Lecture 1:
Quantum Theory of Solids

- Quantum mechanics
- Free electrons in a box (Fermi gas)
- Band theory of solids
- Fermi/Dirac distribution function
- Doping

Quantum mechanics of free particles:

$|\Psi(\vec{r},t)|^2$ is probability of finding an electron at point r at time t.

Ψ is complex, and both real and imaginary parts are physical.

For a free particle:

$\omega = E/\hbar$

$$\Psi(\vec{r},t) \sim e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

Momentum:

$$\vec{p} = \hbar\vec{k}$$

Energy:

$$E = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$$

Schrodinger equation:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)$$

(1 dimension)

(Time dependent)

Let $$\Psi(x,t) = A\cdot e^{i(kx-\omega t)}$$

A is a (complex) constant.

Then

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}A\cdot e^{i(kx-\omega t)} = i\hbar(-i\omega)A\cdot e^{i(kx-\omega t)}$$

$$= E\cdot A\cdot e^{i(kx-\omega t)} = E\cdot\Psi(x,t)$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(A\cdot e^{i(kx-\omega t)}\right) = \left(-\frac{\hbar^2}{2m}\right)(ik)^2\left(A\cdot e^{i(kx-\omega t)}\right)$$

$$= \frac{\hbar^2k^2}{2m}\left(A\cdot e^{i(kx-\omega t)}\right) = \frac{p^2}{2m}\Psi(x,t)$$

Schrodinger equation: (3 dimensions)

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = -\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi(\vec{r},t) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(\vec{r},t)$$

Let $\Psi(\vec{r},t) = A\cdot e^{i(\vec{k}\cdot\vec{r}-\omega t)} = A\cdot e^{i\left((k_x\cdot x+k_y\cdot y+k_z\cdot z)-\omega t\right)}$

Then $i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = i\hbar(-i\omega)\Psi(\vec{r},t) = E\cdot\Psi(\vec{r},t)$ as before.

But:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(\vec{r},t) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\left(A\cdot e^{i(\vec{k}\cdot\vec{r}-\omega t)}\right)$$

$$= \left(-\frac{\hbar^2}{2m}\right)\left((ik_x)^2+(ik_y)^2+(ik_z)^2\right)\left(A\cdot e^{i(\vec{k}\cdot\vec{r}-\omega t)}\right) = \left(\frac{\hbar^2(k_x^{\,2}+k_y^{\,2}+k_z^{\,2})}{2m}\right)\Psi(\vec{r},t)$$

$$= \frac{\hbar^2k^2}{2m}\left(A\cdot e^{i(\vec{k}\cdot\vec{r}-\omega t)}\right) = \frac{p^2}{2m}\Psi(\vec{r},t)$$

Quantum mechanics of free particles:

$$\Psi(\vec{r},t) \sim e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

Generally,

$$\Psi(\vec{r},t) = \sum_n A_n e^{i(k_n x-\omega_n t)} \rightarrow \int dk A(k) e^{i(kx-\omega t)}$$

is also a possibility.

Time-independent Schrodinger equation

$$\Psi(\vec{r},t) = A\cdot e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

$$= A\cdot e^{i\left((k_x\cdot x+k_y\cdot y+k_z\cdot z)-\omega t\right)} = \underbrace{A\cdot e^{i(k_x\cdot x+k_y\cdot y+k_z\cdot z)}}_{\text{Call this } \psi(\vec{r})}\cdot e^{-i\omega t}$$

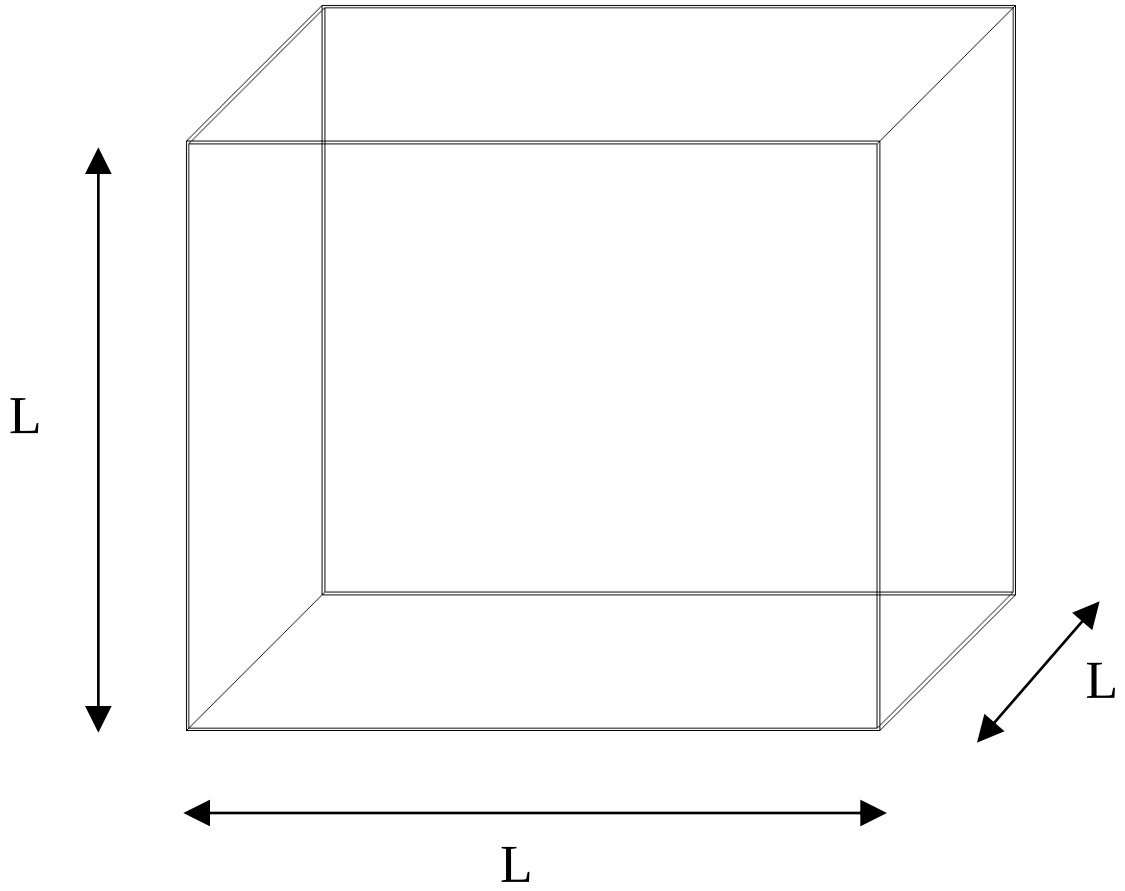
$$\Rightarrow \Psi(\vec{r},t) = \psi(\vec{r})\cdot e^{-i\omega t}$$

From: $$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = -\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi(\vec{r},t)$$

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r})\cdot e^{-i\omega t} = i\hbar(-i\omega)\psi(\vec{r})\cdot e^{-i\omega t} = E\cdot\psi(\vec{r})\cdot e^{-i\omega t} = -\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi(\vec{r},t) = -\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{r})\cdot e^{-i\omega t}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{r}) = E\cdot\psi(\vec{r})$$

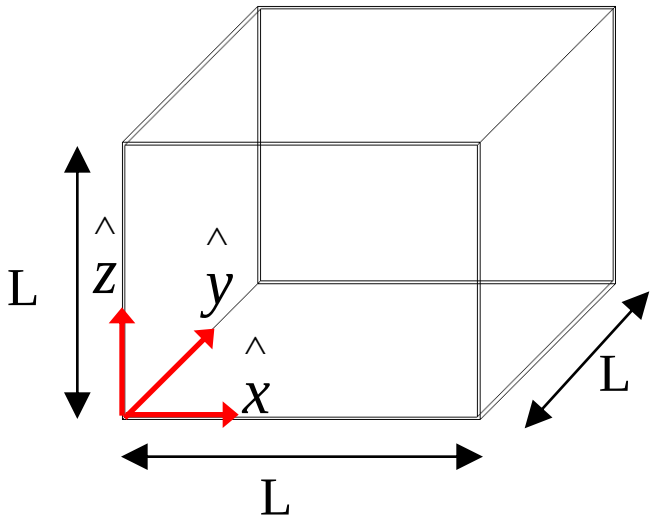
Confined particles: A box



Goal: find $\psi(\vec{r})$

Similar to electric field inside the box.

Goal: find $\psi(\vec{r})$



Everywhere outside the box

$$|\psi(\vec{r})|^2 = 0$$

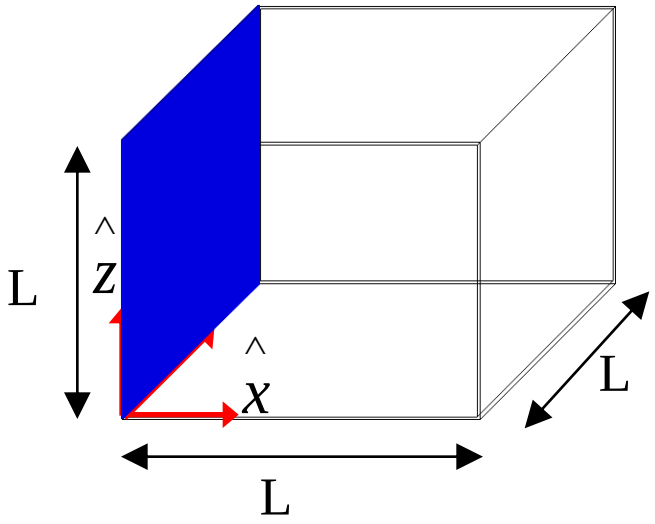
In particular,

$$|\psi(\vec{r})|^2 = 0$$

on the boundaries.

As before, we will consider all six surfaces:

Boundary conditions:



The plane x=0:

Try:

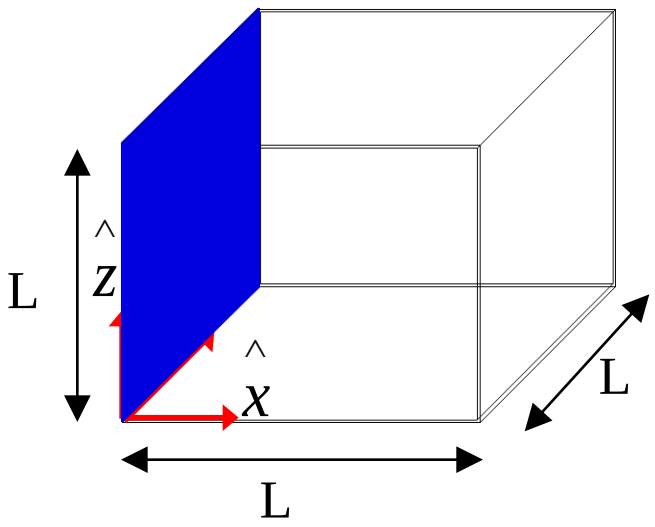
$$\psi(\vec{r}) = A \cdot e^{i(k_x \cdot x + k_y \cdot y + k_z \cdot z)}$$

$$\psi(x=0,y,z) = A \cdot e^{i(k_x \cdot x + k_y \cdot y + k_z \cdot z)} = A \cdot e^{i(k_y \cdot y + k_z \cdot z)}$$

$k_x \cdot x \rightarrow 0$

Does not solve boundary condition!!!

Boundary conditions: The plane x=0:



Let's try something:

$$\psi(\vec{r}) = A \cdot e^{i(k_x \cdot x + k_y \cdot y + k_z \cdot z)}$$

$$-A \cdot e^{i(-k_x \cdot x + k_y \cdot y + k_z \cdot z)}$$

$$\psi(\vec{r}) = A \cdot \left(e^{ik_x \cdot x} - e^{-ik_x \cdot x} \right) \cdot e^{i(k_y \cdot y + k_z \cdot z)}$$

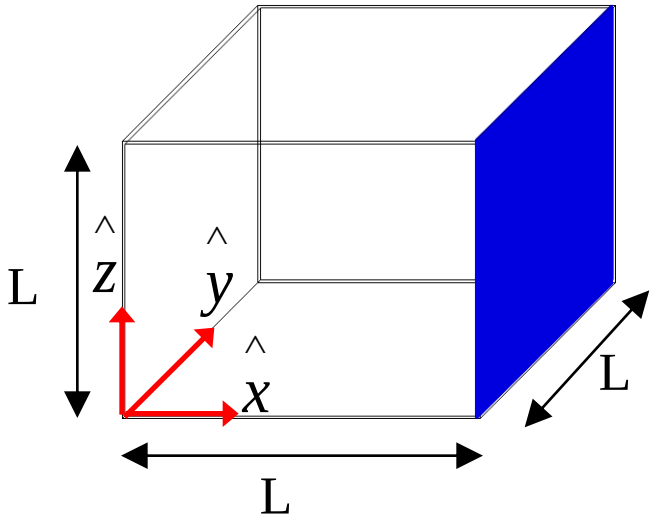
$$e^{a \cdot b} = e^a \cdot e^b$$

$$\psi(x=0, y, z) = A \cdot \left(e^{ik_x \cdot 0} - e^{-ik_x \cdot 0} \right) \cdot e^{i(k_y \cdot y + k_z \cdot z)}$$

$$= A \cdot \left(e^0 - e^0 \right) \cdot e^{i(k_y \cdot y + k_z \cdot z)} = 0$$

Does solve boundary condition!!!

Boundary conditions: The plane x=L:



$$\psi(\vec{r}) = A\cdot\left(e^{ik_x\cdot x} - e^{-ik_x\cdot x}\right)\cdot e^{i(k_y\cdot y + k_z\cdot z)}$$

$$= 2iA\cdot\sin(k_x x)\cdot e^{i(k_y\cdot y + k_z\cdot z)}$$

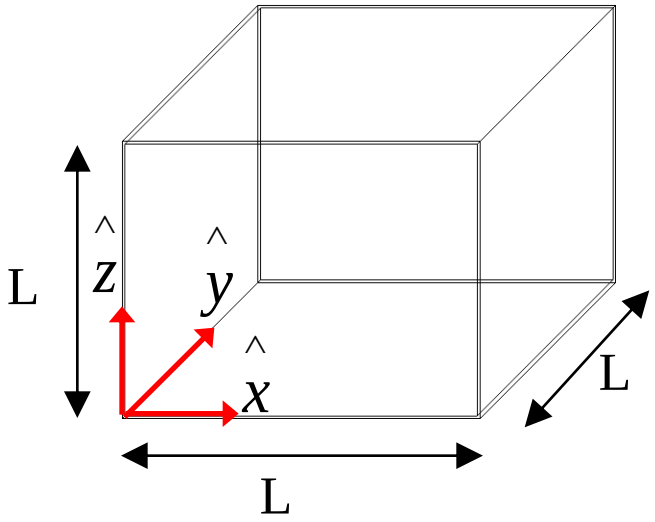
$$\sin(\theta) = \frac{1}{2i}\left(e^{i\theta} - e^{-i\theta}\right)$$

$$\psi(x = L, y, z) = 2iA\cdot\sin(k_x L)\cdot e^{i(k_y\cdot y + k_z\cdot z)} = 0?$$

If and only if:

$$k_n = n\pi / L$$

Boundary conditions:



We can do the same for y, z:

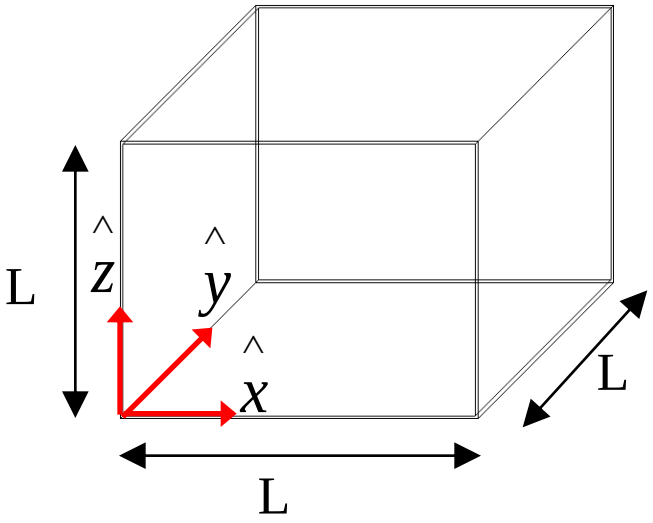
$$\psi(\vec{r}) = (2i)^3 A \cdot \sin(k_{n_x} x) \cdot \sin(k_{n_y} y) \cdot \sin(k_{n_z} z)$$

$$k_{n_x} = n_x \pi / L$$
$$k_{n_y} = n_y \pi / L$$
$$k_{n_z} = n_z \pi / L$$

$$E = \frac{\hbar^2 (k_{n_x}{}^2 + k_{n_y}{}^2 + k_{n_z}{}^2)}{2m} = \frac{\hbar^2 (\pi / L)^2}{2m} (n_x{}^2 + n_y{}^2 + n_z{}^2)$$

These are the allowed energy levels, or "quantum states"

Many electrons:

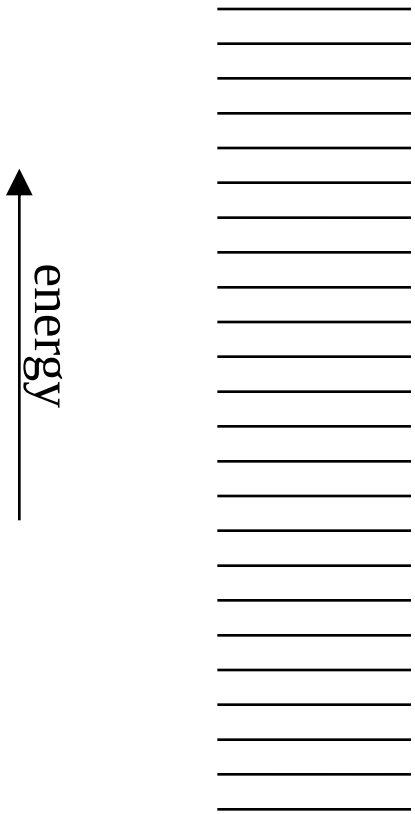


$$E = \frac{\hbar^2 (\pi / L)^2}{2m} (n_x^{\,2} + n_y^{\,2} + n_z^{\,2})$$

These are the allowed energy levels, or "quantum states"

Pauli exclusion principle: Each unique combination of n_x, n_y, n_z can only have two electrons (spin up, spin down).

Energy spectrum of free particles:



$n_x=2, n_y=1, n_z=1$

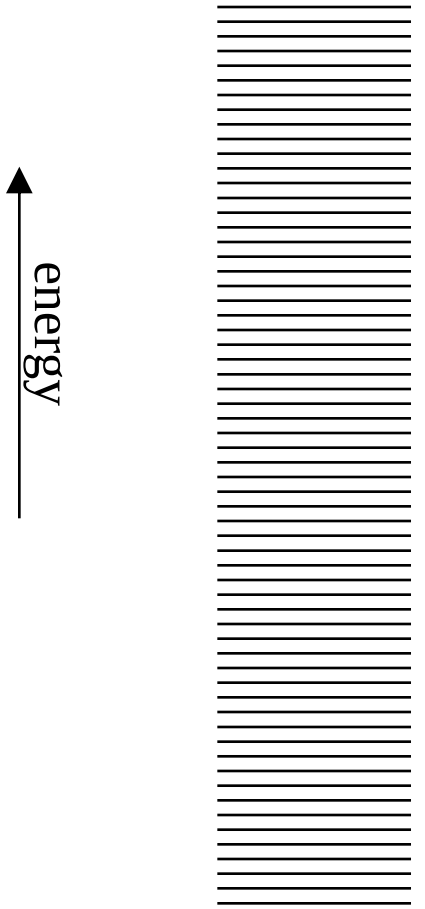
$n_x=1, n_y=1, n_z=1$

Etc.

$n_x=1, n_y=2, n_z=1$

$n_x=1, n_y=1, n_z=2$

Density of states:



If L is large, states are very close together.
Approximate as a continuum.

How many states?

$$N_E dE = ?$$

Number of states with energy between E and E + dE

$$\rho(E) dE = ?$$

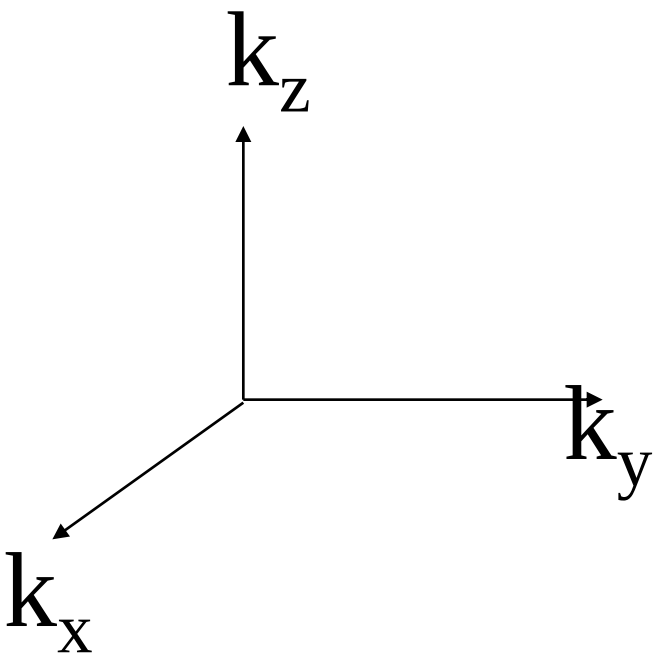
Number of states with energy between E and E + dE *per volume*.

Density of states:

Easier first to think of in k-space:

Density of states in k-space is uniform:

One state per $(\pi/L)^3$:



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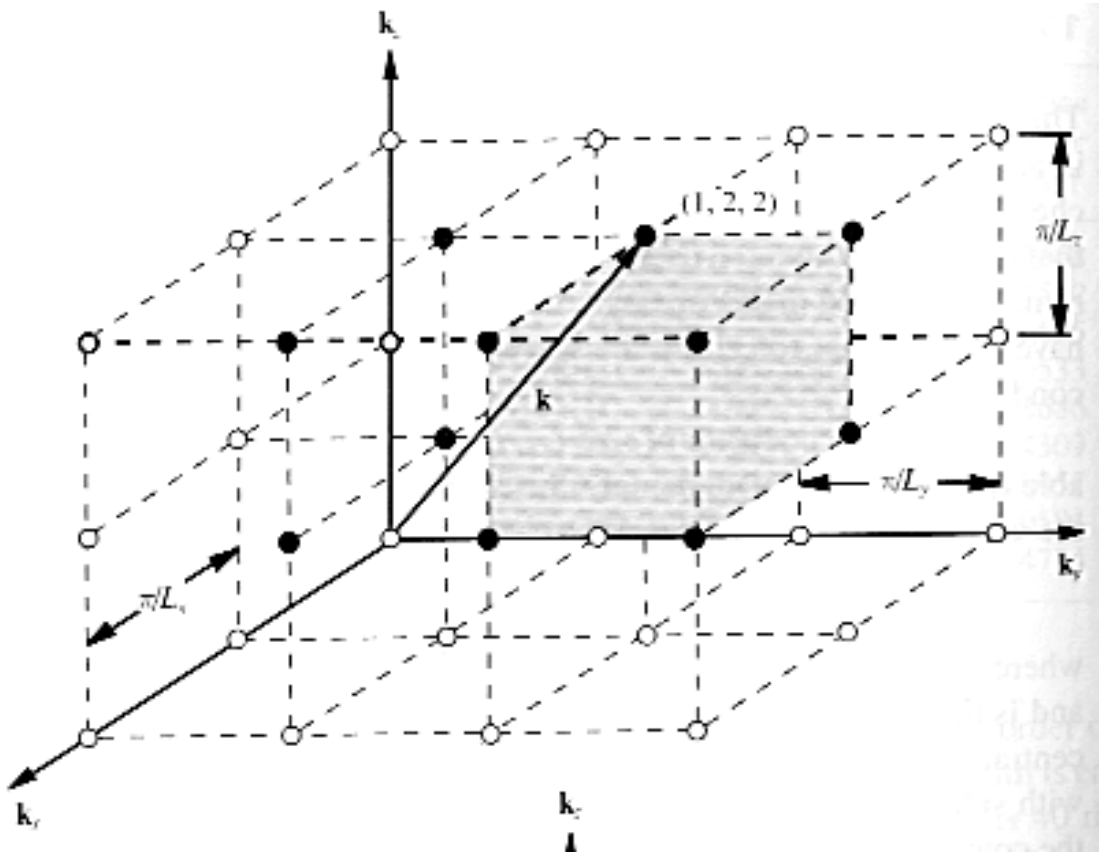
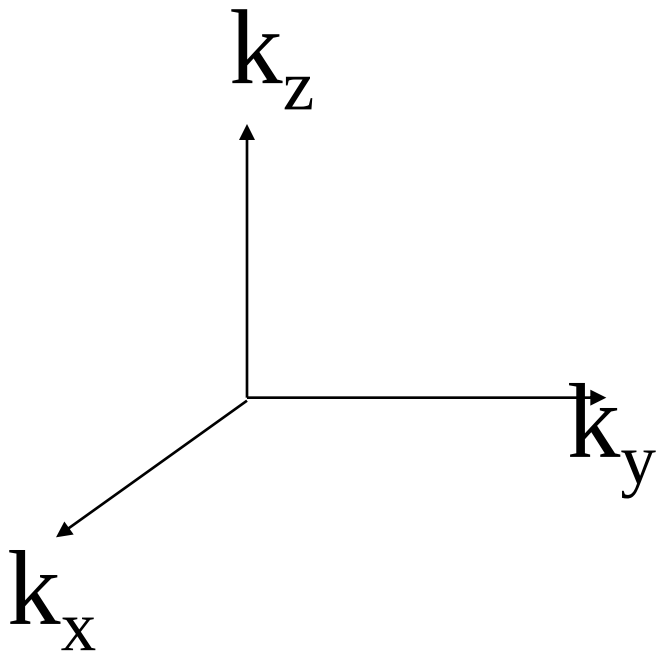
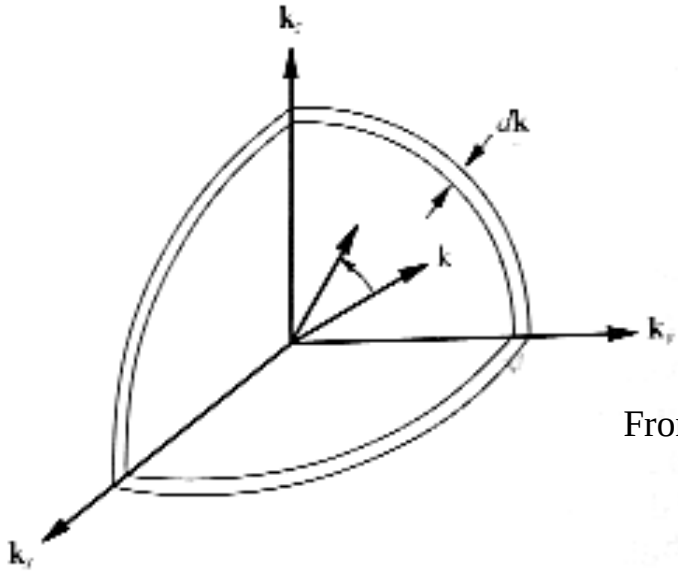


From Verdeyen

Density of states:
Number of states between k, k+dk:

$$N_k dk = ?$$





From Verdeyen

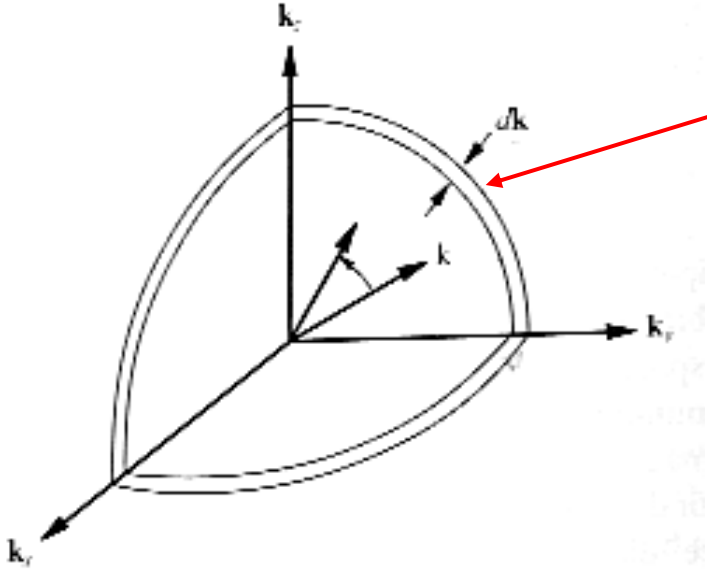
$$k \equiv \sqrt{k_x^2 + k_y^2 + k_z^2}$$

$$k_{n_x} = n_x \pi / L$$

$$k_{n_y} = n_y \pi / L$$

$$k_{n_z} = n_z \pi / L$$

$N_k dk = ?$



Volume of spherical shell
$=4\pi k^2 dk/8$
8 is for upper right quadrant

Number of states in volume=
Volume x States/volume

States/volume = $1 / (\pi/L)^3$:

$$N_k dk = \left(4\pi k^2 dk / 8\right) \cdot \left(\frac{1}{(\pi / L)^3} \right) \cdot 2 = L^3 \frac{k^2 dk}{\pi^2}$$

$$\rho_k dk \equiv \frac{N_k dk}{\text{volume}} = \frac{k^2 dk}{\pi^2}$$

HW you will do calculation for 2 dimensional world.

$\rho(E)dE = ?$

We use:

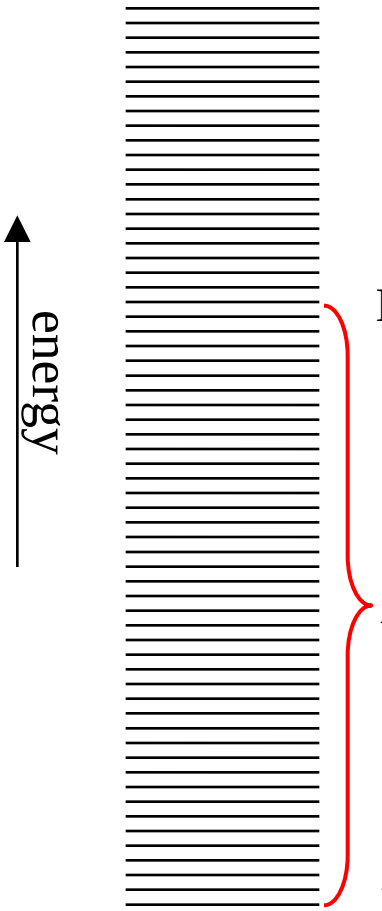
$$\rho_k dk = \rho(E)dE$$

$$\rho_k dk = \frac{k^2 dk}{\pi^2}$$

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \sqrt{\frac{2mE}{\hbar^2}} \Rightarrow dk = \sqrt{\frac{2m}{\hbar^2}} \frac{dE}{2\sqrt{E}}$$

$$\rho(E)dE = \frac{2^{3/2} m^{3/2}}{2\pi^2 \hbar^3} \cdot E^{1/2} dE$$

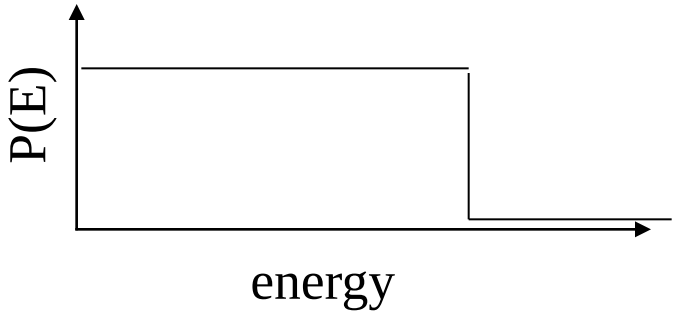
Fermi gas:



At zero temperature, as we add electrons to the box, we gradually fill up all the states. (DISCUSS PAULI EXCLUSION PRINCIPLE -IMPORTANT!)

When we are done filling the box, the energy of the last electron is called the "Fermi energy."

"Gas" means we neglect electron-electron interactions.



Fermi energy:

$$\#\ \text{electrons} = \int_0^{E_f} N_E \, dE = \int_0^{E_f} L^3 \frac{2^{3/2} m^{3/2}}{2\pi^2 \hbar^3} \cdot E^{1/2} dE$$

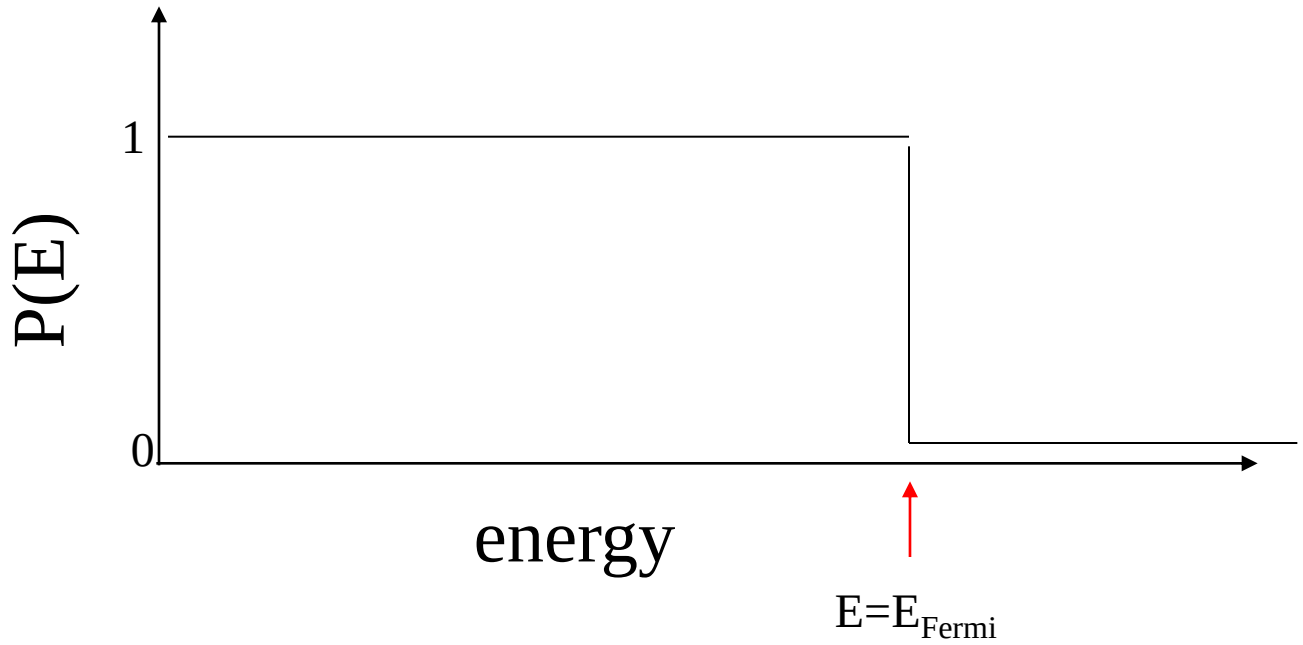
$$\#\ \text{electrons} = L^3 \frac{2^{3/2} m^{3/2}}{2\pi^2 \hbar^3} \cdot \frac{2}{3} E_f^{3/2}$$

$$\Rightarrow E_f = \frac{\hbar^2 3^{2/3} \pi^{4/3}}{2m} \left(\frac{\#\ \text{electrons}}{L^3} \right)^{2/3}$$

In a typical metal, L ~ 0.1 nm.

E_f ~ 10 eV

Occupation probability:



P(E) = probability of occupying a state with energy E

What about finite temperature?

Boltzmann:

Recall Boltzmann factor P(ε):

"The probability for a physical system to be in a state with energy ε is proportional to $e^{-\varepsilon/k_B T}$."

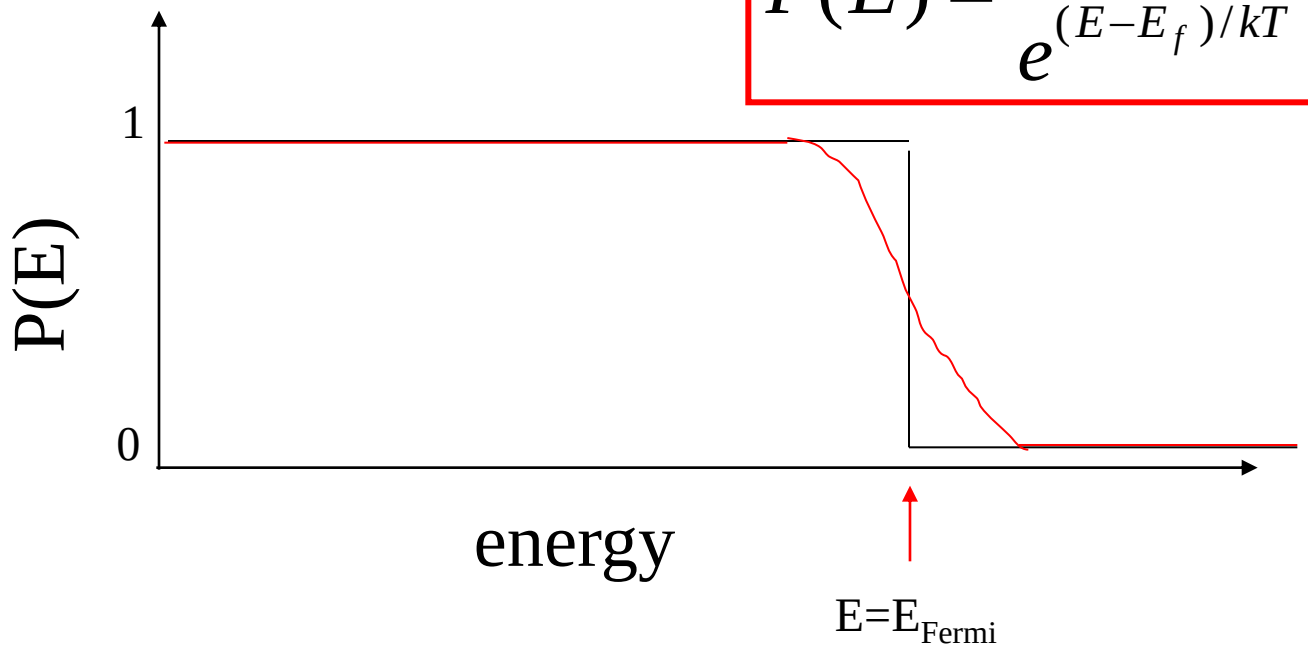
This is actually not quite true. It is classical. A quantum calculation shows for electrons:

$$P(E) = \frac{1}{e^{(E-E_f)/kT} + 1}$$

Called Fermi-Dirac distribution function. Boltzman is high-energy limit (discuss!)

Fermi-Dirac:

$$P(E) = \frac{1}{e^{(E-E_f)/kT} + 1}$$

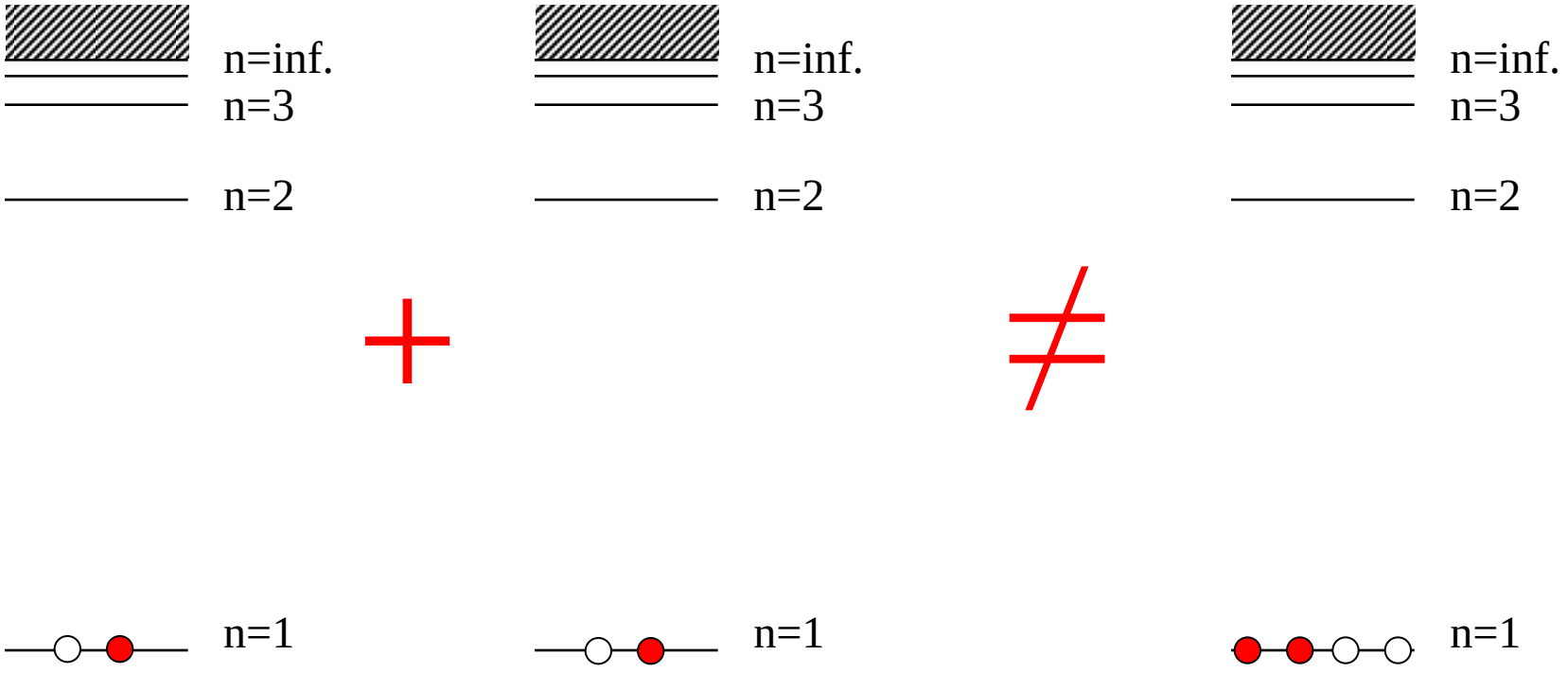


P=1/2 at E_f for all temperatures.

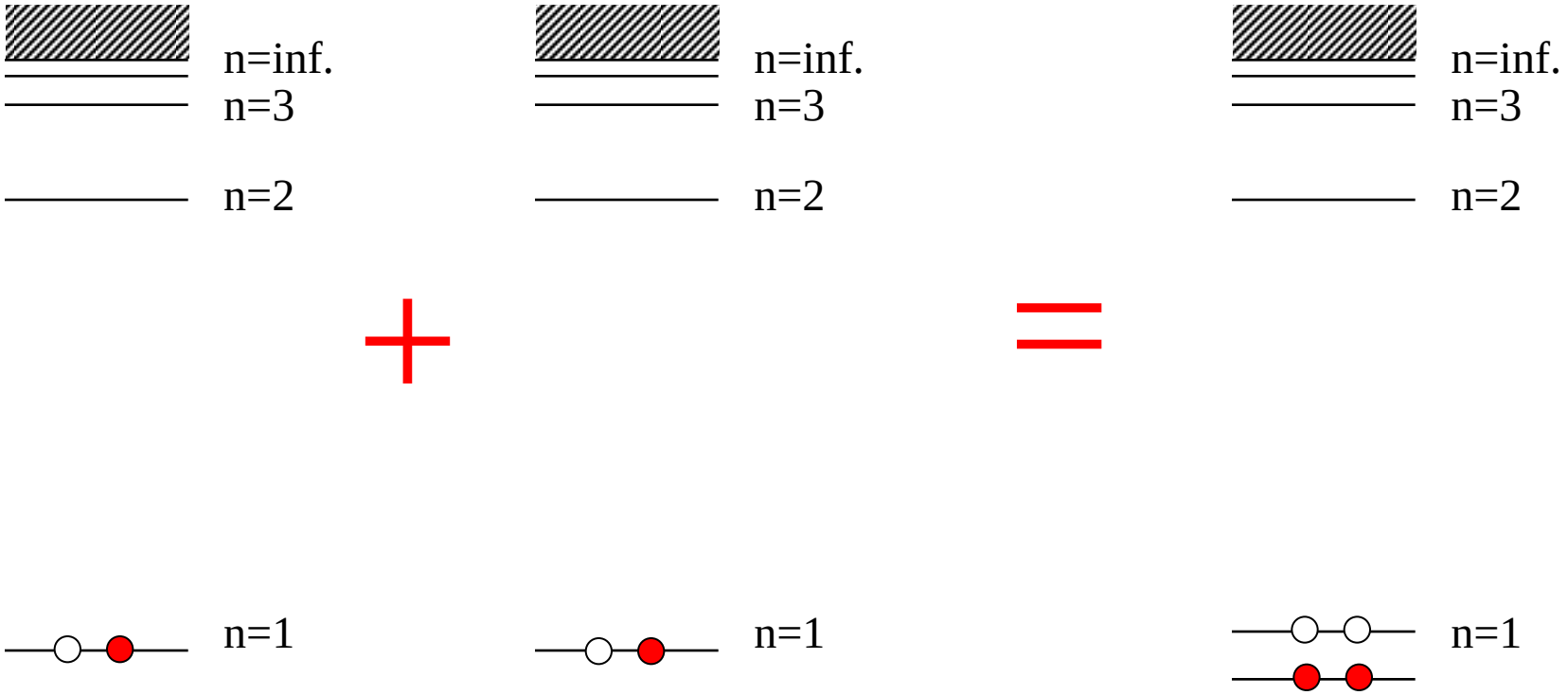
Forget about free electrons for now.

Back to the hydrogen atom.

Chemical bonds:

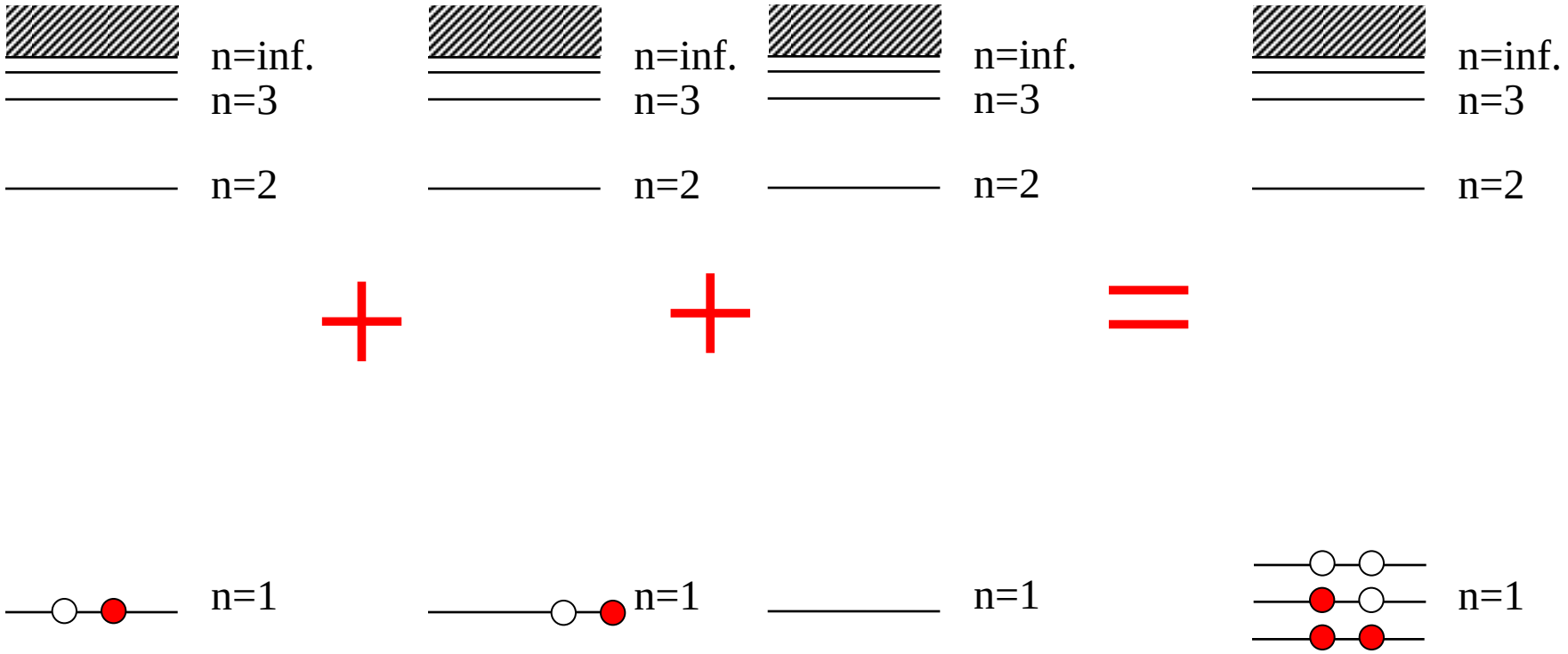


Chemical bonds:



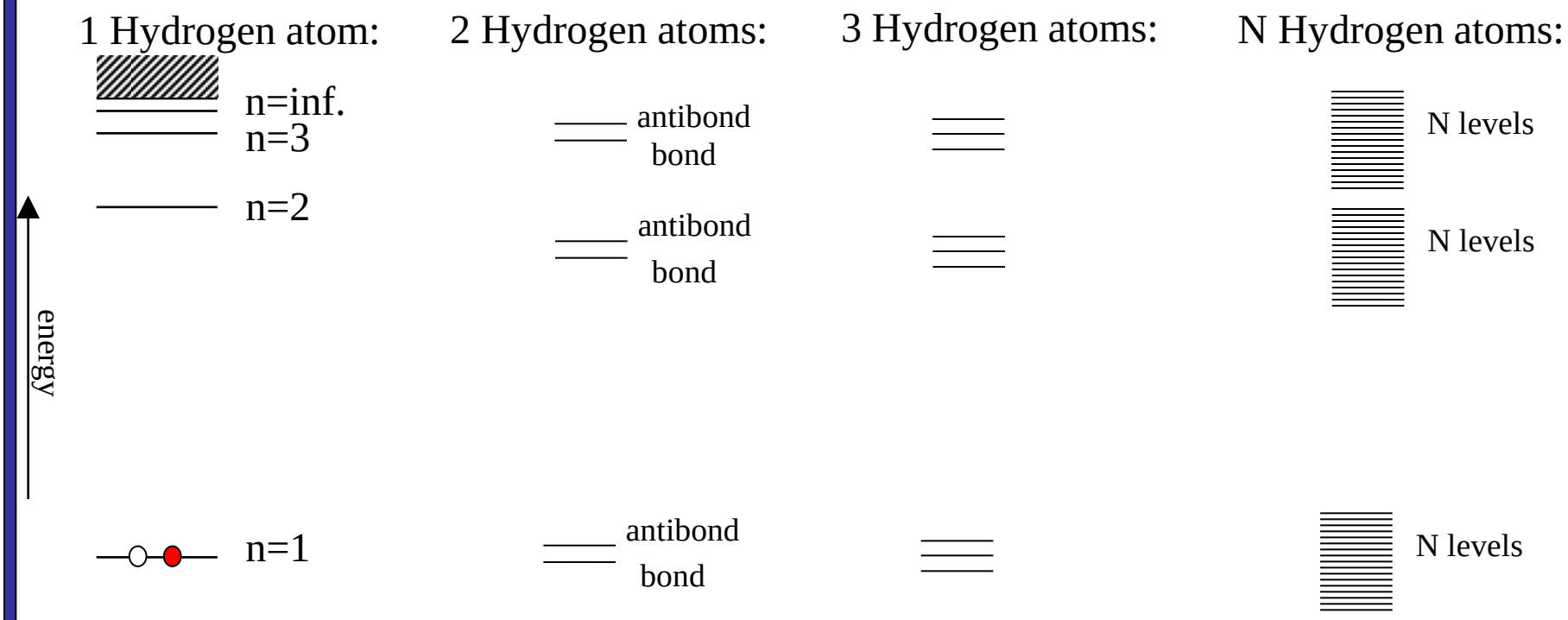
"Bonding and anti-bonding"

Chemical bonds:



"N atoms give N levels"

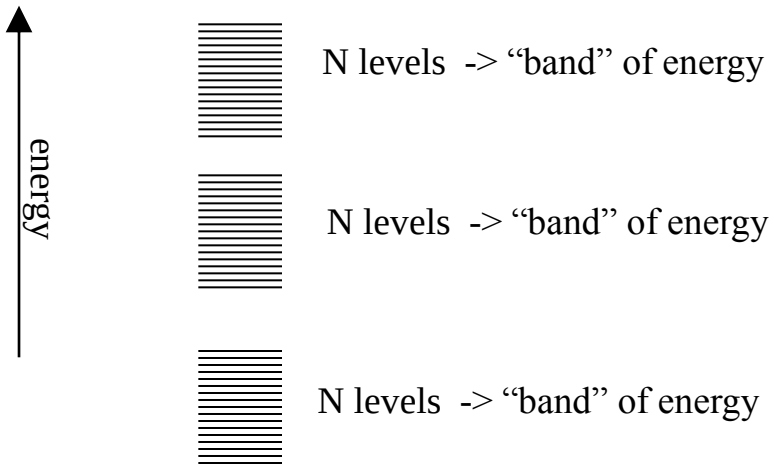
Band theory of solids:



Band theory of solids:

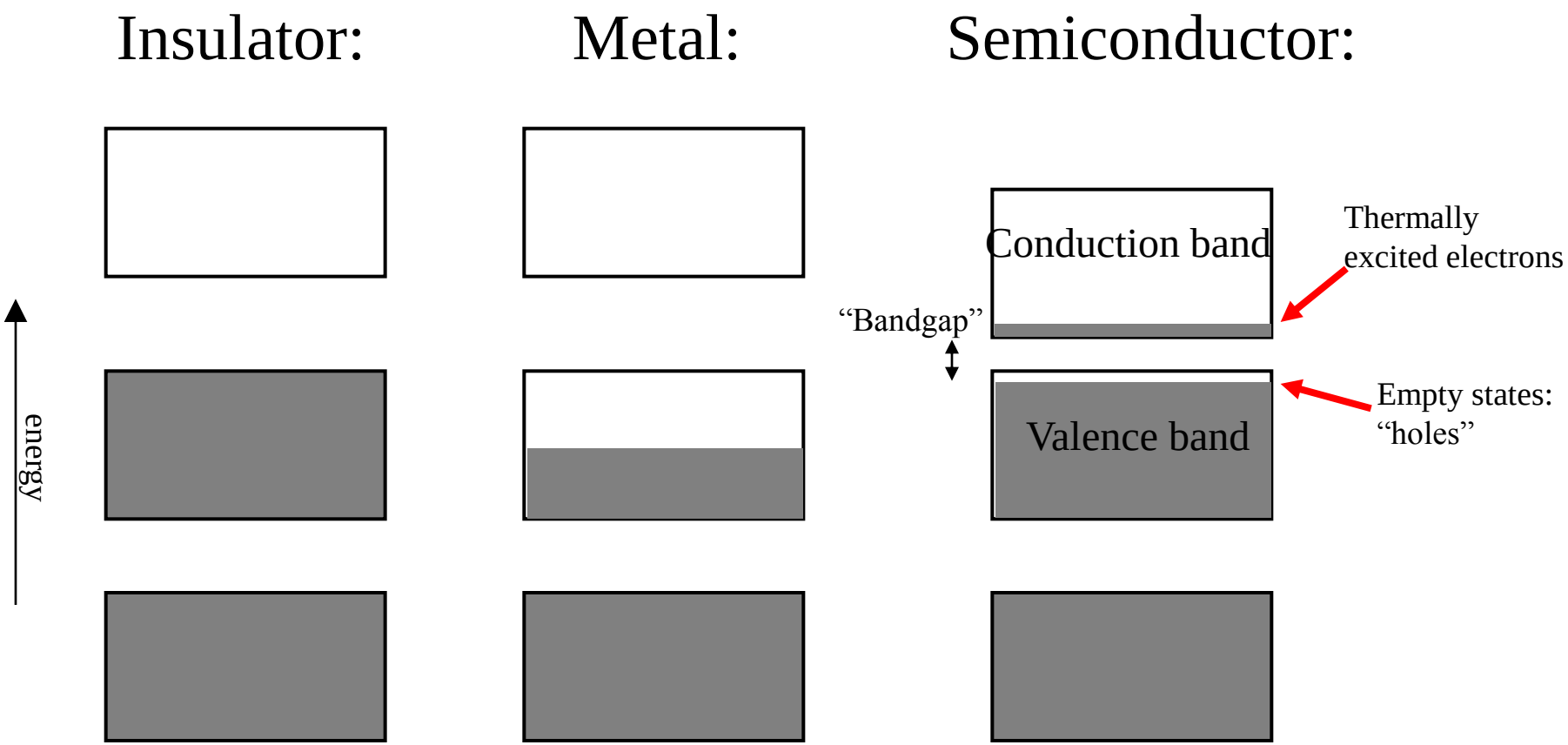
N Hydrogen atoms:

N -> infinity



Band theory of solids:

Filled bands do not conduct electricity!

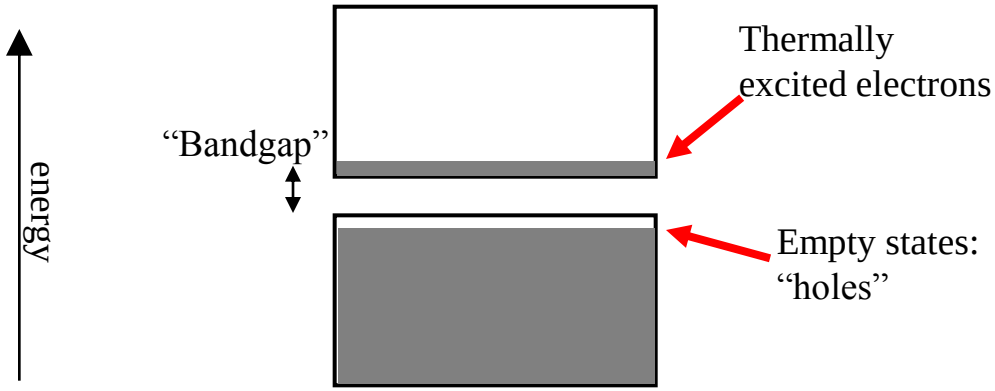


We usually don't care about lower bands.

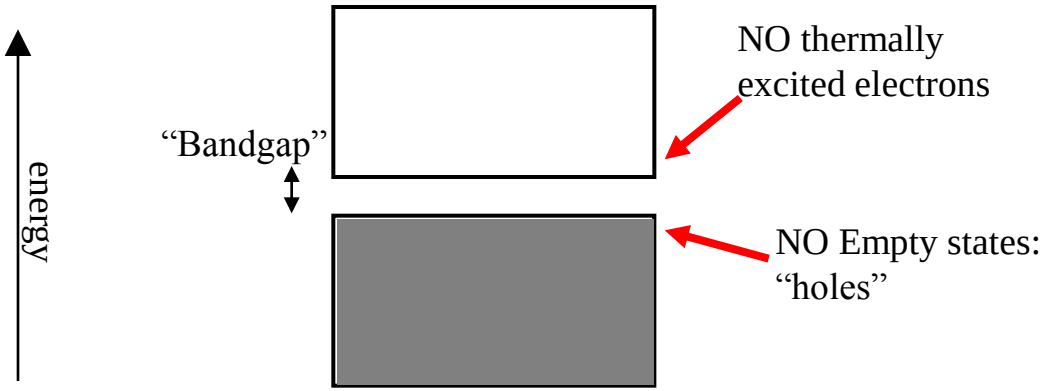
LASER will be formed by electrons going from conduction to valence band...

Semiconductors:

Finite temperature:



Zero temperature:



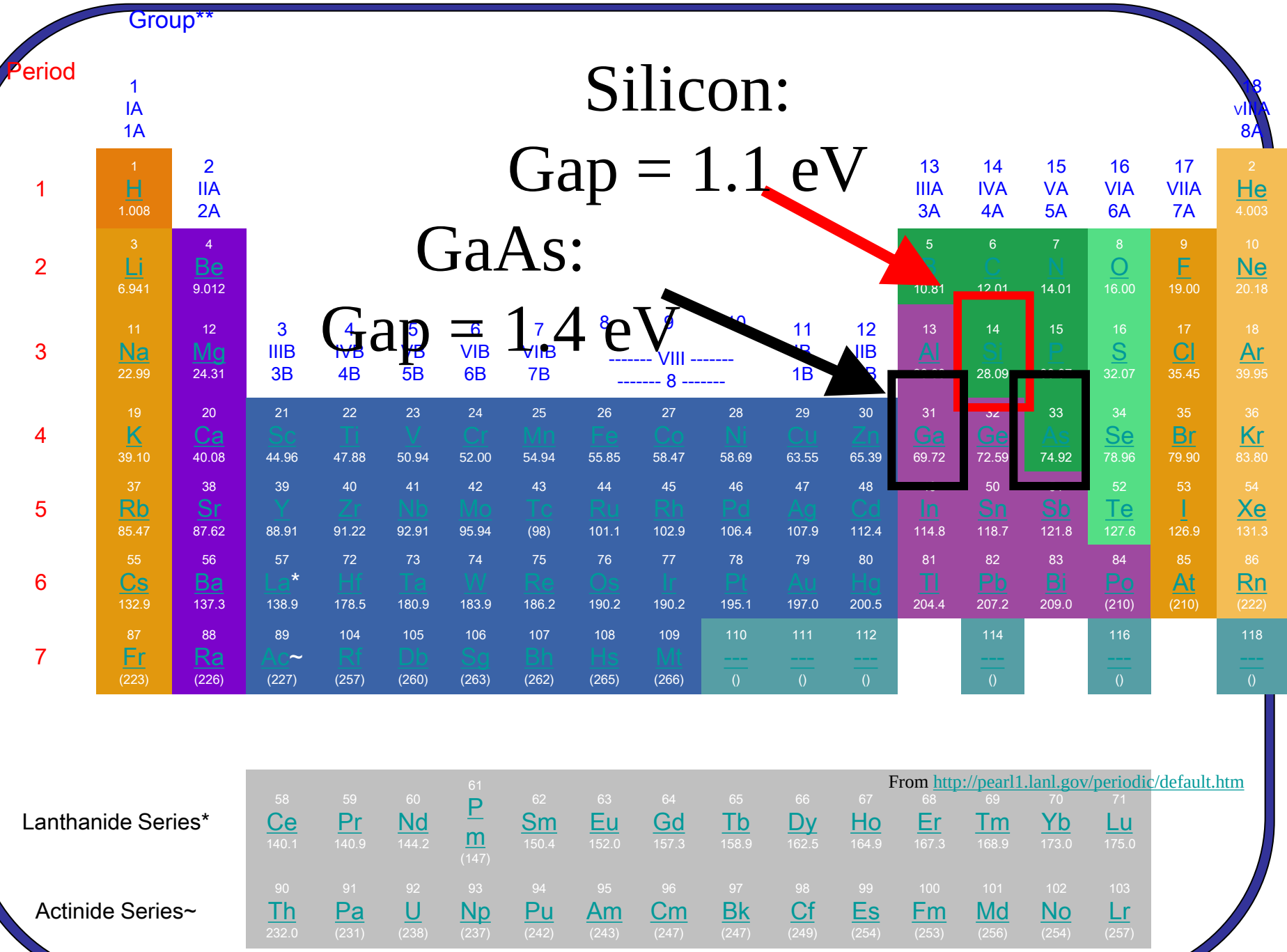
NO CONDUCTION
AT ZERO TEMPERATURE.
Only at finite temperature.
Hence the name, "semi"conductors.

Silicon:

Gap = 1.1 eV

GaAs:

Gap = 1.4 eV



From http://pearl1.lanl.gov/periodic/default.htm

Lanthanide Series*

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.1	140.9	144.2	(147)	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0

Actinide Series~

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.0	(231)	(238)	(237)	(242)	(243)	(247)	(247)	(249)	(254)	(253)	(256)	(254)	(257)

Remember free electrons now.

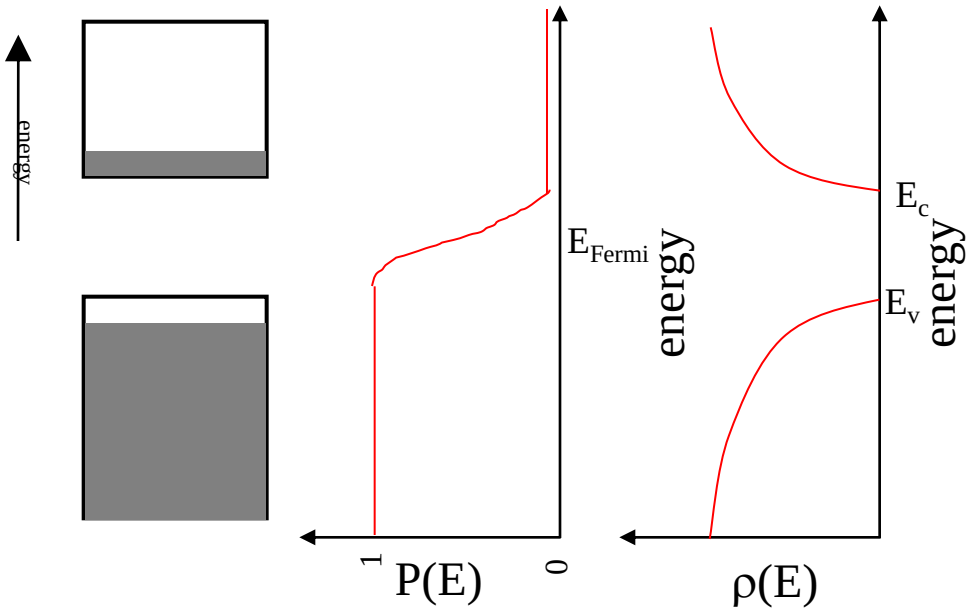
Even though electrons in a semiconductor live in "bands of energy", we can treat them like free electrons, except for the gap.

The price we pay for treating a complicated system like free electrons:

1) E_{Fermi} is in the middle of the gap.
3) Density of states origin is referred to edge of band.
2) Electrons, holes have different "effective" mass values.

We now discuss these three points:

How many electrons in conduction band?



$$n_i = \int_{E_c}^{\infty} P(E)\rho(E)dE$$

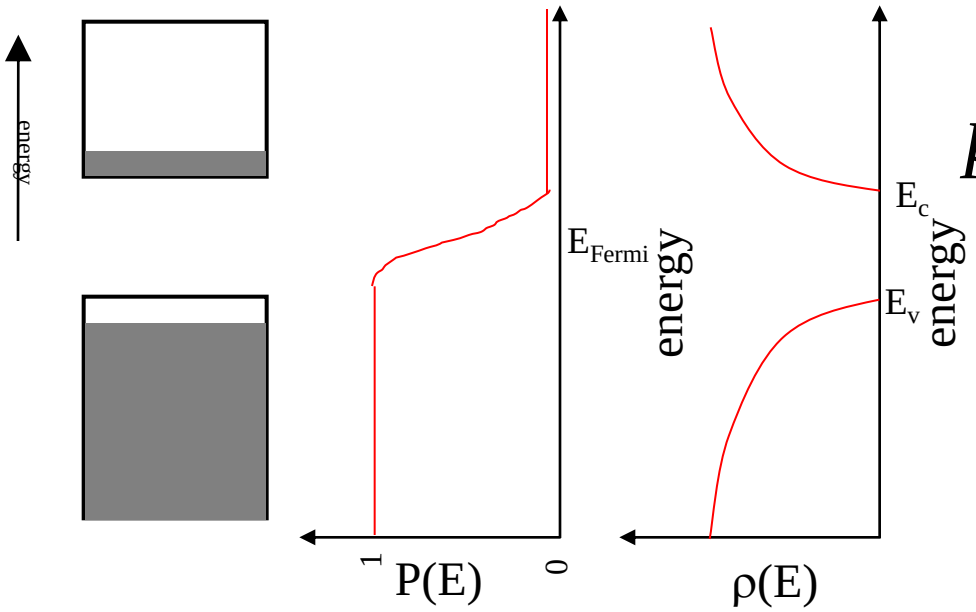
$$\rho_{electrons}(E)dE = \frac{2^{1/2}m^{3/2}}{\pi^2\hbar^{3/2}} \cdot (E - E_c)^{1/2} dE$$

$$P(E) = \frac{1}{e^{(E-E_f)/kT} + 1}$$

(Discuss high energy appr. on board.)

$$n_i = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_f - E_c)/kT}$$

How many holes in valence band?



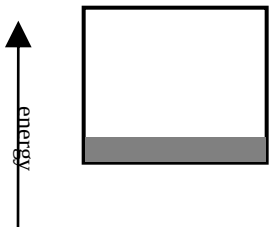
$$p_i = \int_{E_c}^{-\infty} [1 - P(E)]\rho(E)dE$$

$$\rho_{electrons}(E)dE = \frac{2^{1/2} m^{3/2}}{\pi^2 \hbar^{3/2}} \cdot (E - E_c)^{1/2} dE$$

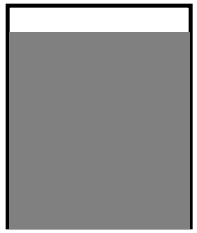
$$P(E) = \frac{1}{e^{(E-E_f)/kT} + 1}$$

$$p_i = 2\left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_v - E_f)/kT}$$

Holes and electrons



$$p_i = 2\left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_v - E_f)/kT} \equiv N_v e^{(E_v - E_f)/kT}$$



$$n_i = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_f - E_c)/kT} \equiv N_c e^{(E_f - E_c)/kT}$$

But $E_f - E_c = (1/2)\, E_{gap}$ and $E_v - E_f = (1/2)\, E_{gap}$.
With some algebra,

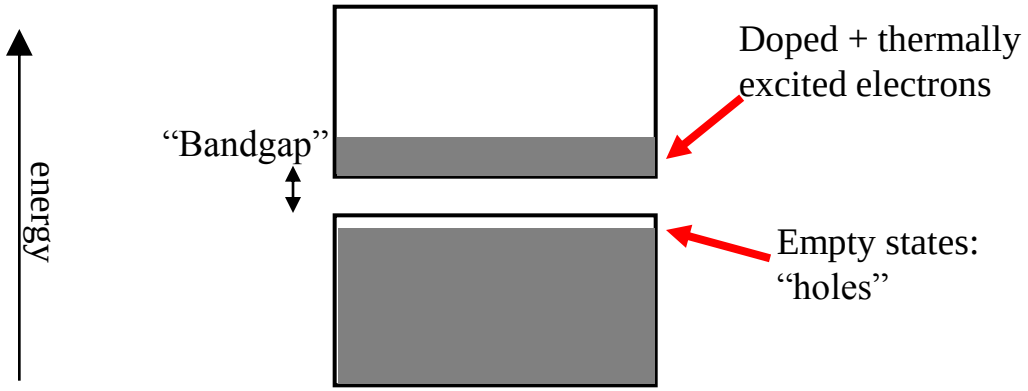
$$n_i = p_i = 2\left(\frac{kT}{2\pi\hbar^2}\right)^{3/2} \left(m_e^* m_h^*\right)^{3/4} e^{-E_g/2kT}$$

$$n_i \sim 10^6 cm^{-3} (GaAs)$$

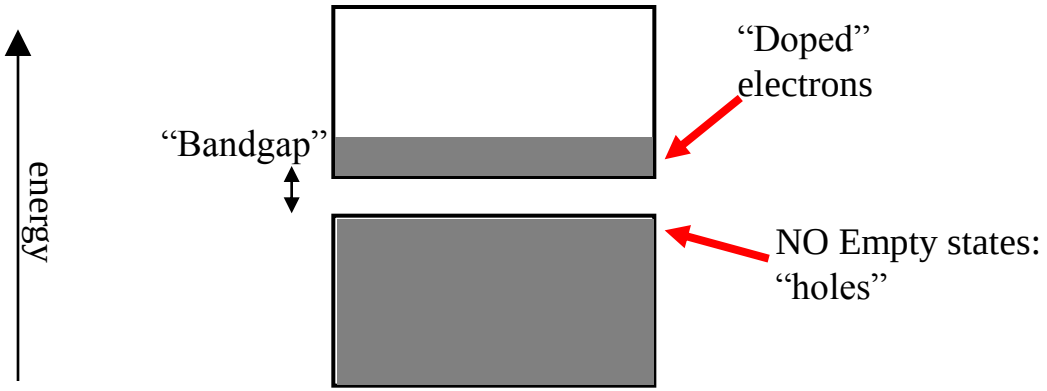
$$n_i \sim 10^{10} cm^{-3} (Si)$$

n-type doped semiconductors:

Finite temperature:

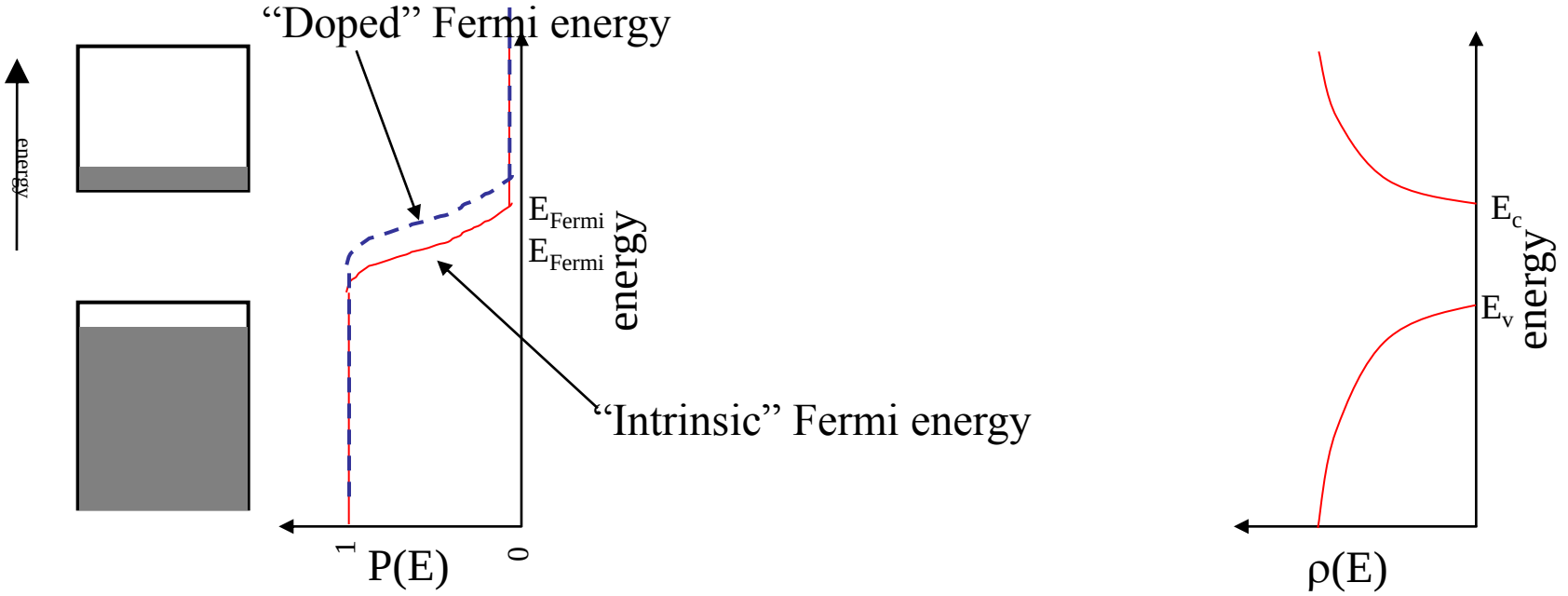


"Low" temperature:



CONDUCTION
AT LOW TEMPERATURE!

How many electrons in conduction band?



"Law of mass action"

$$n \cdot p = n_i^{\,2} = N_c N_v e^{-E_g/kT}$$

$$p - n = N_{acceptors} - N_{donors}$$

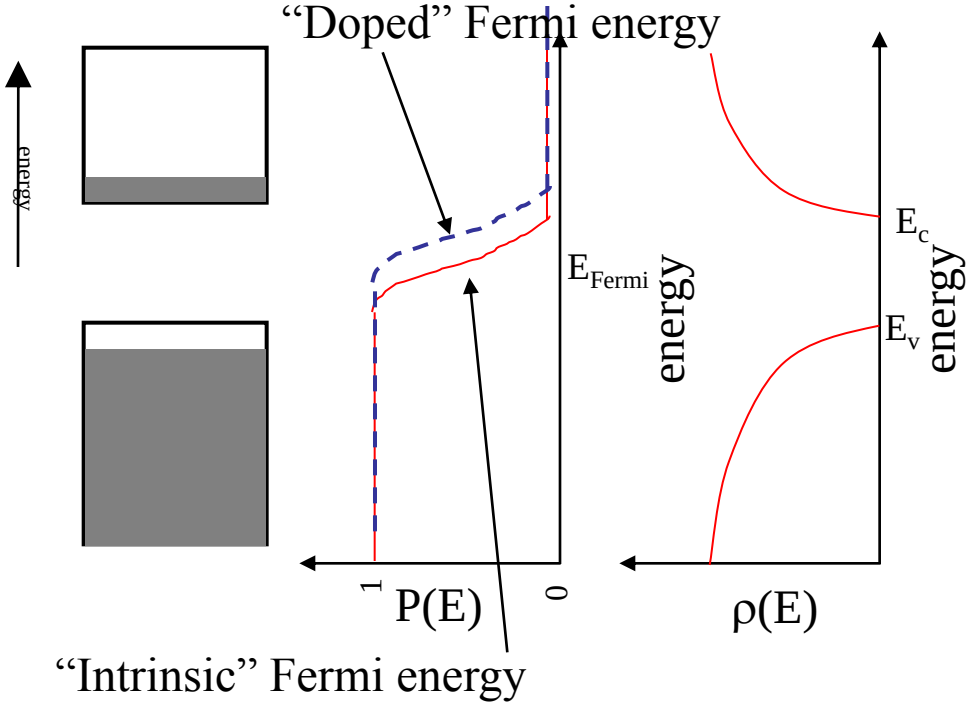
$$p - n = N_d$$

$$n_i^{\,2}/n - n = N_d$$

$$n = \frac{\sqrt{N_d^{\,2} + 4n_i^{\,2}} + N_d}{2} \approx N_d$$

How many electrons in conduction band?

A method to calculate if E_{fermi} is known:



$$n = \int_{E_c}^{\infty} P(E)\rho(E)dE$$

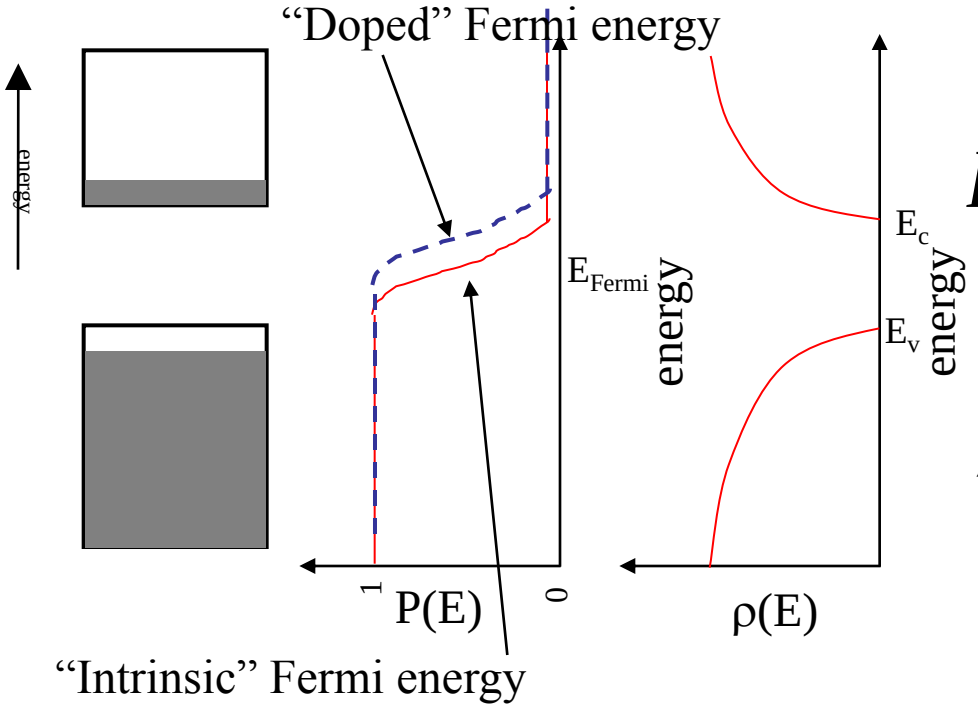
$$\rho_{electrons}(E)dE = \frac{2^{1/2}m^{3/2}}{\pi^2\hbar^{3/2}} \cdot (E - E_c)^{1/2}dE$$

$$P(E) = \frac{1}{e^{(E-E_f)/kT} + 1}$$

$$n = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_f - E_c)/kT}$$

How many holes in valence band?

A method to calculate if E_{fermi} is known:



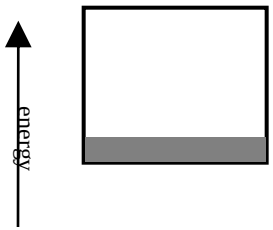
$$p = \int_{E_c}^{-\infty} [1 - P(E)]\rho(E)dE$$

$$\rho_{electrons}(E)dE = \frac{2^{1/2} m^{3/2}}{\pi^2 \hbar^{3/2}} \cdot (E - E_c)^{1/2} dE$$

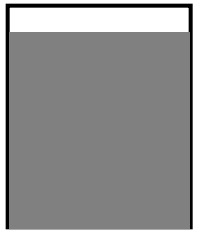
$$P(E) = \frac{1}{e^{(E-E_f)/kT} + 1}$$

$$p = 2\left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_v - E_f)/kT}$$

Holes and electrons when doped n-type



$$p = 2\left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_v - E_f)/kT}$$



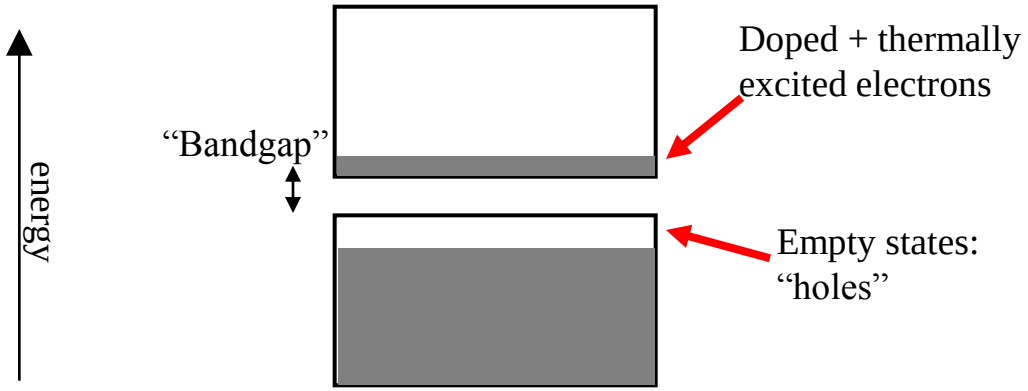
$$n = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_f - E_c)/kT}$$

But $E_f - E_c \neq (1/2)\, E_{gap}$ and $E_v - E_f \neq (1/2)\, E_{gap}$!

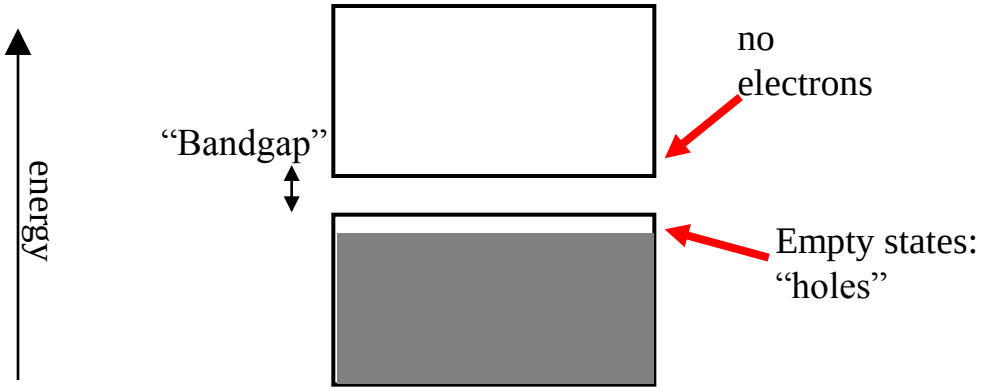
$$n > p$$

p-type doped semiconductors:

Finite temperature:

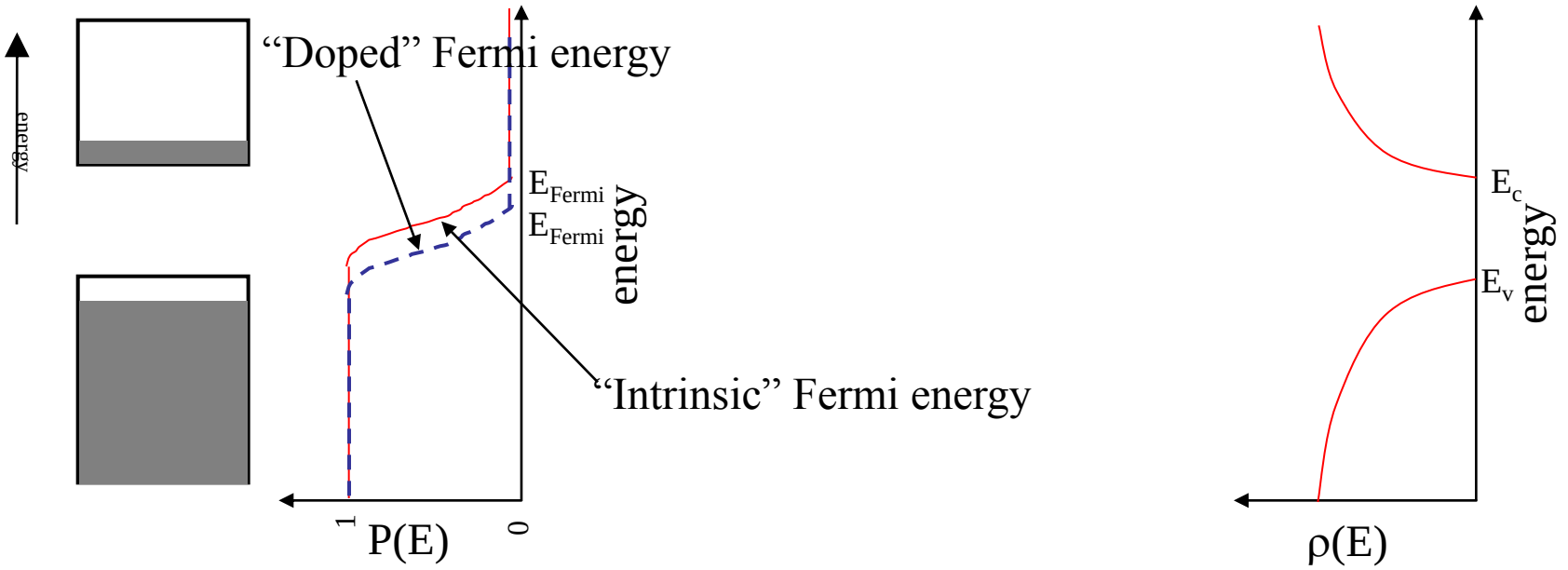


"Low" temperature:



CONDUCTION
AT LOW TEMPERATURE!

How many holes in valence band?



$$n \cdot p = n_i^2$$

$$p - n = N_{acceptors} - N_{donors}$$

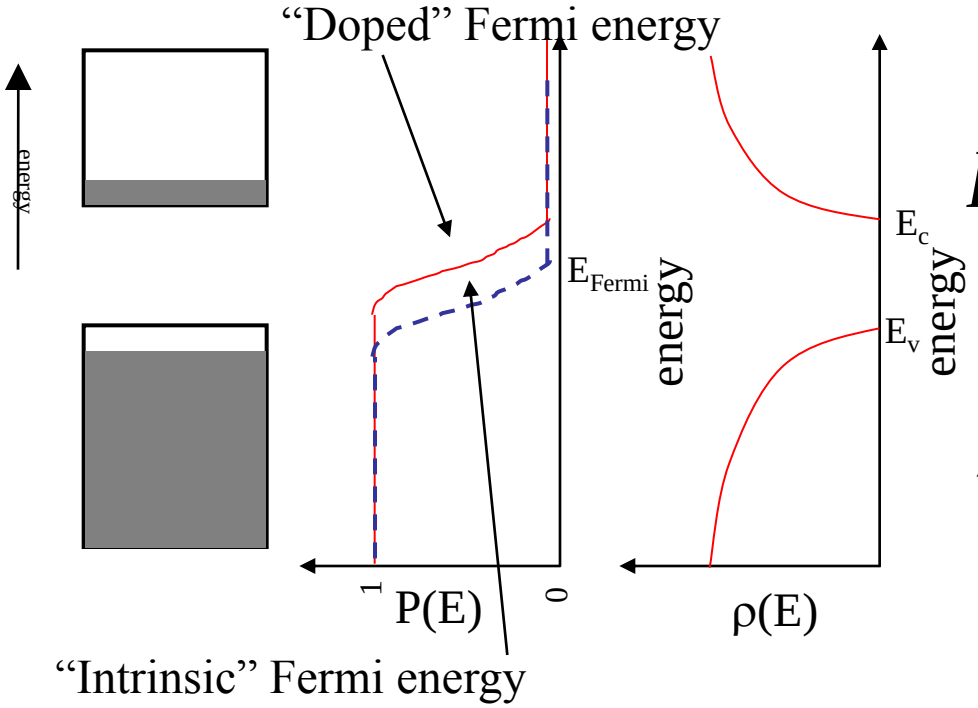
$$p - n = N_a$$

$$p - n_i^2 / p = N_a$$

$$p = \frac{\sqrt{N_a^2 + 4n_i^2} + N_a}{2} \approx N_a$$

How many holes in valence band?

A method to calculate if E_{fermi} is known:



$$p = \int_{E_c}^{-\infty} [1 - P(E)]\rho(E)dE$$

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How many electrons in conduction band?

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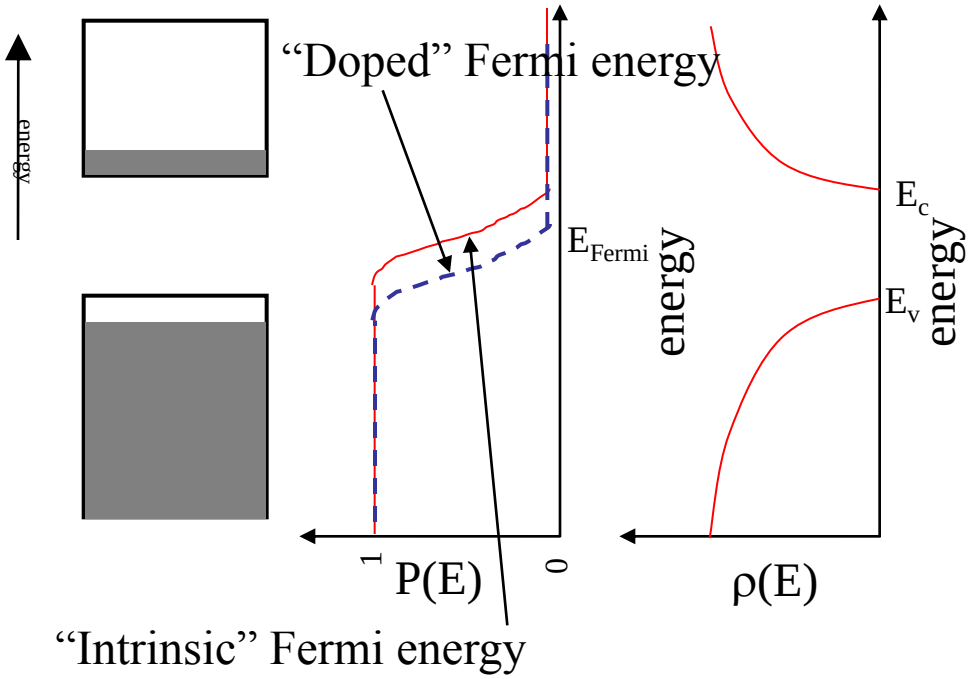

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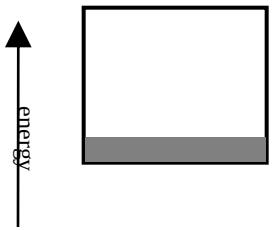
$$\rho_{electrons}(E)dE = \frac{2^{1/2}m^{3/2}}{\pi^2\hbar^{3/2}} \cdot (E - E_c)^{1/2} dE$$

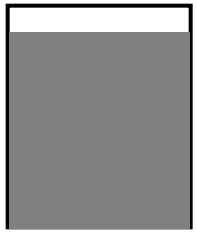
$$P(E) = \frac{1}{e^{(E-E_f)/kT} + 1}$$

$$n = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_f - E_c)/kT}$$

Holes and electrons when doped



$$p = 2\left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_v - E_f)/kT}$$



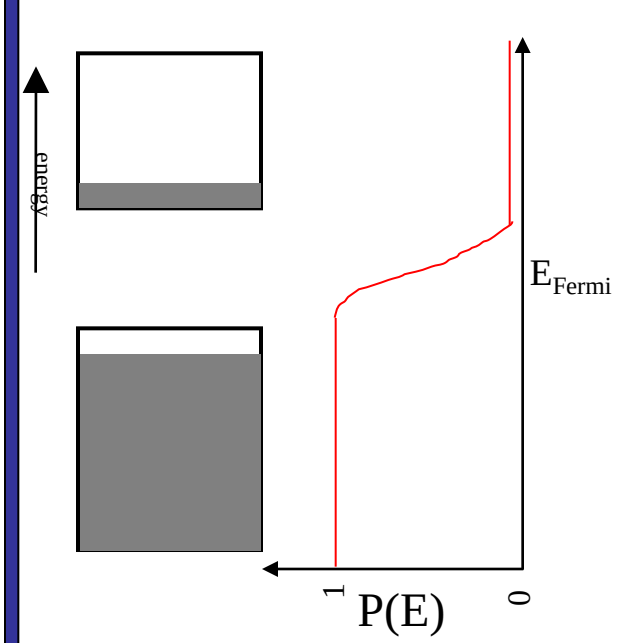
$$n = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_f - E_c)/kT}$$

But $E_f - E_c \neq (1/2)\, E_{gap}$ and $E_v - E_f \neq (1/2)\, E_{gap}$!

$$n < p$$

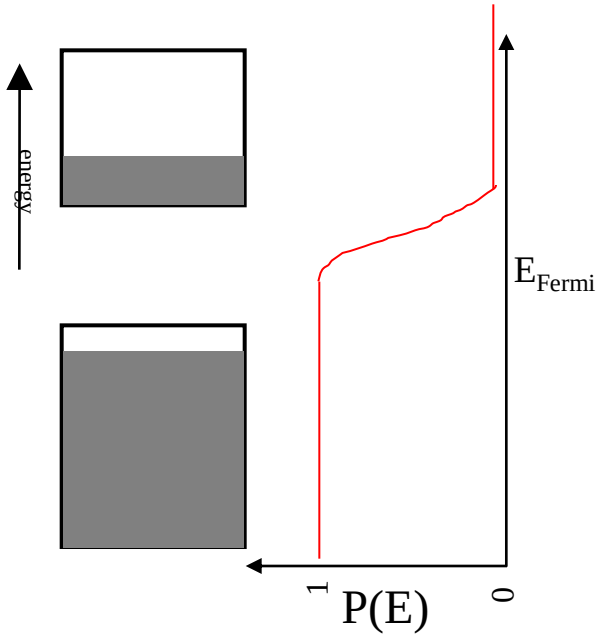
In conclusion:

Intrinsic:



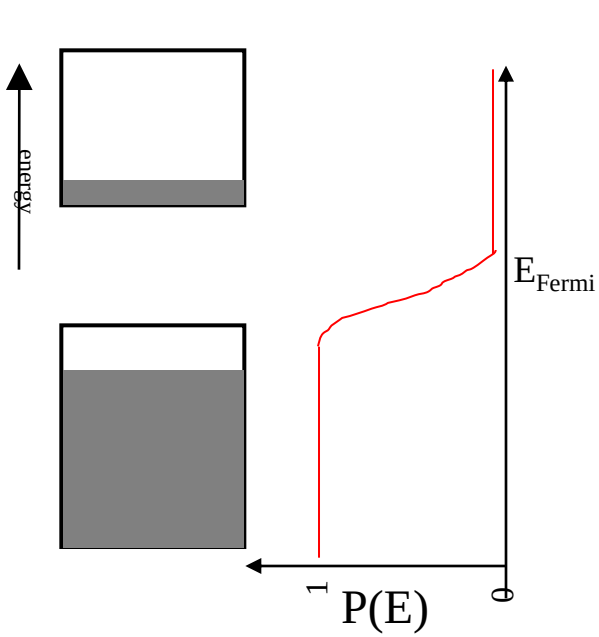
$n = p$

n-type:



$n > p$

p-type:



$n < p$

What we've done:

- Free electron density of states
- Fermi-Dirac distrubution function
- Band theory of solids (metal, insulator, semiconductor)
- Effective mass, density of states in semiconductors
- Electron, hole carrier concentrations in semiconductors