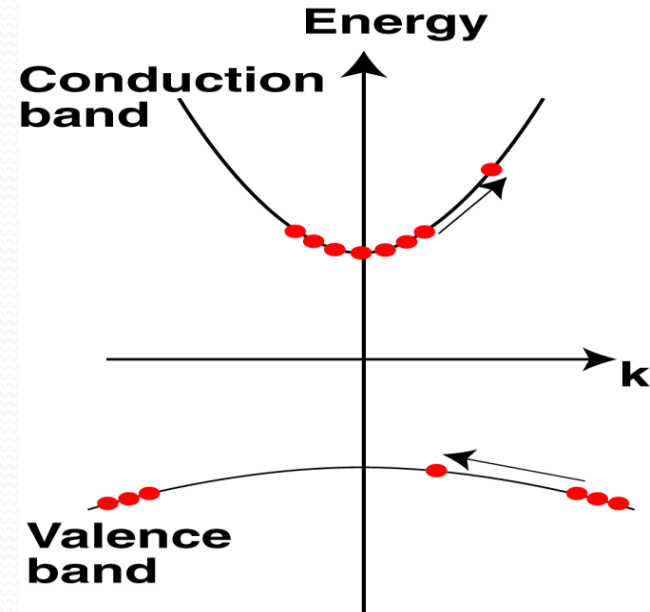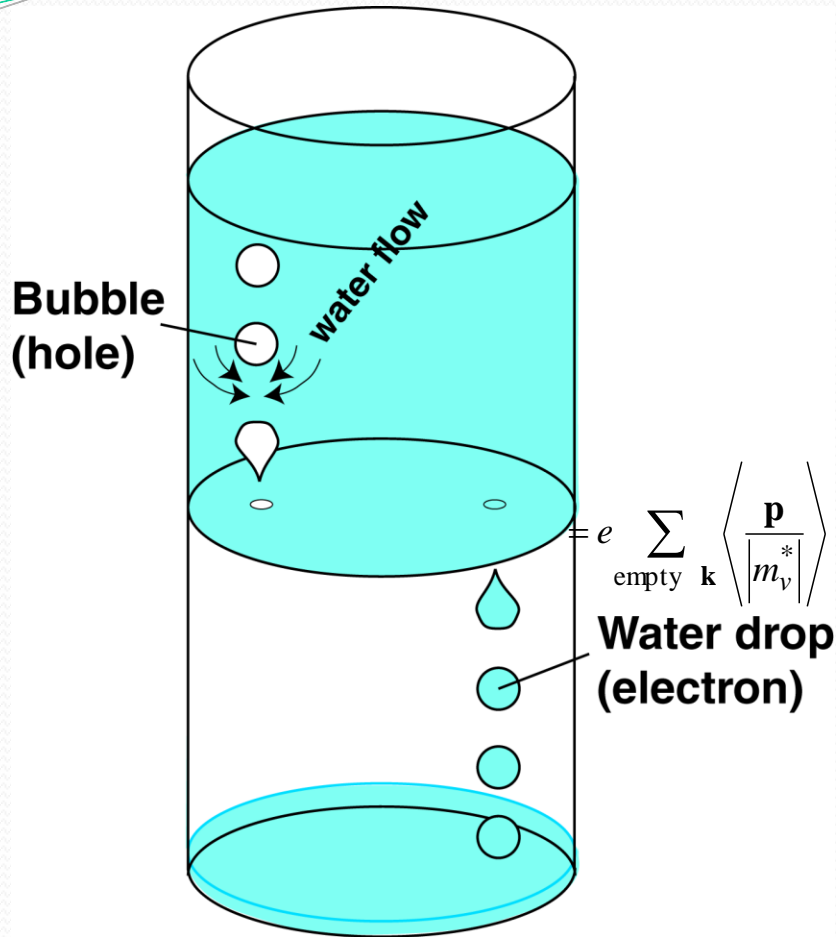
$$\approx E_b + \frac{1}{2!} \frac{\partial^2 E}{\partial k_i \partial k_j} k_i k_j$$

If isotropic: $\quad E_b(\mathbf{k}) \approx E_b + \frac{1}{2} \frac{\partial^2 E}{\partial k^2} k^2 = E_b + \frac{\hbar^2 k^2}{2m*}$

$\mathbf{m*} \equiv \hbar^2 / \left(d^2 E / dk^2 \right)$ **is <u>defined</u> as the <u>effective mass</u>**

- **Effective mass (EM) approximation is the most important and useful approximation of all the results from the band theory. <u>It allows us to treat carriers as free particles</u>. <u>Many classical transport concepts are valid as long as the mass is EM</u>. For the rest of this course, everything will be done with effective mass approximation.**
- **Effective masses in various semiconductors are measured. A huge amount of work and published literature is concerned with measuring these values.**

An important EM results: holes

Bubble (hole)

water flow

Water drop (electron)

$$= e \sum_{\text{empty } \mathbf{k}} \left\langle \frac{\mathbf{p}}{\left| m_v^* \right|} \right\rangle$$

Energy

Conduction band

k

Valence band

$$J_{\text{net}} = J_{\text{all}} - (-e) \sum_{\text{empty } \mathbf{k}} \left\langle \psi_{v;\mathbf{k}} \left| \frac{\mathbf{p}}{\left| m_v^* \right|} \right| \psi_{v;\mathbf{k}} \right\rangle$$

$$E_{\text{elect}} = -\frac{\hbar^2 k^2}{2\left| m^*_v \right|} = -E_{\text{hole}} \Rightarrow E_{\text{hole}} = \frac{\hbar^2 k^2}{2\left| m^*_v \right|}$$

- **The absence of an electron in the valence band extremum (with negative effective mass) behaves like a <u>positive charge particle with valence effective mass</u>, defined as <u>hole</u>.**
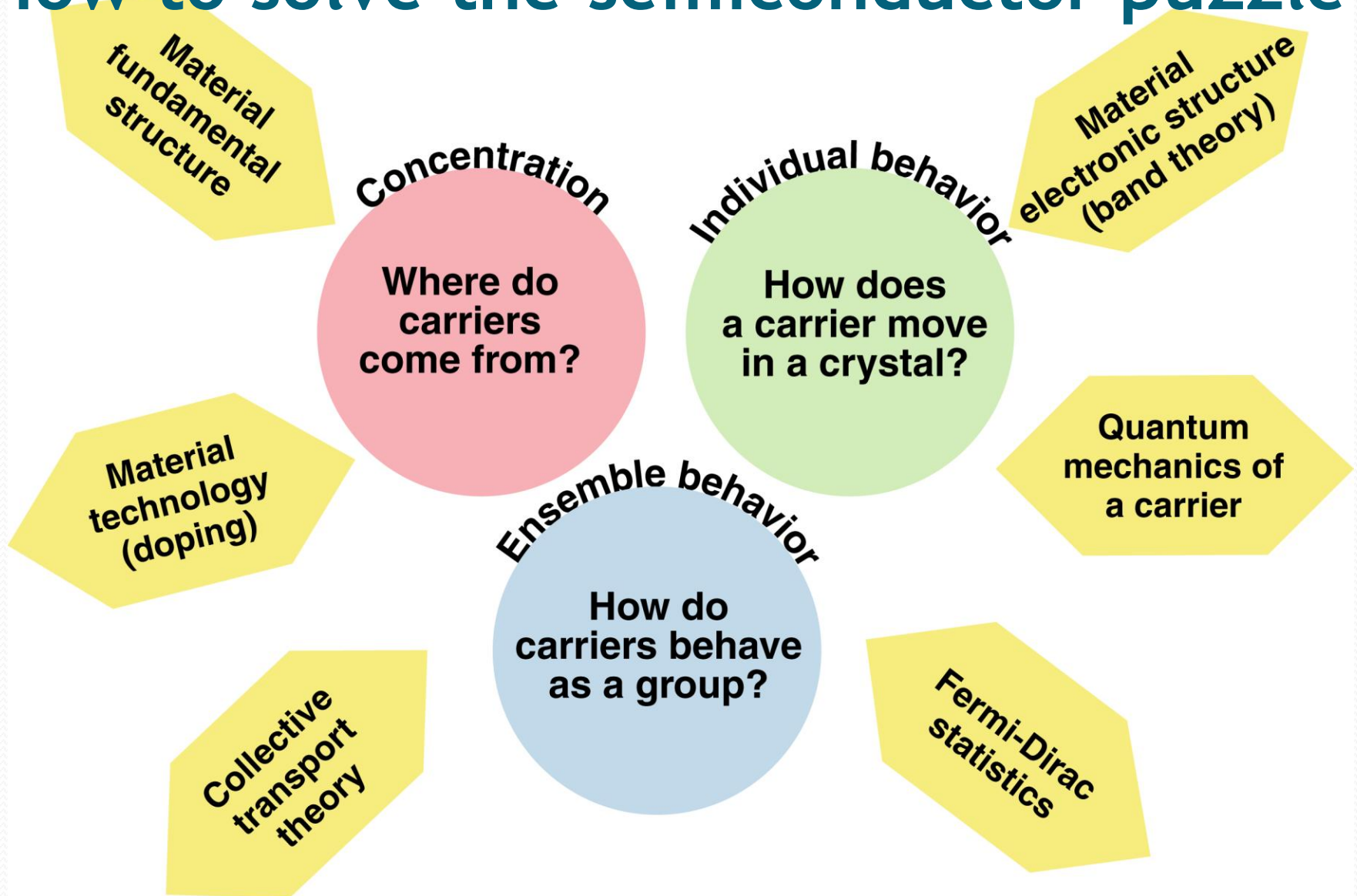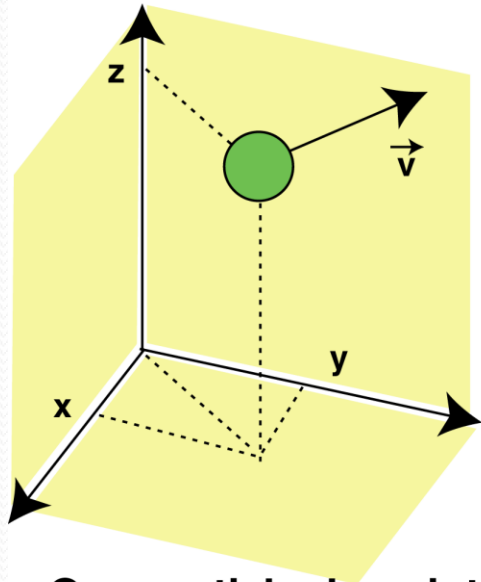
How to solve the semiconductor puzzle
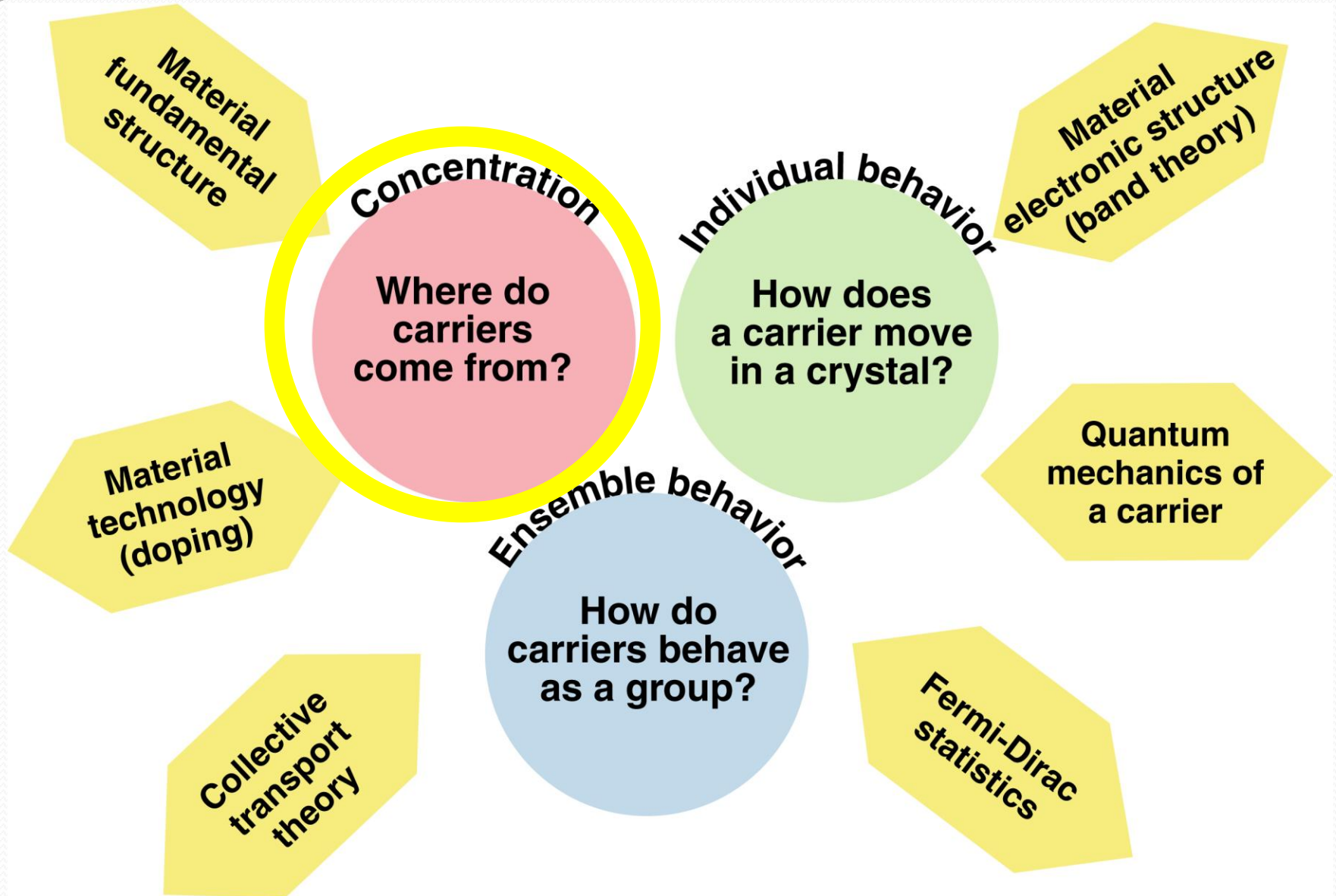
How do semiconductors have charge carriers?

- **Intrinsic: thermal excitation from the valence band to the conduction band**

- **Extrinsic: carriers from dopants, impurities, defects**

  ☐ ¨ **Donor (D): donates extra electrons to the conduction band; single or multiple; D^+: ionized donor.**
  ☐ ¨ **Acceptor (A): accepts valence electrons, leave behind holes; single or multiple. A^-: ionized acceptor.**
  ☐ ¨ **Amphoteric dopant: either D or A, depending on site.**
  ☐ ¨ **Shallow donor/acceptor: electron/hole energy level close to conduction band/valence band edge.**
  ☐ ¨ **Deep levels, deep traps: D e or A h energy level near mid gap.**
  ☐ ¨ **Lightly/heavily doped: result in nondegenerate/degenerate carrier population**
  ☐ ¨ **Majority/minority carrier, ambipolar population**

How to solve the semiconductor puzzle

Material fundamental structure

Concentration

Individual behavior

Material electronic structure (band theory)

Where do carriers come from?

How does a carrier move in a crystal?

Material technology (doping)

Ensemble behavior

Quantum mechanics of a carrier

How do carriers behave as a group?

Collective transport theory

Fermi-Dirac statistics

Statistical mechanics concepts


One particle description
(x,y,z,vx,vy,vz,
internal degree of freedom)
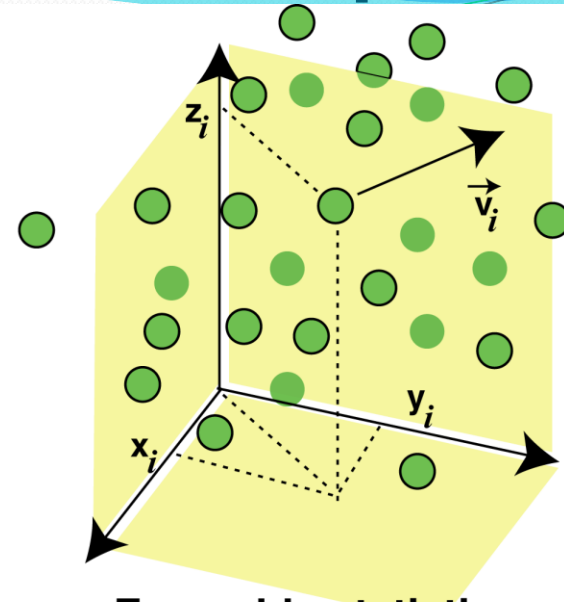
Ensemble statistics

Distribution functions

- **Example 1:** : **Fraction of atoms in r and r+Δr, with velocity between v and v+Δv at time t: global distribution.** $$f(\mathbf{r}, \mathbf{v}, t)\Delta\mathbf{r}\Delta\mathbf{v}$$

- **Example 2:** $f(E)$ **is the probability of having particles occupying states with energy** E**: also called <u>occupation</u> number: relative distribution.**

How to use occupation number
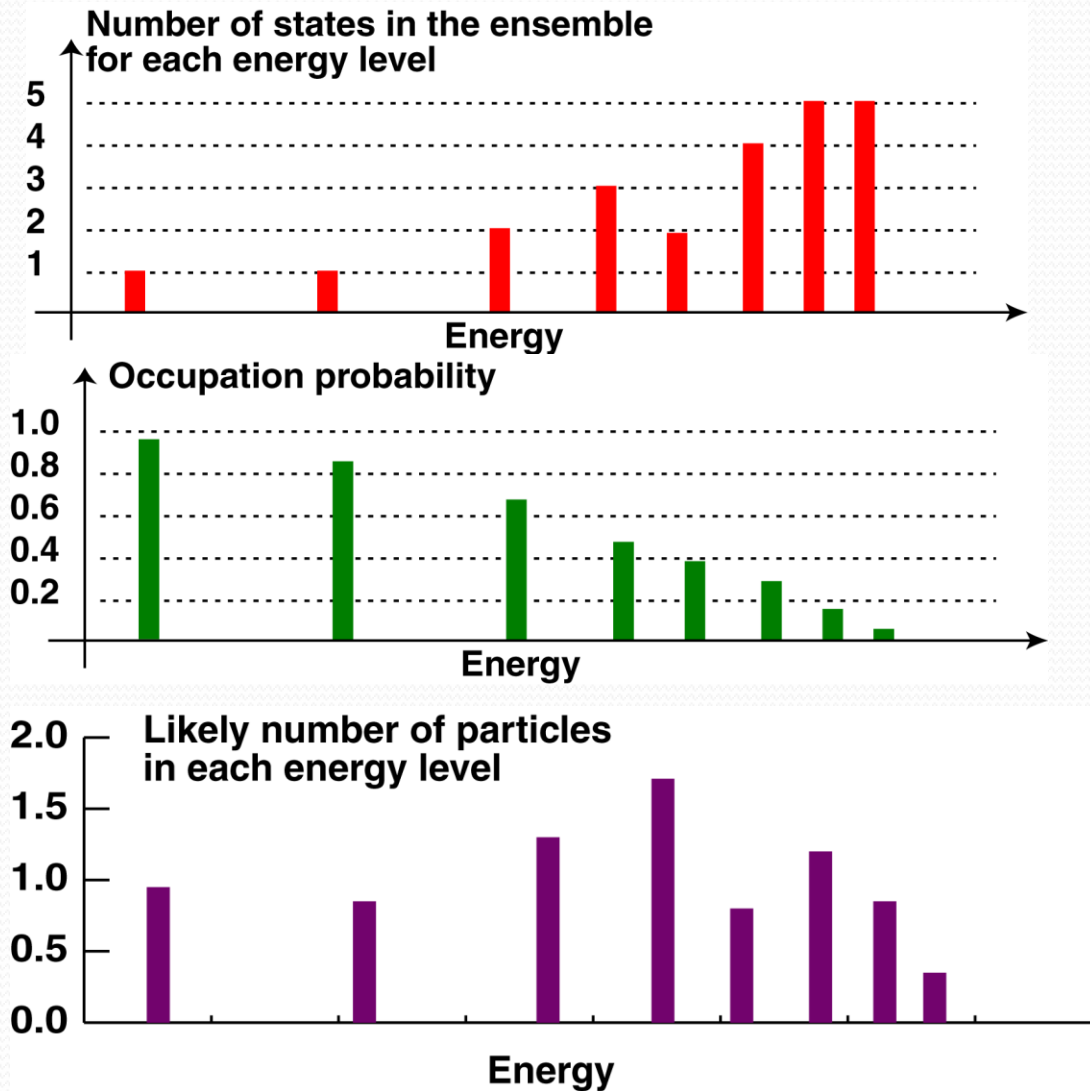
Sum of Occ. Prob. x Number of states = Total number of particles
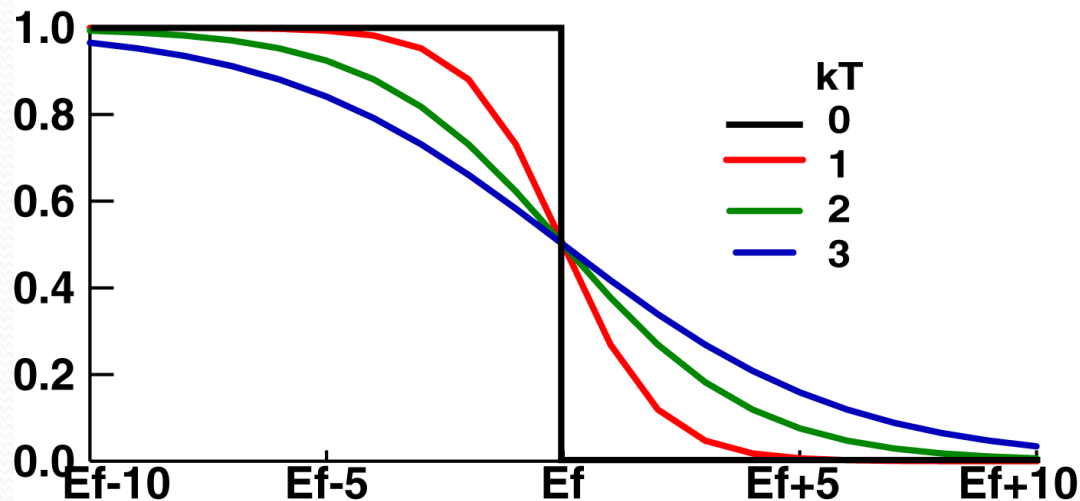
Distribution for dense or continuous energy
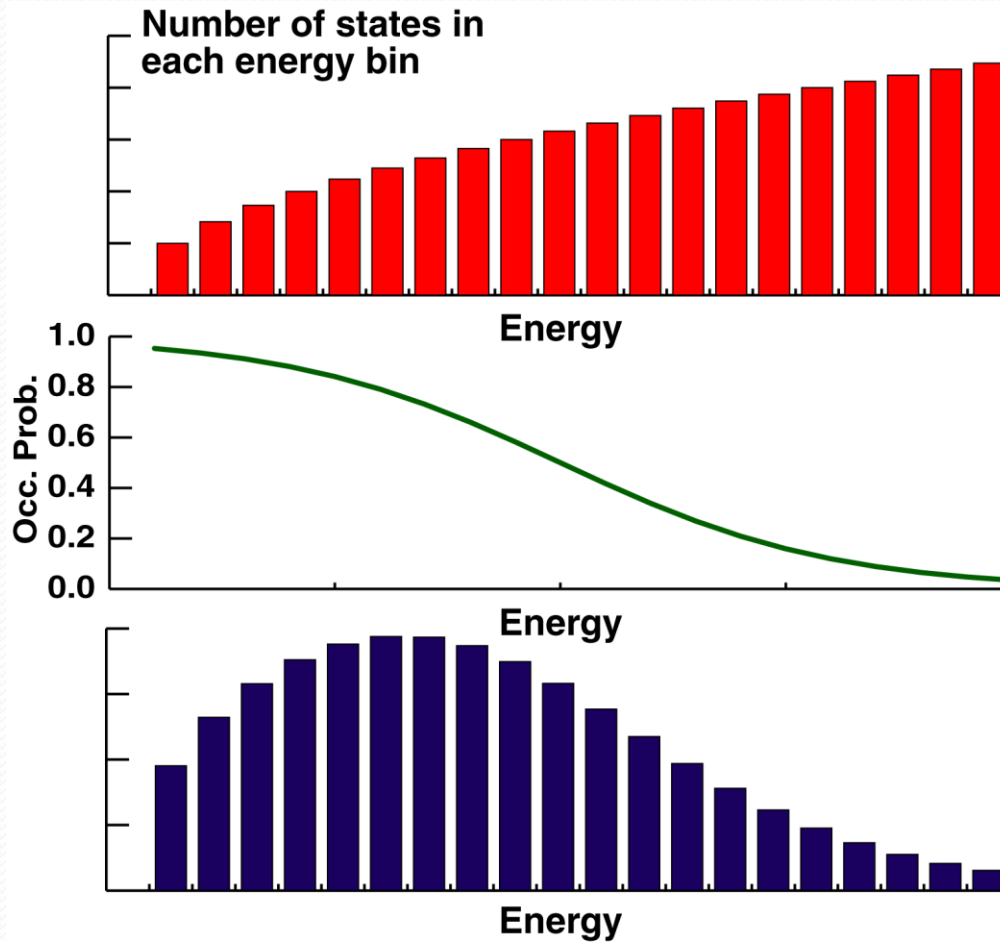
$$n = \int f(E)D(E)dE$$

Fermi-Dirac distribution function

$$f\left(E; E_f\right) = \frac{1}{1 + e^{\left(E - E_f\right)/k_B T}}$$

where: k_B is the Boltzmann's constant=0.08617 eV/Kelvin, T is the absolute temperature, and E_f is the energy that separates the filled and unfilled states at zero T, called <u>Fermi level</u>

In a given system, E_f is determined by the equation: $n = \int f\left(E; E_f\right) D(E) dE$

Terminology and units

1. Electron/hole density: # of electron/hole per unit volume, e. g. cm^3
2. (Ionized) Donor/Acceptor density: # of D/A / unit vol. (ionized or not)
3. Semiconductor units of length and energy

Length   Donor Bohr radius a_B^* $a_B^* = \dfrac{\varepsilon_o \hbar^2}{m_e^* e^2}$

Energy   Donor Rydberg energy Ry^* $Ry^* = \dfrac{e^2}{2\varepsilon_o a_B^*}$

m_e^* is the electron effective mass, ε_o is the dielectric constant
Relation of these in terms of atomic units

$$a_B^* = \frac{\varepsilon_o \hbar^2}{m_e^* e^2} = \varepsilon_o \frac{m_o}{m_e^*} a_B$$

$$Ry^* = \frac{e^2}{2\varepsilon_o a_B^*} = \frac{1}{\varepsilon_o} \frac{a_B}{a_B^*} R_\infty = \frac{1}{\varepsilon_o^2} \frac{m_e^*}{m_o} R_\infty$$

· **Charge neutrality:** $n_o + D^+ = p_o + A^-$ **n$_o$, p$_o$ are electron/hole densities at thermal equilibrium, D$^+$/A$^-$ are ionized donor/acceptor densities**

• **At thermal equilibrium:** $n_o = N_c e^{-(E_c - E_f)/k_B T}$; $p_o = N_v e^{-(E_f - E_v)/k_B T}$

where $N_C = g_c \dfrac{2}{a_B^{*3}} \left(\dfrac{k_B T}{4\pi Ry*} \right)^{3/2}$ $N_V = g_v \left(\dfrac{m_h^*}{m_e^*} \right)^{3/2} \dfrac{2}{a_B^{*3}} \left(\dfrac{k_B T}{4\pi Ry*} \right)^{3/2} = \dfrac{g_v}{g_c} \left(\dfrac{m_h^*}{m_e^*} \right)^{3/2} N_C$

• **N$_c$, N$_v$ referred to as effective density of states are NOT really DOS, but only quantities for approximation convenience; g$_c$, g$_v$ are denegeracy factors of conduction and valence band.**
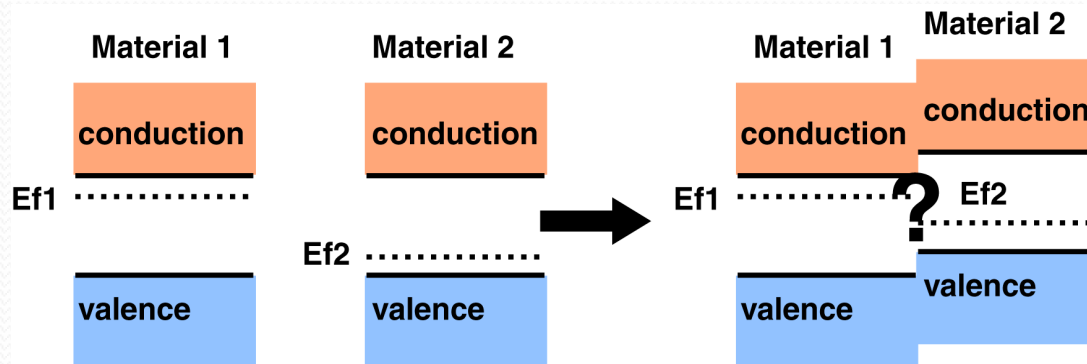**Approximation: intrinsic n$_i$, p$_i$ at <u>low intrinsic densities</u>**

$$n_i = p_i = \sqrt{N_c N_v} e^{-E_g/k_B T}$$

Approximation at <u>low doping densities</u>:

$$n_o p_o = n_i p_i = n_i^2$$

Fermi level across dissimilar materials

Rate of electron going from 1 (left) to 2 (right):
$$N_1(E)f_1(E) \times N_2(E)[1 - f_2(E)]$$

Rate of electron going from 2 (right) to 1 (left):
$$N_2(E)f_2(E) \times N_1(E)[1 - f_1(E)]$$

At equilibrium, the two rates must be equal; canceling all terms involving N:
$$f_1(E) = f_2(E)$$

$$\left[1 + e^{(E - E_{f1})/k_B T}\right]^{-1} = \left[1 + e^{(E - E_{f2})/k_B T}\right]^{-1}$$

$$E_{f1} = E_{f2}$$