

# Lecture 12: Free electrons

- Quantum mechanics
- Free electrons in a box
- Fermi gas
- Fermi-Dirac distribution function
- Covers Verdeyen ch. 11
- Please ask questions!

# Free electron theory of solids

- Each atom in the solid “gives up” one electron
- Each electron is free to move where-ever it wants, with no scattering
- Completely the opposite of atom lasers, where each electron is bound to each atom
- Amazingly, this simple idea makes predictions that are true!
- Not for semiconductors, but metals
- Still need to understand this for semiconductors

Electrons are waves, too.

# Quantum mechanics of free particles:

$$|\Psi(\vec{r}, t)|^2$$

is probability of finding an electron at point  $r$  at time  $t$ .

$\Psi$  is complex, and both real and imaginary parts are physical.

For a free particle:

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

$\omega = E / \hbar$

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

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) &= i\hbar \frac{\partial}{\partial t} A \cdot e^{i(kx - \omega t)} = i\hbar(-i\omega) A \cdot e^{i(kx - \omega t)} \\ &= E \cdot A \cdot e^{i(kx - \omega t)} = E \cdot \Psi(x, t) \end{aligned}$$

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

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

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:

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

# 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

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

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

Call this  $\psi(\vec{r})$

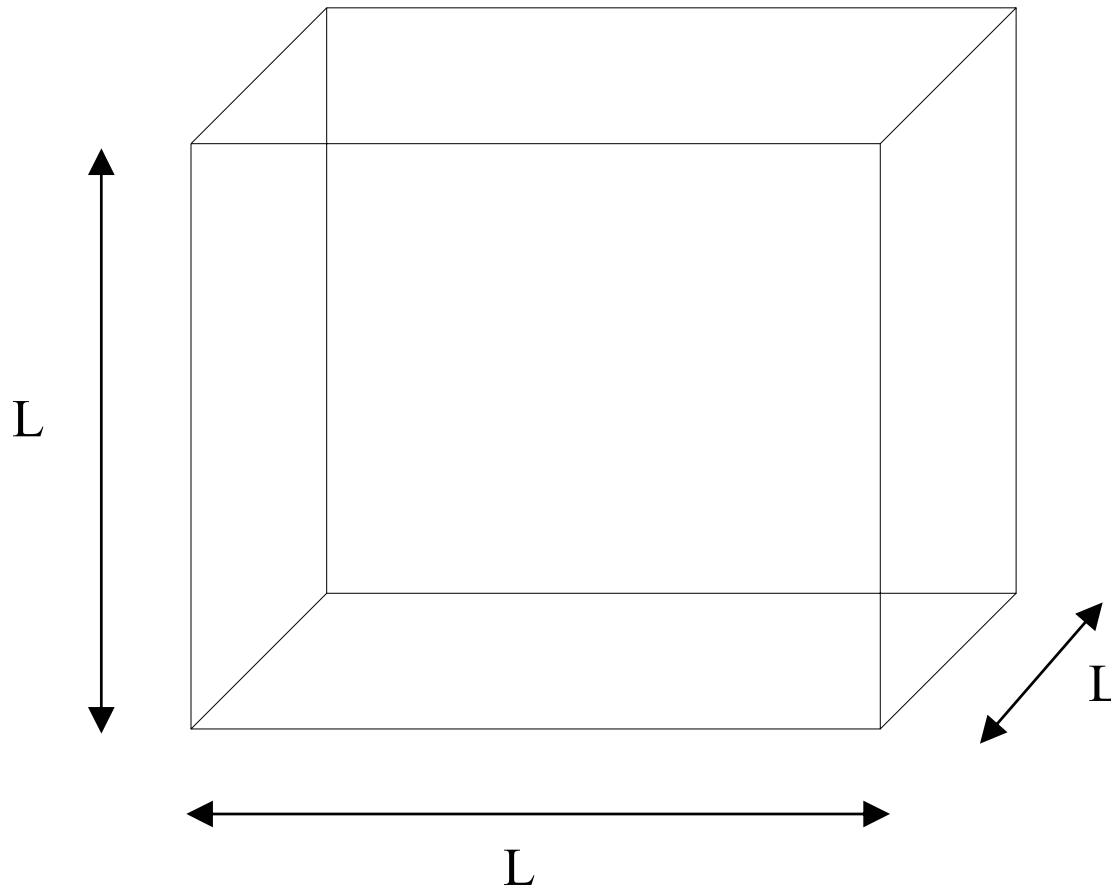
$$\Rightarrow \Psi(\vec{r}, t) = \psi(\vec{r}) \cdot e^{-i\omega t}$$

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

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

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

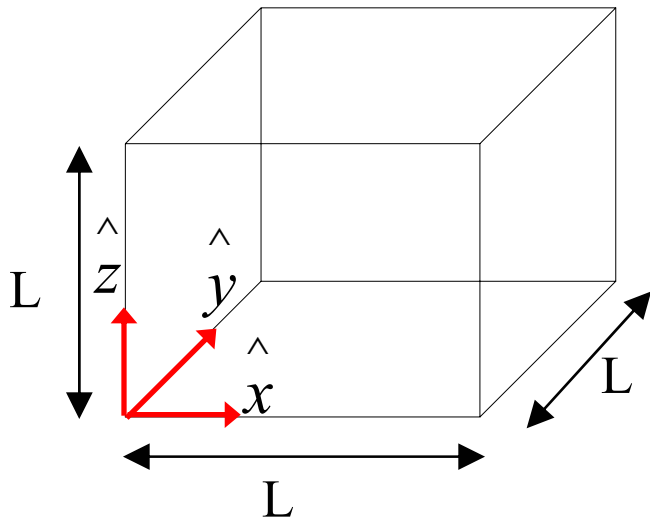
# Confined particles: A box



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

Similar to electric field inside the box.

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



Everywhere outside the box

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

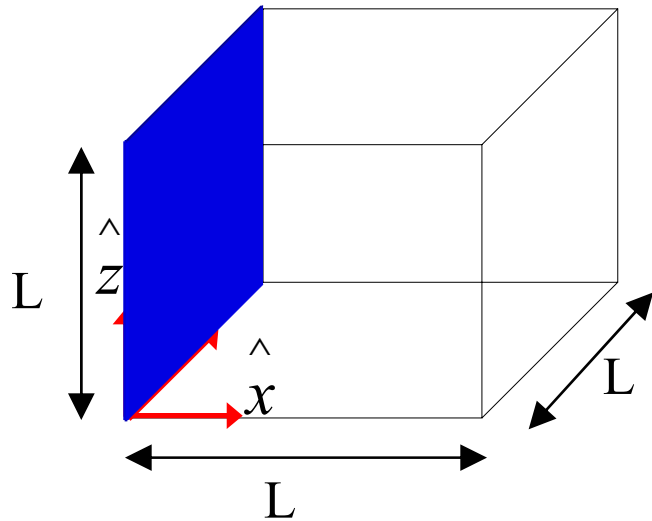
In particular,

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

on the boundaries.

As before, we will consider all six surfaces:

# Boundary conditions:



The plane  $x=0$ :

Try:

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

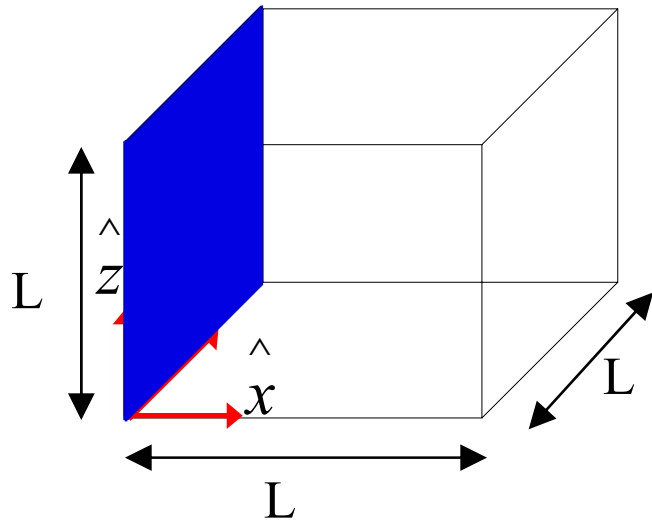
$$\psi(x=0, y, z) = A \cdot e^{i(k_x \cdot \cancel{x} + k_y \cdot y + k_z \cdot z)} = A \cdot e^{i(k_y \cdot y + k_z \cdot z)}$$

Does not solve boundary condition!!!

# Boundary conditions: The plane $x=0$ :

Let's try something:

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



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

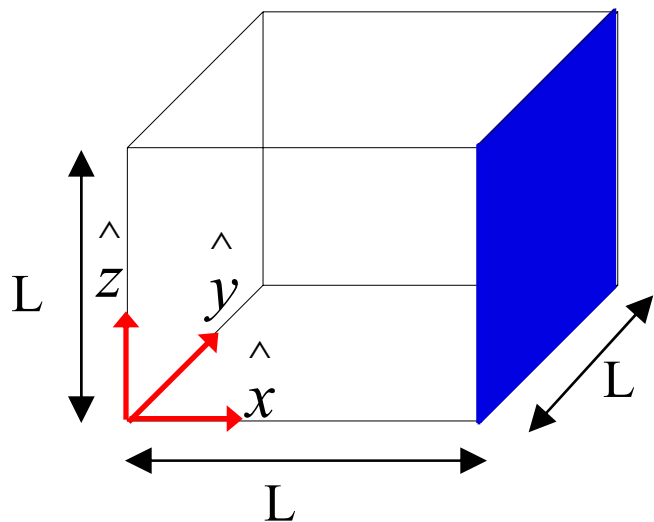
$$\psi(\vec{r}) = A \cdot (e^{ik_x \cdot x} - e^{-ik_x \cdot x}) \cdot e^{i(k_y \cdot y + k_z \cdot z)}$$

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

$$\begin{aligned} \psi(x=0, y, z) &= A \cdot (e^{ik_x \cdot x} - e^{-ik_x \cdot x}) \cdot e^{i(k_y \cdot y + k_z \cdot z)} \\ &= A \cdot (e^0 - e^0) \cdot e^{i(k_y \cdot y + k_z \cdot z)} = 0 \end{aligned}$$

Does solve boundary condition!!!

# Boundary conditions: The plane $x=L$ :



$$\begin{aligned}\psi(\vec{r}) &= A \cdot \left( e^{ik_x \cdot x} - e^{-ik_x \cdot x} \right) \cdot e^{i(k_y \cdot y + k_z \cdot z)} \\ &= 2iA \cdot \sin(k_x x) \cdot e^{i(k_y \cdot y + k_z \cdot z)}\end{aligned}$$

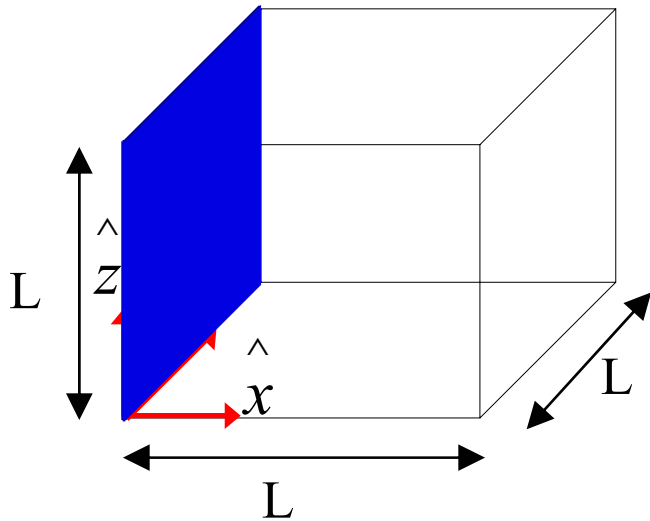
$$\sin(\theta) = \frac{1}{2i} (e^{i\theta} - e^{-i\theta})$$

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

If and only if:

$$k_n = n\pi / L$$

# Boundary conditions:



We can do the same for y, z:

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

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

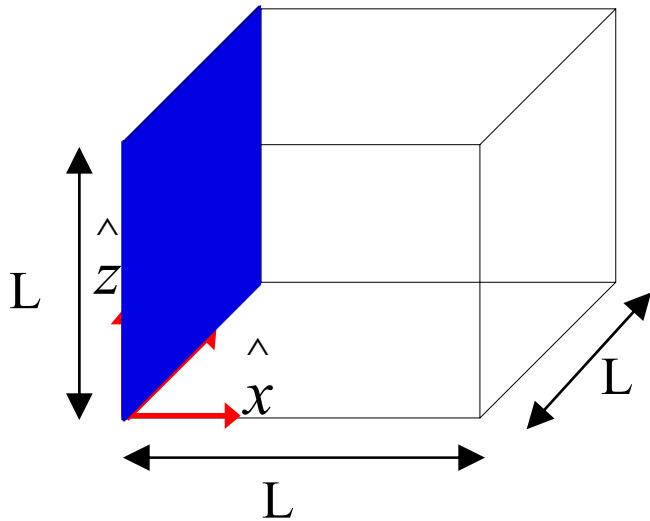
$$k_{n_y} = n_y \pi / L$$

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

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

These are the allowed energy levels, or “quantum states”

# Many electrons:

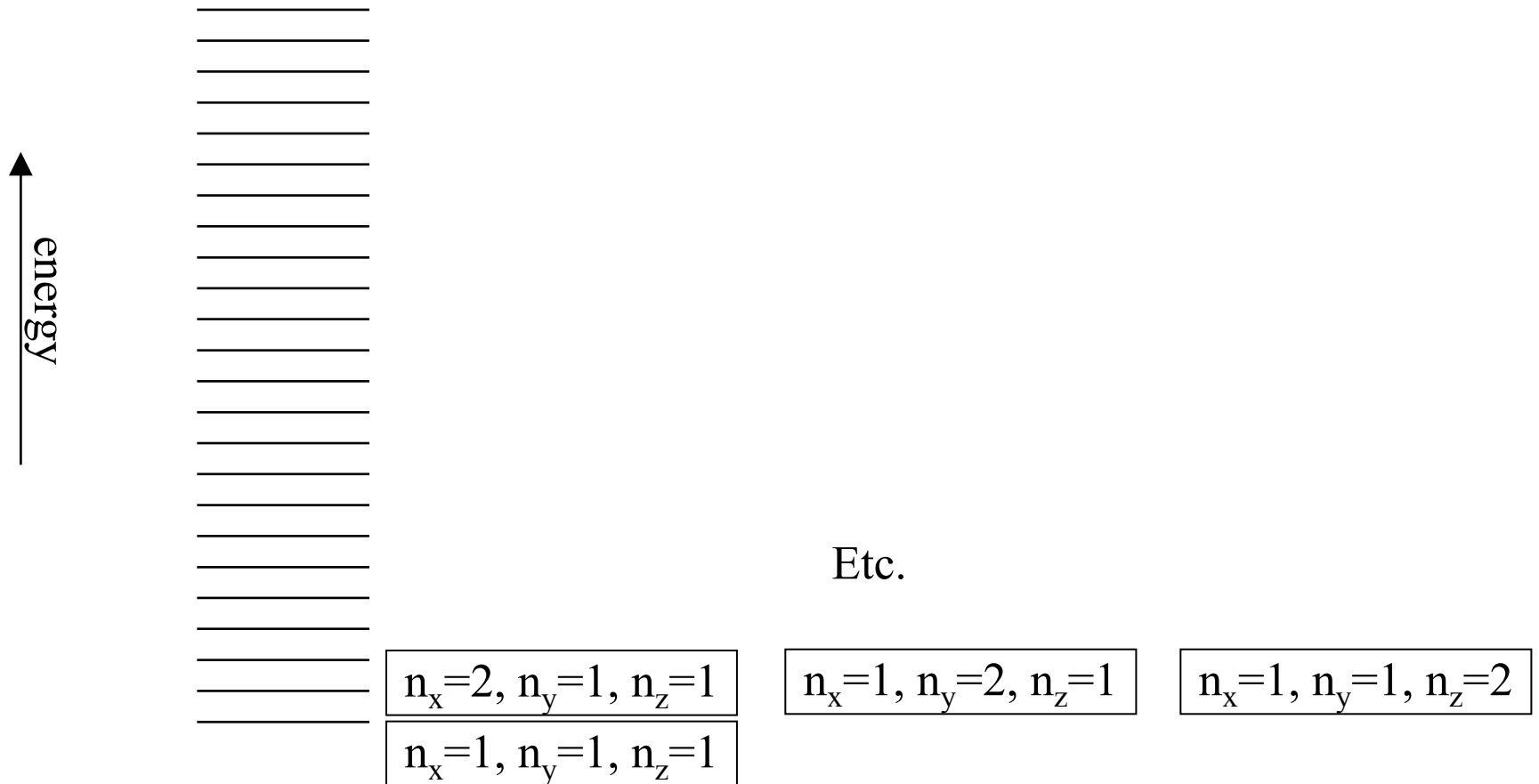


$$E = \frac{\hbar^2 (\pi / L)^2}{2m} (n_x^2 + n_y^2 + n_z^2)$$

These are the allowed energy levels,  
or “quantum states”

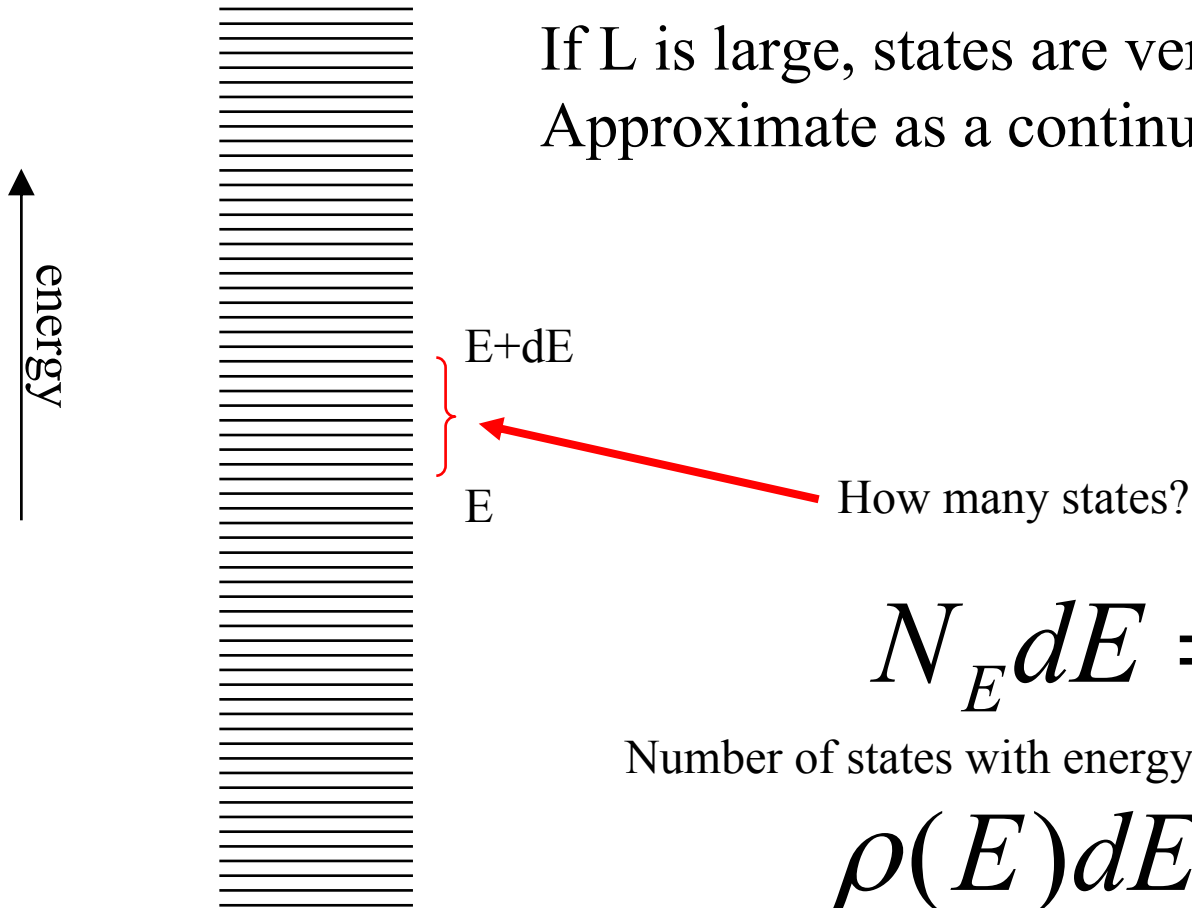
Pauli exclusion principle: Each unique combination of  $n_x$ ,  $n_y$ ,  $n_z$  can only have two electrons (spin up, spin down).

# Energy spectrum of free particles:



# Density of states:

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



$$N_E dE = ?$$

Number of states with energy between  $E$  and  $E + dE$

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

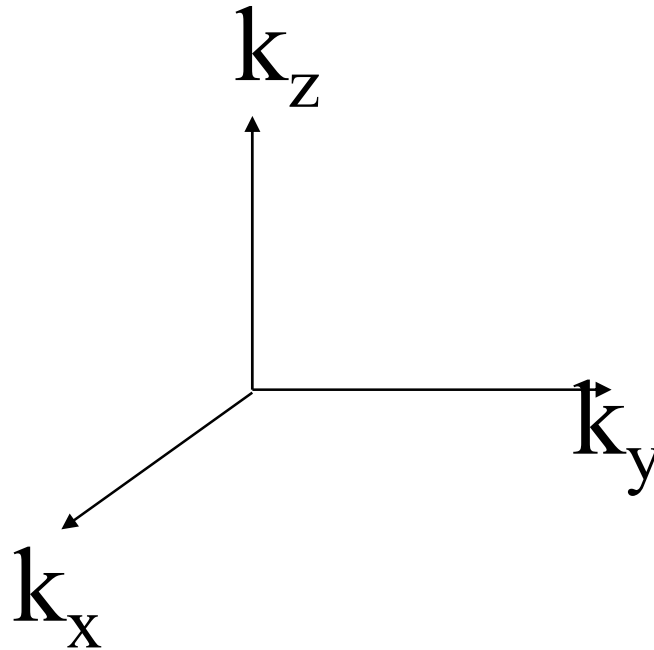
Number of states with energy between  $E$  and  $E + dE$  *per volume*.

# Density of states:

Easier first to think of in  $k$ -space:

Density of states in  $k$ -space is uniform:

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

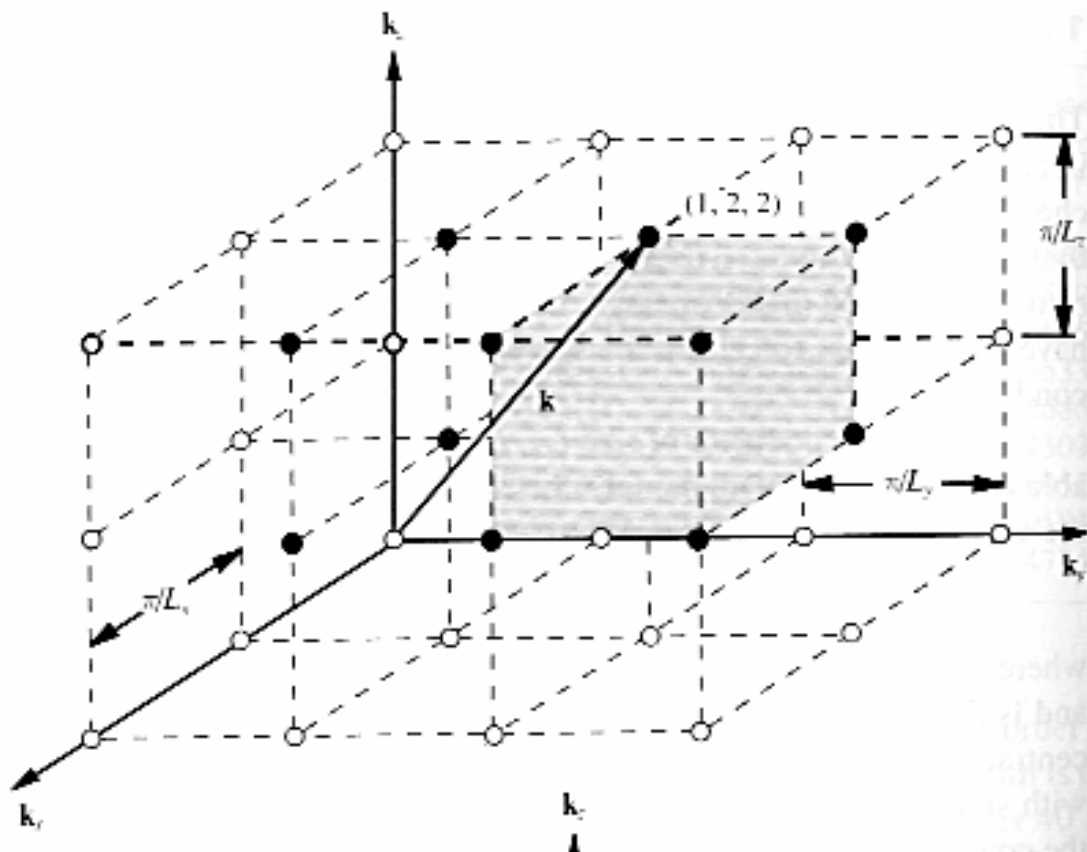


# Density of states:

Easier first to think of in k-space:

Density of states in k-space is uniform:

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

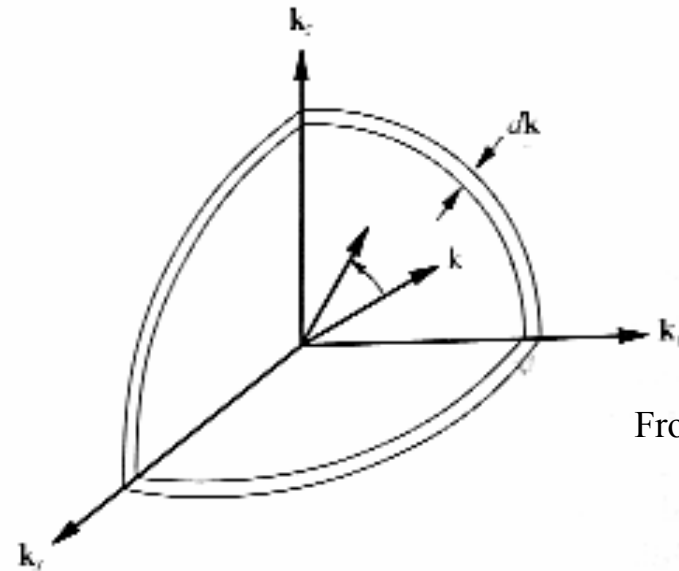
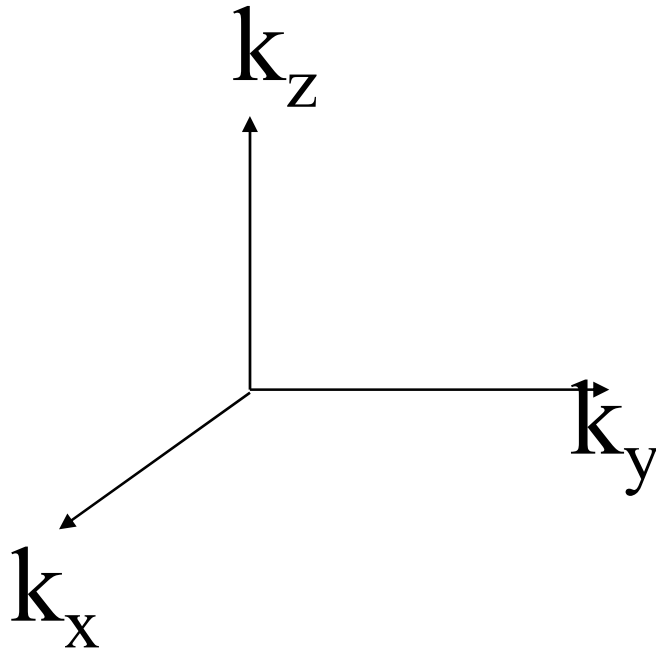


From Verdeyen

# Density of states:

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

$$N_k dk = ?$$



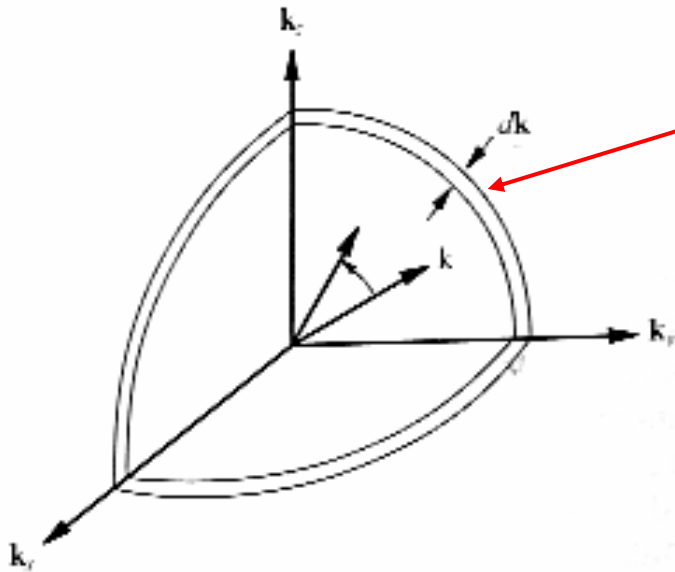
$$k \equiv \sqrt{k_x^2 + k_y^2 + k_z^2}$$

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

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

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

$$N_k dk = ?$$



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:

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

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

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

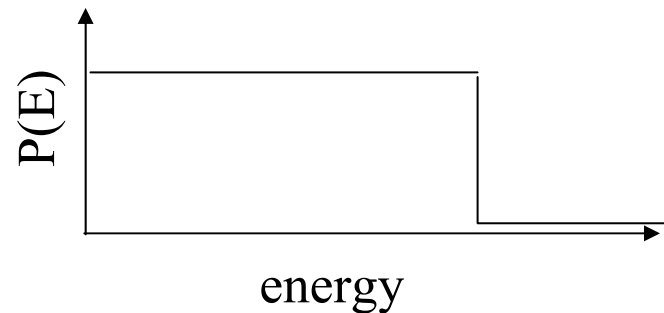
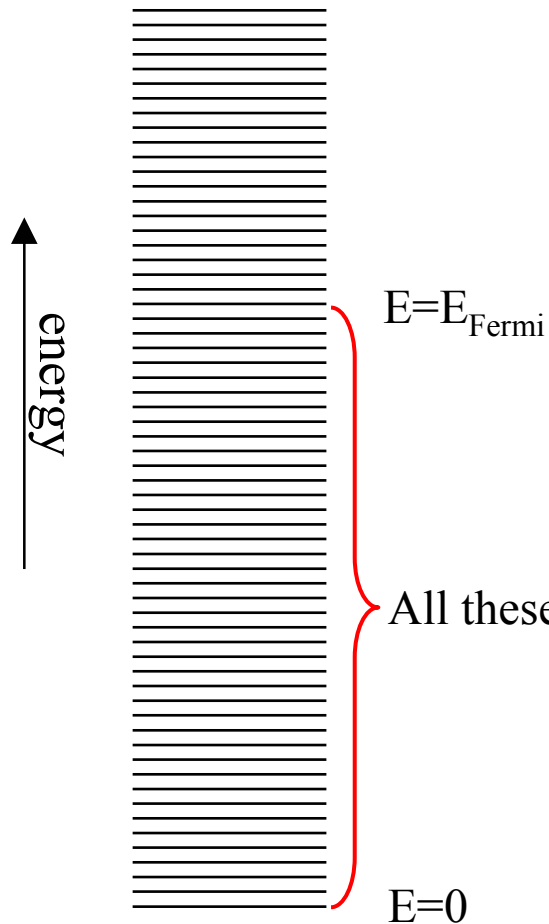
$$\rho(E)dE = \frac{2^{1/2} m^{3/2}}{\pi^2 \hbar^3} \cdot E^{1/2} dE$$

# 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.

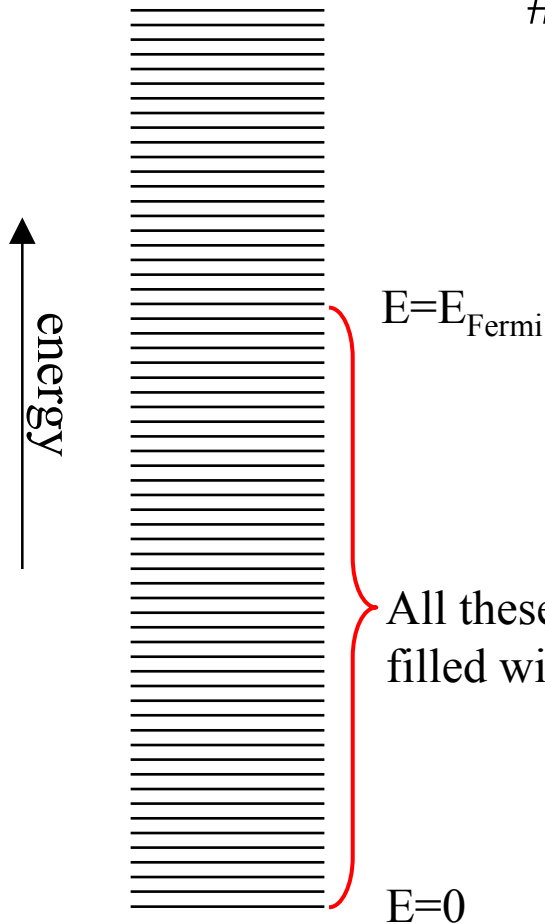


# Fermi energy:

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

$$\# \text{ electrons} = L^3 \frac{2^{1/2} m^{3/2}}{\pi^2 \hbar^3} \frac{2}{3} E_f^{3/2}$$

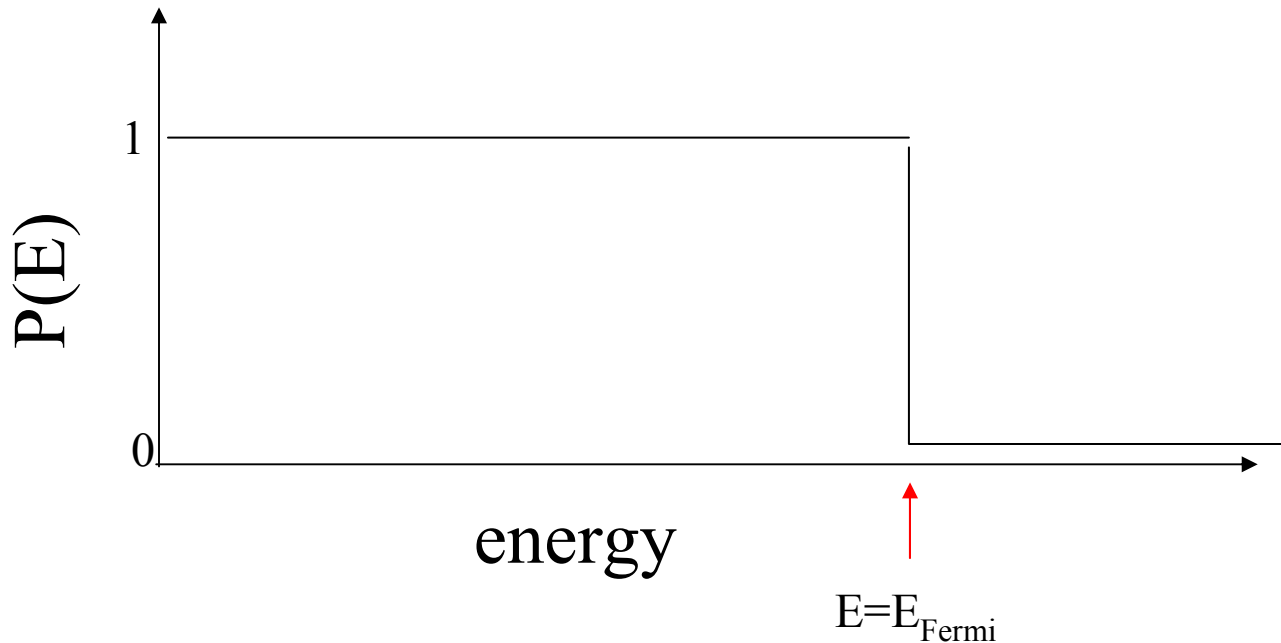
$$\Rightarrow E_f = \frac{\hbar^2 3^{2/3} \pi^{4/3}}{2m} \left( \frac{\# \text{ electrons}}{L^3} \right)^{2/3}$$



In a typical metal,  $L \sim 0.1 \text{ nm}$ .

$$E_f \sim 10 \text{ eV}$$

# Occupation probability:



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

What about finite temperature?

# Boltzmann:

Recall Boltzmann factor  $P(\varepsilon)$ :

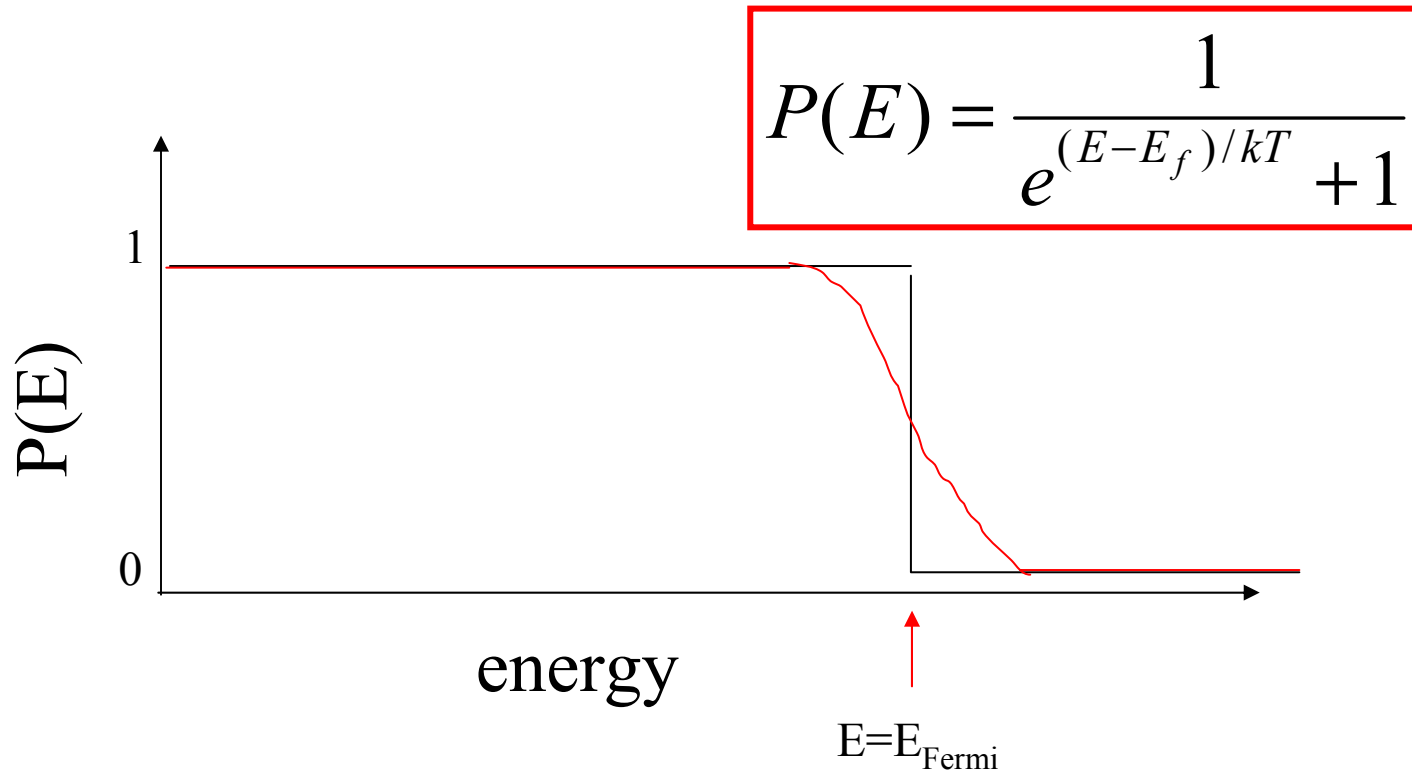
“The probability for a physical system to be in a state with energy  $\varepsilon$  is proportional to  $e^{-\varepsilon/k_B T}$ .”

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.

# Fermi-Dirac:



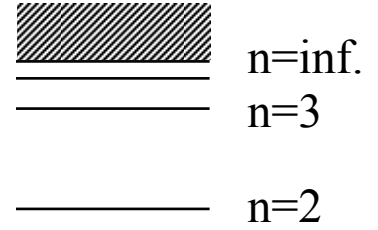
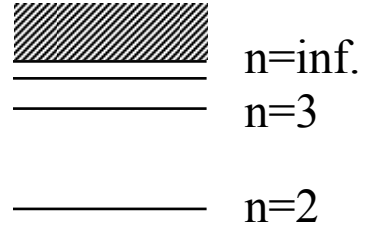
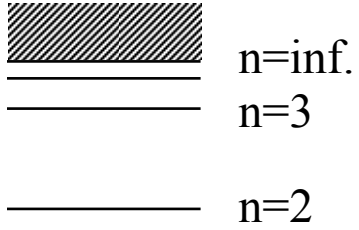
$P=1/2$  at  $E_f$  for all temperatures.

$kT$

Forget about free electrons for now.

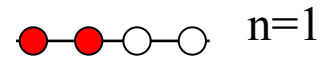
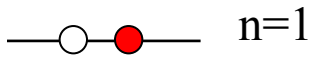
Back to the hydrogen atom.

# Chemical bonds:

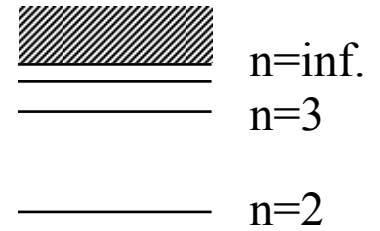
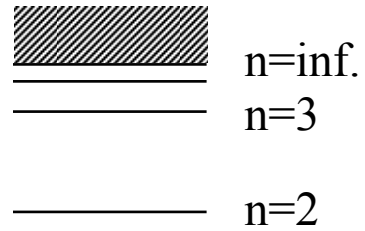
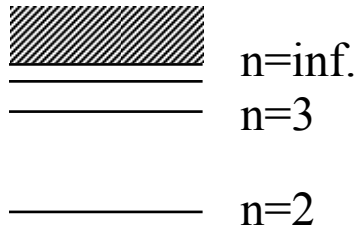


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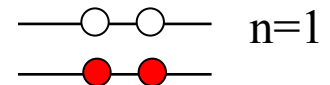
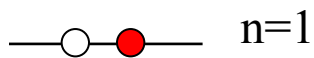


# Chemical bonds:



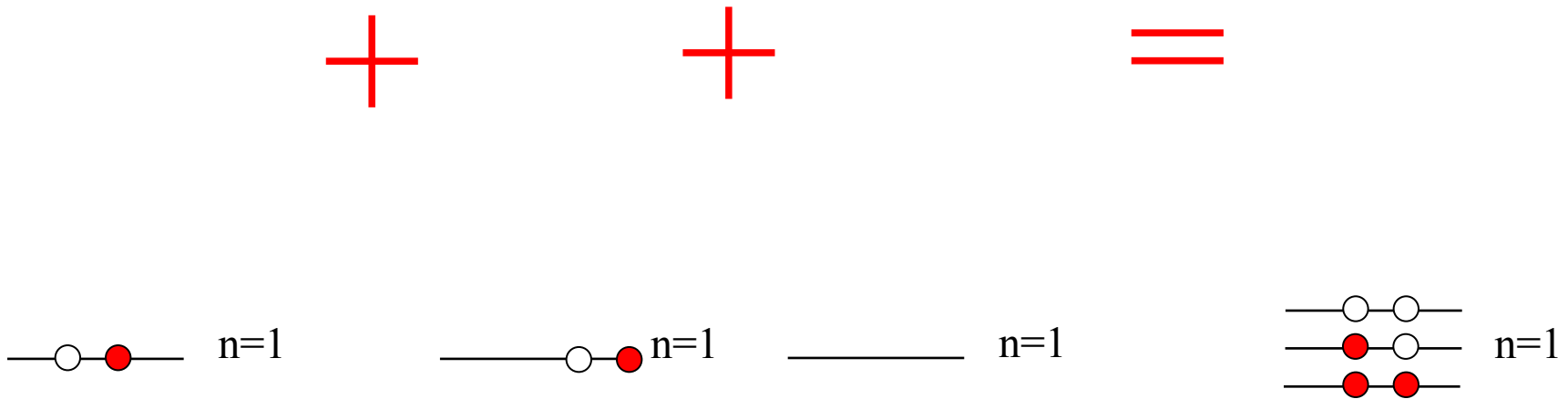
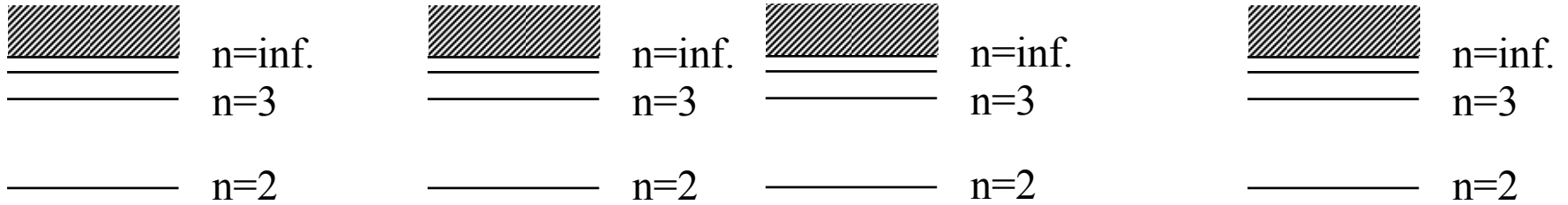
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“Bonding and anti-bonding”

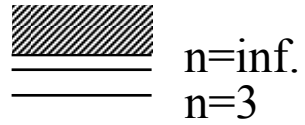
# Chemical bonds:



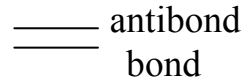
“N atoms give N levels”

# Band theory of solids:

1 Hydrogen atom:



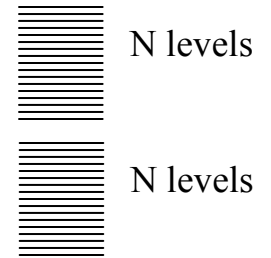
2 Hydrogen atoms:



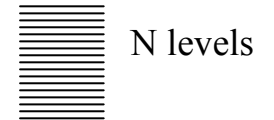
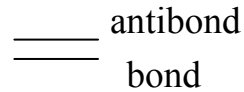
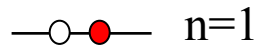
3 Hydrogen atoms:



N Hydrogen atoms:



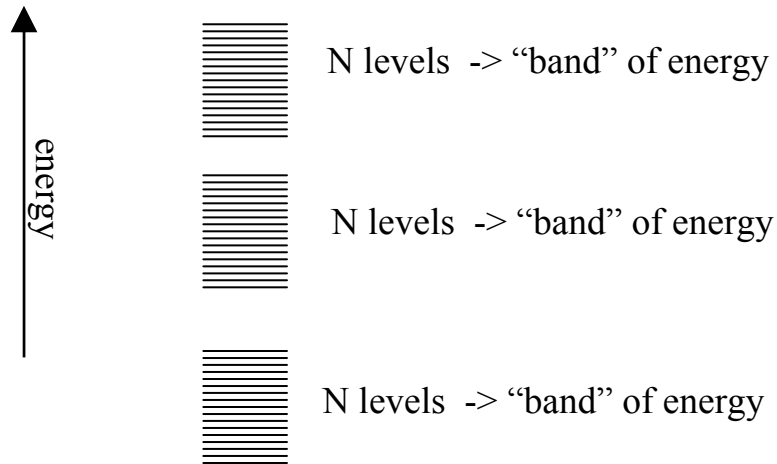
energy ↑



# Band theory of solids:

N Hydrogen atoms:

N  $\rightarrow$  infinity



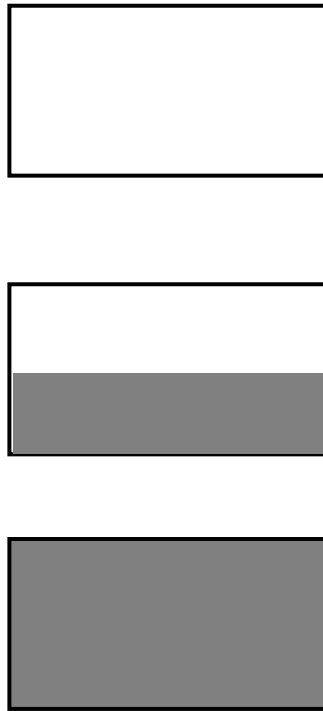
# Band theory of solids:

## Filled bands do not conduct electricity!

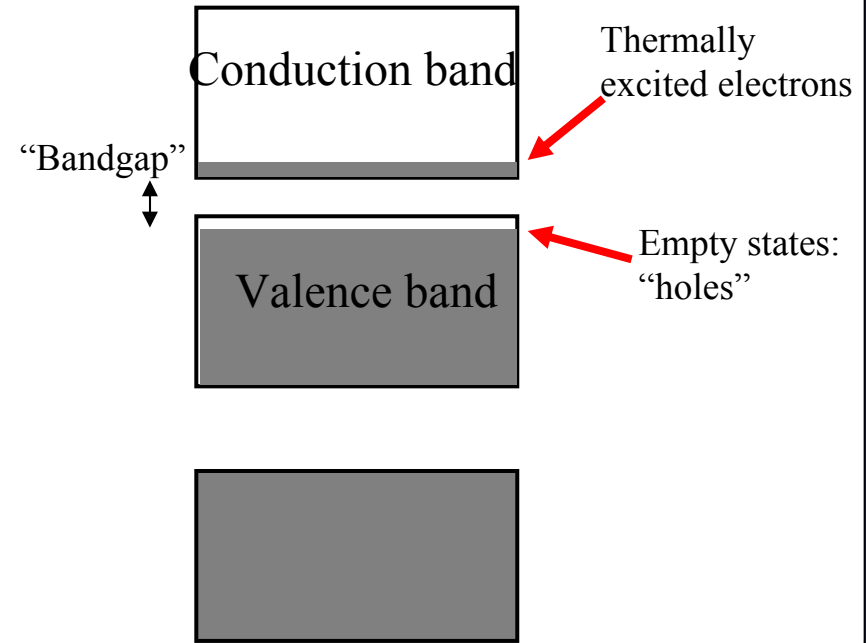
Insulator:



Metal:



Semiconductor:

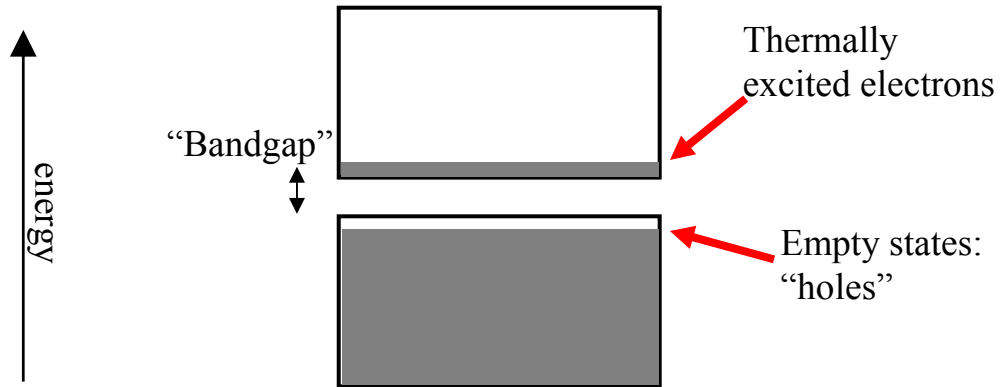


We usually don't care about lower bands.

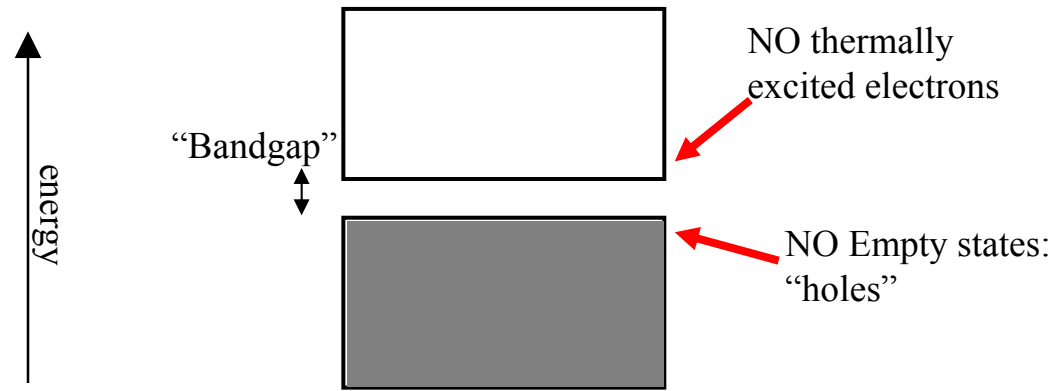
LASER will be formed by electrons going from conduction to valence band...

# Semiconductors:

## Finite temperature:



## Zero temperature:



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

# Silicon:

## Gap = 1.1 eV

Group\*\*

Period

1	1 IA 1A	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A	
1	1 <u>H</u> 1.008																		2 <u>He</u> 4.003
2	3 <u>Li</u> 6.941	4 <u>Be</u> 9.012											5 <u>B</u> 10.81	6 <u>C</u> 12.01	7 <u>N</u> 14.01	8 <u>O</u> 16.00	9 <u>F</u> 19.00	10 <u>Ne</u> 20.18	
3	11 <u>Na</u> 22.99	12 <u>Mg</u> 24.31	13 IIIB 3B	14 IVB 4B	15 VB 5B	16 VIB 6B	17 VIIB 7B	18 VIII 8	19 VIII 8	20 VIII 8	21 IB 1B	22 IIB 2B	31 <u>Al</u> 26.98	32 <u>Si</u> 28.09	33 <u>P</u> 30.97	34 <u>S</u> 32.07	35 <u>Cl</u> 35.45	36 <u>Ar</u> 39.95	
4	19 <u>K</u> 39.10	20 <u>Ca</u> 40.08	21 <u>Sc</u> 44.96	22 <u>Ti</u> 47.88	23 <u>V</u> 50.94	24 <u>Cr</u> 52.00	25 <u>Mn</u> 54.94	26 <u>Fe</u> 55.85	27 <u>Co</u> 58.47	28 <u>Ni</u> 58.69	29 <u>Cu</u> 63.55	30 <u>Zn</u> 65.39	31 <u>Ga</u> 69.72	32 <u>Ge</u> 72.59	33 <u>As</u> 74.92	34 <u>Se</u> 78.96	35 <u>Br</u> 79.90	36 <u>Kr</u> 83.80	
5	37 <u>Rb</u> 85.47	38 <u>Sr</u> 87.62	39 <u>Y</u> 88.91	40 <u>Zr</u> 91.22	41 <u>Nb</u> 92.91	42 <u>Mo</u> 95.94	43 <u>Tc</u> (98)	44 <u>Ru</u> 101.1	45 <u>Rh</u> 102.9	46 <u>Pd</u> 106.4	47 <u>Ag</u> 107.9	48 <u>Cd</u> 112.4	49 <u>In</u> 114.8	50 <u>Sn</u> 118.7	51 <u>Sb</u> 121.8	52 <u>Te</u> 127.6	53 <u>I</u> 126.9	54 <u>Xe</u> 131.3	
6	55 <u>Cs</u> 132.9	56 <u>Ba</u> 137.3	57 <u>La*</u> 138.9	72 <u>Hf</u> 178.5	73 <u>Ta</u> 180.9	74 <u>W</u> 183.9	75 <u>Re</u> 186.2	76 <u>Os</u> 190.2	77 <u>Ir</u> 190.2	78 <u>Pt</u> 195.1	79 <u>Au</u> 197.0	80 <u>Hg</u> 200.5	81 <u>Tl</u> 204.4	82 <u>Pb</u> 207.2	83 <u>Bi</u> 209.0	84 <u>Po</u> (210)	85 <u>At</u> (210)	86 <u>Rn</u> (222)	
7	87 <u>Fr</u> (223)	88 <u>Ra</u> (226)	89 <u>Ac~</u> (227)	104 <u>Rf</u> (257)	105 <u>Db</u> (260)	106 <u>Sg</u> (263)	107 <u>Bh</u> (262)	108 <u>Hs</u> (265)	109 <u>Mt</u> (266)	110 ---	111 ---	112 ---		114 ---		116 ---		118 ---	

Lanthanide Series\*

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

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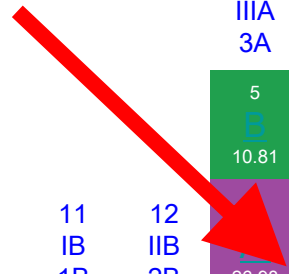
Actinide Series~

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

Period

Ge:



1	1 IA 1A	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A	
1	1 <u>H</u> 1.008																		2 <u>He</u> 4.003
2	3 <u>Li</u> 6.941	4 <u>Be</u> 9.012											5 <u>B</u> 10.81	6 <u>C</u> 12.01	7 <u>N</u> 14.01	8 <u>O</u> 16.00	9 <u>F</u> 19.00	10 <u>Ne</u> 20.18	
3	11 <u>Na</u> 22.99	12 <u>Mg</u> 24.31	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 ----- VIII ----- 8	9	10	11 IB 1B	12 IIB 2B	13 <u>Al</u> 26.98	14 <u>Si</u> 28.09	15 <u>P</u> 30.97	16 <u>S</u> 32.07	17 <u>Cl</u> 35.45	18 <u>Ar</u> 39.95	
4	19 <u>K</u> 39.10	20 <u>Ca</u> 40.08	21 <u>Sc</u> 44.96	22 <u>Ti</u> 47.88	23 <u>V</u> 50.94	24 <u>Cr</u> 52.00	25 <u>Mn</u> 54.94	26 <u>Fe</u> 55.85	27 <u>Co</u> 58.47	28 <u>Ni</u> 58.69	29 <u>Cu</u> 63.55	30 <u>Zn</u> 65.39	31 <u>Ga</u> 69.72	32 <u>Ge</u> 72.59	33 <u>As</u> 74.92	34 <u>Se</u> 78.96	35 <u>Br</u> 79.90	36 <u>Kr</u> 83.80	
5	37 <u>Rb</u> 85.47	38 <u>Sr</u> 87.62	39 <u>Y</u> 88.91	40 <u>Zr</u> 91.22	41 <u>Nb</u> 92.91	42 <u>Mo</u> 95.94	43 <u>Tc</u> (98)	44 <u>Ru</u> 101.1	45 <u>Rh</u> 102.9	46 <u>Pd</u> 106.4	47 <u>Ag</u> 107.9	48 <u>Cd</u> 112.4	49 <u>In</u> 114.8	50 <u>Sn</u> 118.7	51 <u>Sb</u> 121.8	52 <u>Te</u> 127.6	53 <u>I</u> 126.9	54 <u>Xe</u> 131.3	
6	55 <u>Cs</u> 132.9	56 <u>Ba</u> 137.3	57 <u>La</u> * 138.9	72 <u>Hf</u> 178.5	73 <u>Ta</u> 180.9	74 <u>W</u> 183.9	75 <u>Re</u> 186.2	76 <u>Os</u> 190.2	77 <u>Ir</u> 190.2	78 <u>Pt</u> 195.1	79 <u>Au</u> 197.0	80 <u>Hg</u> 200.5	81 <u>Tl</u> 204.4	82 <u>Pb</u> 207.2	83 <u>Bi</u> 209.0	84 <u>Po</u> (210)	85 <u>At</u> (210)	86 <u>Rn</u> (222)	
7	87 <u>Fr</u> (223)	88 <u>Ra</u> (226)	89 <u>Ac</u> ~ (227)	104 <u>Rf</u> (257)	105 <u>Db</u> (260)	106 <u>Sg</u> (263)	107 <u>Bh</u> (262)	108 <u>Hs</u> (265)	109 <u>Mt</u> (266)	110 --- ( )	111 --- ( )	112 --- ( )		114 --- ( )		116 --- ( )		118 --- ( )	

Lanthanide Series\*

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

90 <u>Th</u> 232.0	91 <u>Pa</u> (231)	92 <u>U</u> (238)	93 <u>Np</u> (237)	94 <u>Pu</u> (242)	95 <u>Am</u> (243)	96 <u>Cm</u> (247)	97 <u>Bk</u> (247)	98 <u>Cf</u> (249)	99 <u>Es</u> (254)	100 <u>Fm</u> (253)	101 <u>Md</u> (256)	102 <u>No</u> (254)	103 <u>Lr</u> (257)
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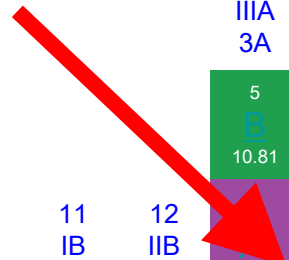
From <http://pearl1.lanl.gov/periodic/default.htm>

Group\*\*

Period

# GaAs:

Gap = 1.4 eV



1	1 IA 1A	2											14	15	16	17	18	
1	1 <u>H</u> 1.008	2 IIA 2A											14 IIIA 3A	15 IVA 4A	16 VA 5A	17 VIA 6A	18 VIIA 7A	2 VIII 8A
2	3 <u>Li</u> 6.941	4 <u>Be</u> 9.012											5 <u>B</u> 10.81	6 <u>C</u> 12.01	7 <u>N</u> 14.01	8 <u>O</u> 16.00	9 <u>F</u> 19.00	10 <u>Ne</u> 20.18
3	11 <u>Na</u> 22.99	12 <u>Mg</u> 24.31	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 ----- VIII ----- 8	9	10	11 IB 1B	12 IIB 2B	13 <u>Al</u> 26.98	14 <u>Si</u> 28.09	15 <u>P</u> 30.97	16 <u>S</u> 32.07	17 <u>Cl</u> 35.45	18 <u>Ar</u> 39.95
4	19 <u>K</u> 39.10	20 <u>Ca</u> 40.08	21 <u>Sc</u> 44.96	22 <u>Ti</u> 47.88	23 <u>V</u> 50.94	24 <u>Cr</u> 52.00	25 <u>Mn</u> 54.94	26 <u>Fe</u> 55.85	27 <u>Co</u> 58.47	28 <u>Ni</u> 58.69	29 <u>Cu</u> 63.55	30 <u>Zn</u> 65.39	31 <u>Ga</u> 69.72	32 <u>Ge</u> 72.59	33 <u>As</u> 74.92	34 <u>Se</u> 78.96	35 <u>Br</u> 79.90	36 <u>Kr</u> 83.80
5	37 <u>Rb</u> 85.47	38 <u>Sr</u> 87.62	39 <u>Y</u> 88.91	40 <u>Zr</u> 91.22	41 <u>Nb</u> 92.91	42 <u>Mo</u> 95.94	43 <u>Tc</u> (98)	44 <u>Ru</u> 101.1	45 <u>Rh</u> 102.9	46 <u>Pd</u> 106.4	47 <u>Ag</u> 107.9	48 <u>Cd</u> 112.4	49 <u>In</u> 114.8	50 <u>Sn</u> 118.7	51 <u>Sb</u> 121.8	52 <u>Te</u> 127.6	53 <u>I</u> 126.9	54 <u>Xe</u> 131.3
6	55 <u>Cs</u> 132.9	56 <u>Ba</u> 137.3	57 <u>La</u> * 138.9	72 <u>Hf</u> 178.5	73 <u>Ta</u> 180.9	74 <u>W</u> 183.9	75 <u>Re</u> 186.2	76 <u>Os</u> 190.2	77 <u>Ir</u> 190.2	78 <u>Pt</u> 195.1	79 <u>Au</u> 197.0	80 <u>Hg</u> 200.5	81 <u>Tl</u> 204.4	82 <u>Pb</u> 207.2	83 <u>Bi</u> 209.0	84 <u>Po</u> (210)	85 <u>At</u> (210)	86 <u>Rn</u> (222)
7	87 <u>Fr</u> (223)	88 <u>Ra</u> (226)	89 <u>Ac</u> ~ (227)	104 <u>Rf</u> (257)	105 <u>Db</u> (260)	106 <u>Sg</u> (263)	107 <u>Bh</u> (262)	108 <u>Hs</u> (265)	109 <u>Mt</u> (266)	110 --- ( )	111 --- ( )	112 --- ( )	113 --- ( )	114 --- ( )	115 --- ( )	116 --- ( )	117 --- ( )	118 --- ( )

Lanthanide Series\*

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

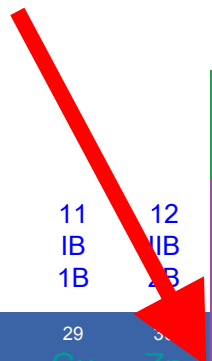
90 <u>Th</u> 232.0	91 <u>Pa</u> (231)	92 <u>U</u> (238)	93 <u>Np</u> (237)	94 <u>Pu</u> (242)	95 <u>Am</u> (243)	96 <u>Cm</u> (247)	97 <u>Bk</u> (247)	98 <u>Cf</u> (249)	99 <u>Es</u> (254)	100 <u>Fm</u> (253)	101 <u>Md</u> (256)	102 <u>No</u> (254)	103 <u>Lr</u> (257)
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From <http://pearl1.lanl.gov/periodic/default.htm>

Group\*\*

Period

InP:



1	1 IA 1A	2											13	14	15	16	17	18
1	1 <u>H</u> 1.008	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
2	3 <u>Li</u> 6.941	4 <u>Be</u> 9.012											5 <u>B</u> 10.81	6 <u>C</u> 12.01	7 <u>N</u> 14.01	8 <u>O</u> 16.00	9 <u>F</u> 19.00	10 <u>Ne</u> 20.18
3	11 <u>Na</u> 22.99	12 <u>Mg</u> 24.31	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 ----- VIII ----- 8	9 ----- VIII ----- 8	10 ----- VIII ----- 8	11 IB 1B	12 IIB 2B	13 <u>Al</u> 26.98	14 <u>Si</u> 28.09	15 <u>P</u> 30.97	16 <u>S</u> 32.07	17 <u>Cl</u> 35.45	18 <u>Ar</u> 39.95
4	19 <u>K</u> 39.10	20 <u>Ca</u> 40.08	21 <u>Sc</u> 44.96	22 <u>Ti</u> 47.88	23 <u>V</u> 50.94	24 <u>Cr</u> 52.00	25 <u>Mn</u> 54.94	26 <u>Fe</u> 55.85	27 <u>Co</u> 58.47	28 <u>Ni</u> 58.69	29 <u>Cu</u> 63.55	30 <u>Zn</u> 65.39	31 <u>Ga</u> 69.72	32 <u>Ge</u> 72.59	33 <u>As</u> 74.92	34 <u>Se</u> 78.96	35 <u>Br</u> 79.90	36 <u>Kr</u> 83.80
5	37 <u>Rb</u> 85.47	38 <u>Sr</u> 87.62	39 <u>Y</u> 88.91	40 <u>Zr</u> 91.22	41 <u>Nb</u> 92.91	42 <u>Mo</u> 95.94	43 <u>Tc</u> (98)	44 <u>Ru</u> 101.1	45 <u>Rh</u> 102.9	46 <u>Pd</u> 106.4	47 <u>Ag</u> 107.9	48 <u>Cd</u> 112.4	49 <u>In</u> 114.8	50 <u>Sn</u> 118.7	51 <u>Sb</u> 121.8	52 <u>Te</u> 127.6	53 <u>I</u> 126.9	54 <u>Xe</u> 131.3
6	55 <u>Cs</u> 132.9	56 <u>Ba</u> 137.3	57 <u>La</u> * 138.9	72 <u>Hf</u> 178.5	73 <u>Ta</u> 180.9	74 <u>W</u> 183.9	75 <u>Re</u> 186.2	76 <u>Os</u> 190.2	77 <u>Ir</u> 190.2	78 <u>Pt</u> 195.1	79 <u>Au</u> 197.0	80 <u>Hg</u> 200.5	81 <u>Tl</u> 204.4	82 <u>Pb</u> 207.2	83 <u>Bi</u> 209.0	84 <u>Po</u> (210)	85 <u>At</u> (210)	86 <u>Rn</u> (222)
7	87 <u>Fr</u> (223)	88 <u>Ra</u> (226)	89 <u>Ac</u> ~ (227)	104 <u>Rf</u> (257)	105 <u>Db</u> (260)	106 <u>Sg</u> (263)	107 <u>Bh</u> (262)	108 <u>Hs</u> (265)	109 <u>Mt</u> (266)	110 --- ( )	111 --- ( )	112 --- ( )	113 --- ( )	114 --- ( )	115 --- ( )	116 --- ( )	117 --- ( )	118 --- ( )

Lanthanide Series\*

58 <u>Ce</u> 140.1	59 <u>Pr</u> 140.9	60 <u>Nd</u> 144.2	61 <u>Pm</u> (147)	62 <u>Sm</u> 150.4	63 <u>Eu</u> 152.0	64 <u>Gd</u> 157.3	65 <u>Tb</u> 158.9	66 <u>Dy</u> 162.5	67 <u>Ho</u> 164.9	68 <u>Er</u> 167.3	69 <u>Tm</u> 168.9	70 <u>Yb</u> 173.0	71 <u>Lu</u> 175.0
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From <http://pearl1.lanl.gov/periodic/default.htm>

Actinide Series~

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

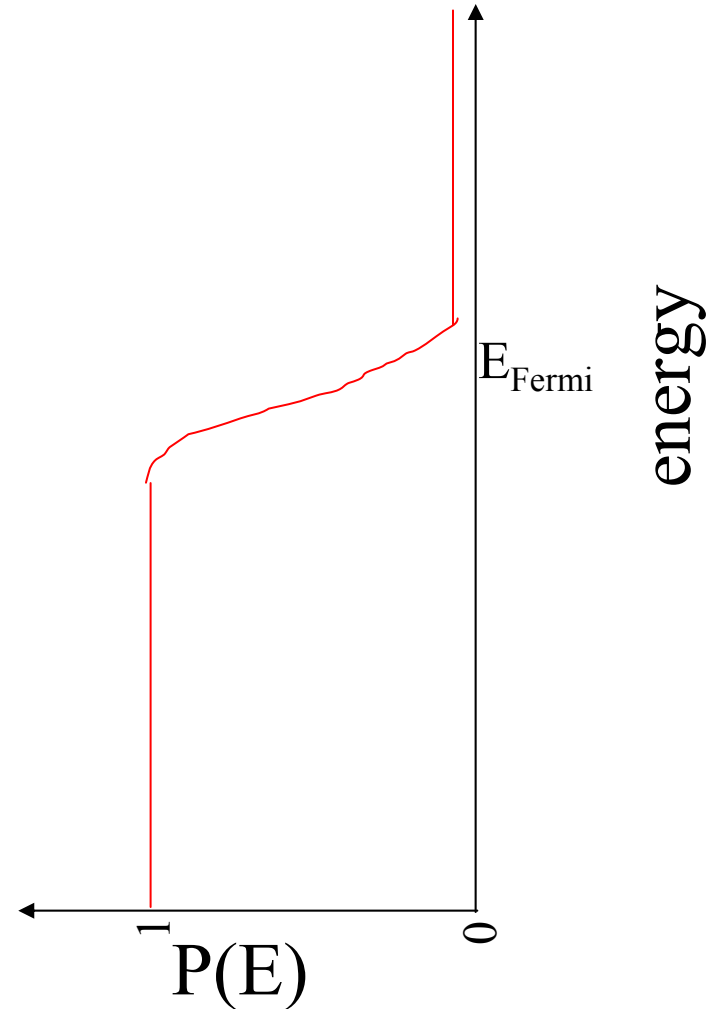
- 1)  $E_{\text{Fermi}}$  is in the middle of the gap.
- 3) Density of states origin is referred to edge of band.
- 2) Electrons, holes have different “effective” mass values.

We now discuss these three points:

# Semiconductors:

1)  $E_{\text{Fermi}}$  in middle of gap:

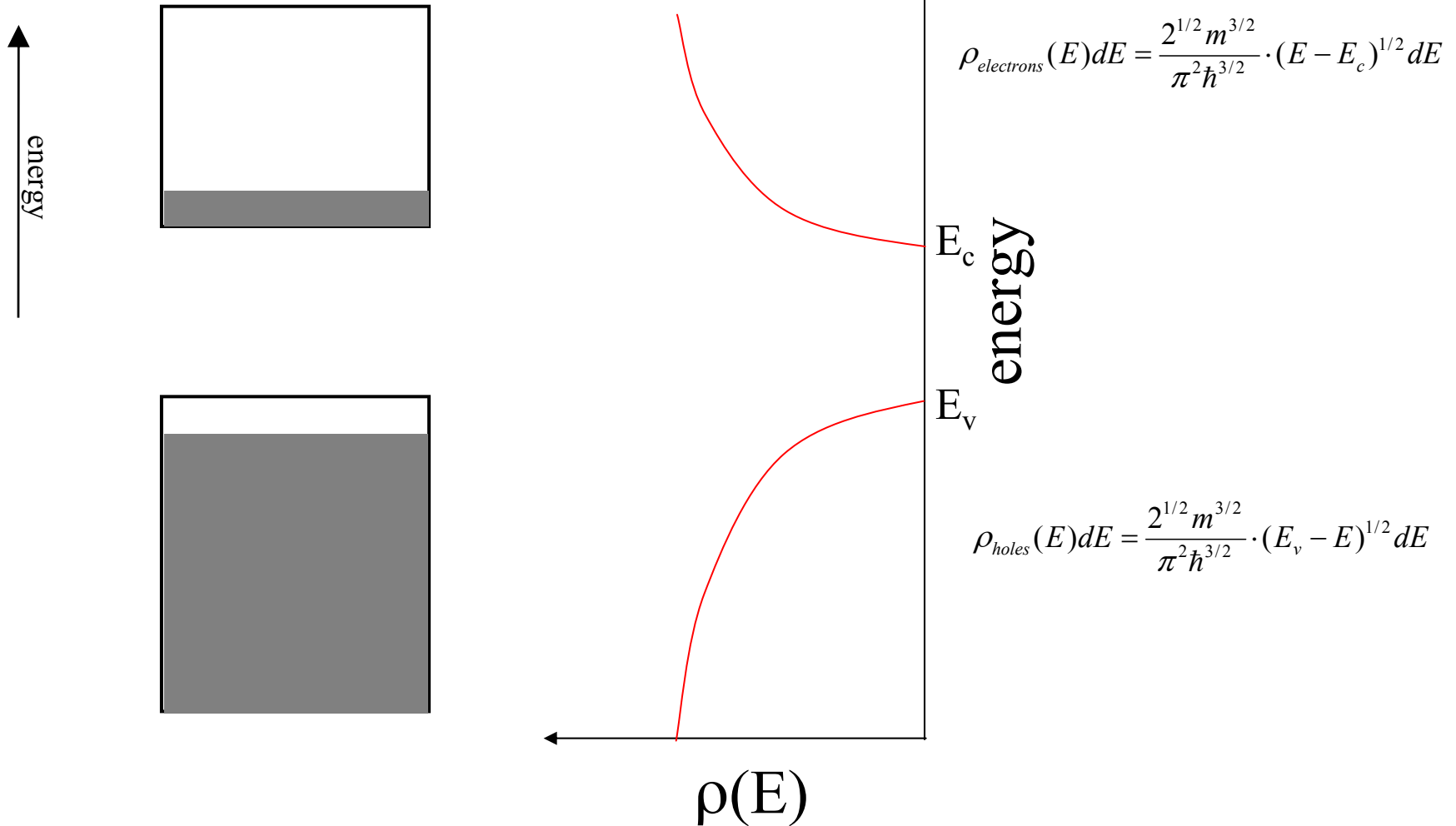
energy ↑



In board,  
discuss magnitude of gap,  
 $kT$  smearing.  
Also high energy appr.  
to Fermi-Dirac, and low  
Probability of excitation!

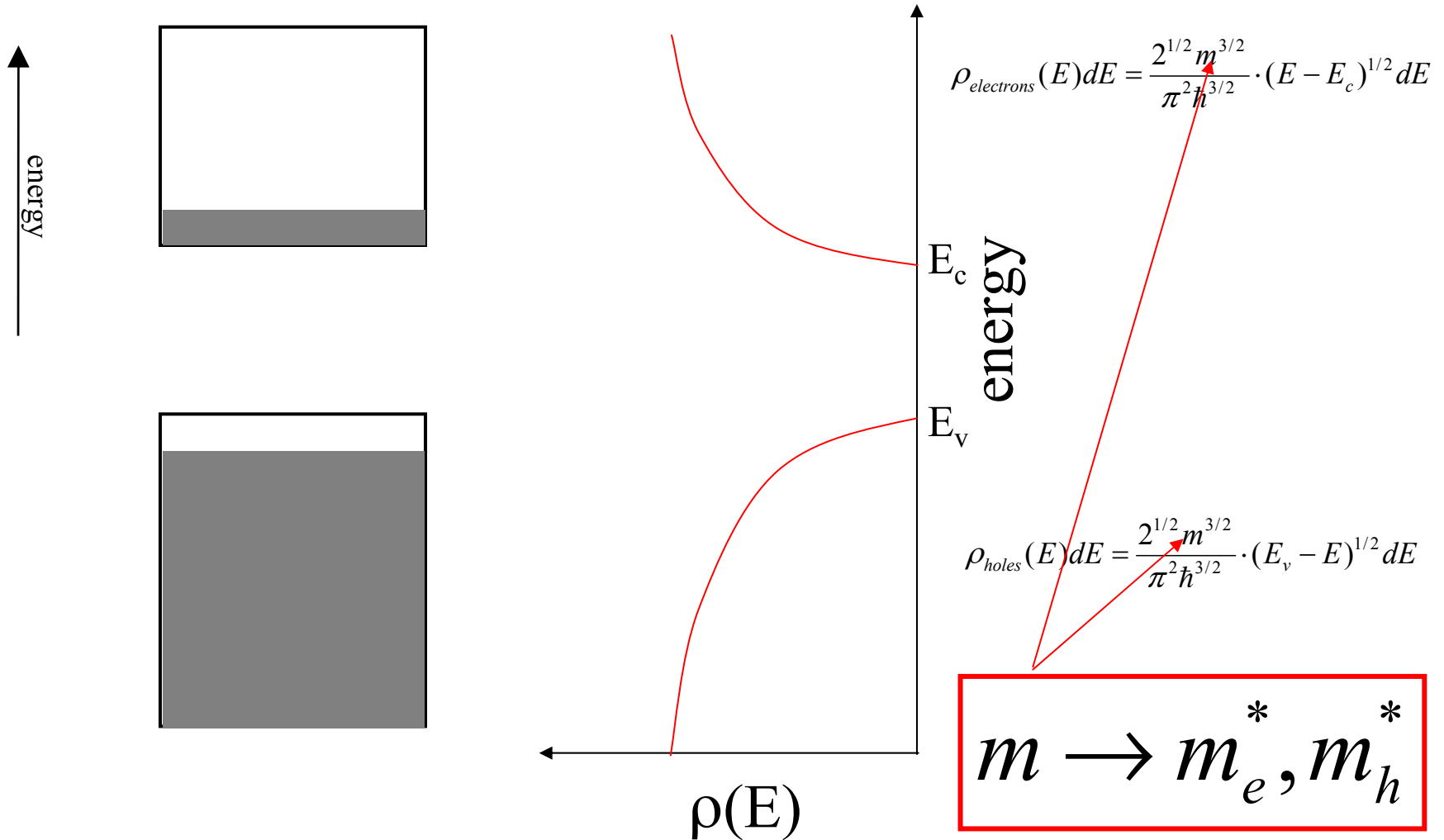
# Semiconductors:

2) Density of states origin is referred to edge of band :

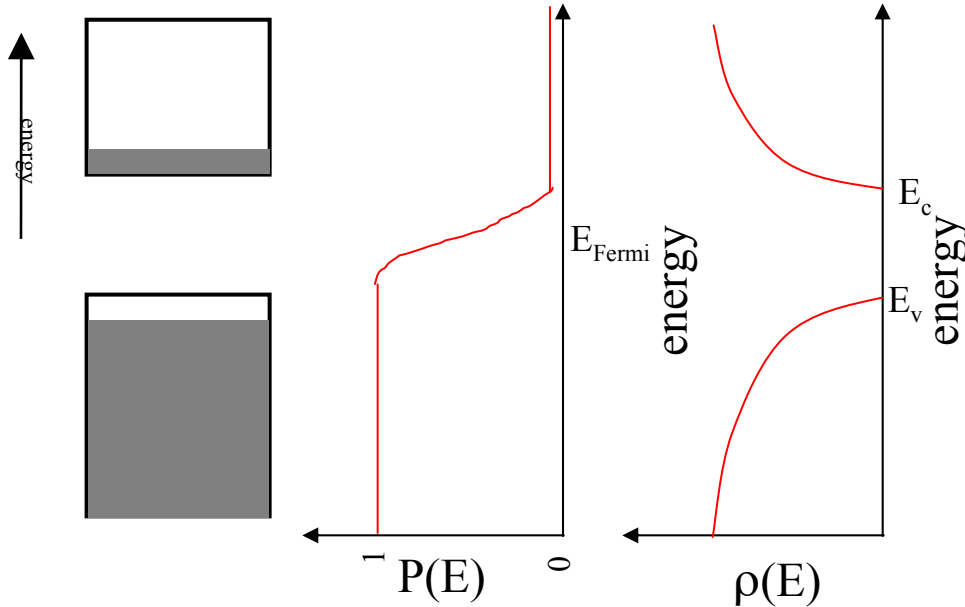


# Semiconductors:

## 3) Effective mass of electrons, holes:



# How many electrons in conduction band?



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

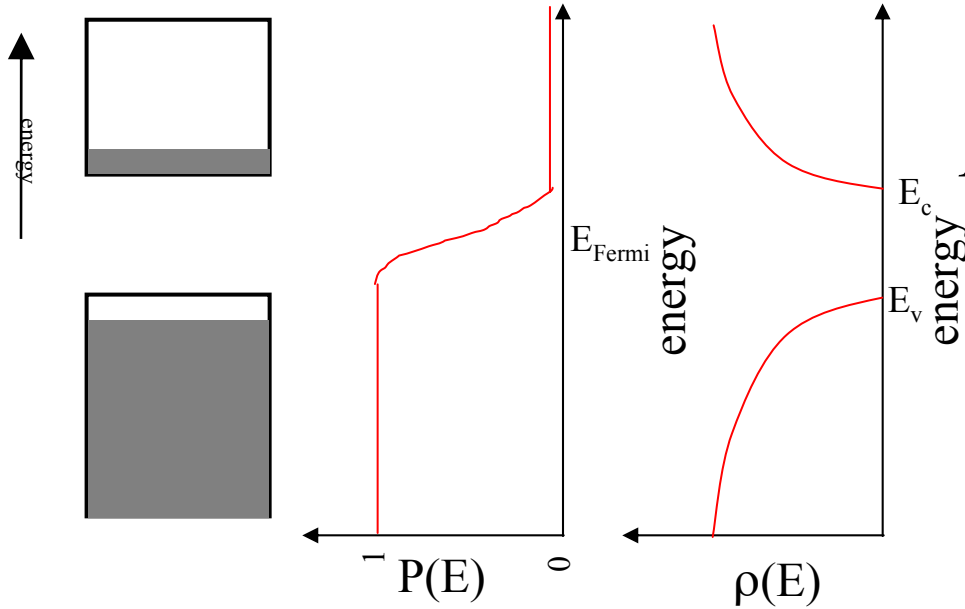
$$\rho_{electrons}(E) dE = \frac{2^{1/2} m^{3/2}}{\pi^2 \hbar^3} \cdot (E - E_c)^{1/2} dE$$

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

(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?



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

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

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

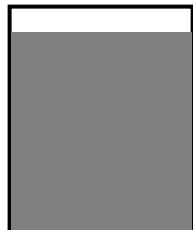
$$p_i = 2 \left( \frac{m_h^* kT}{2\pi \hbar^2} \right)^{3/2} e^{(E_v - E_f)/kT}$$

# Holes and electrons

energy ↑



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



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

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

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

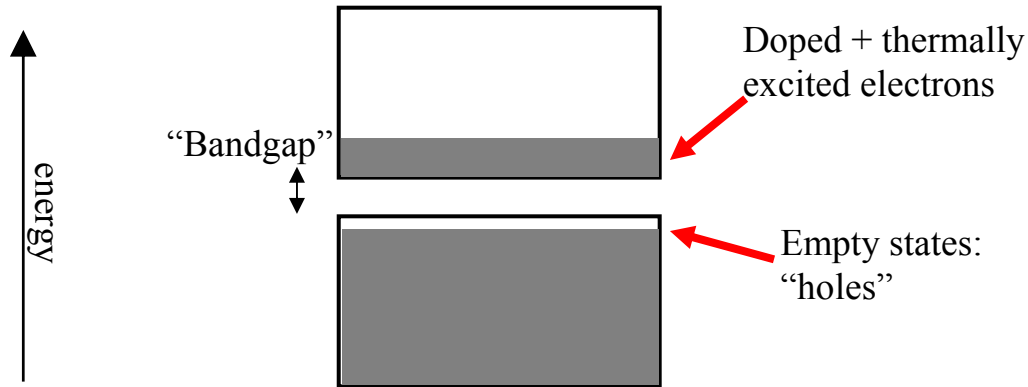
# Doping

- If we purposely include some “impurities” in the crystal, we can add more electrons.
- This works if the impurity atoms have one more electron per atom than the host semiconductor.
- Since we increase # of electrons, Fermi energy increases
- Intrinsic means no doping.
- Examples discussed for Si on next slide:

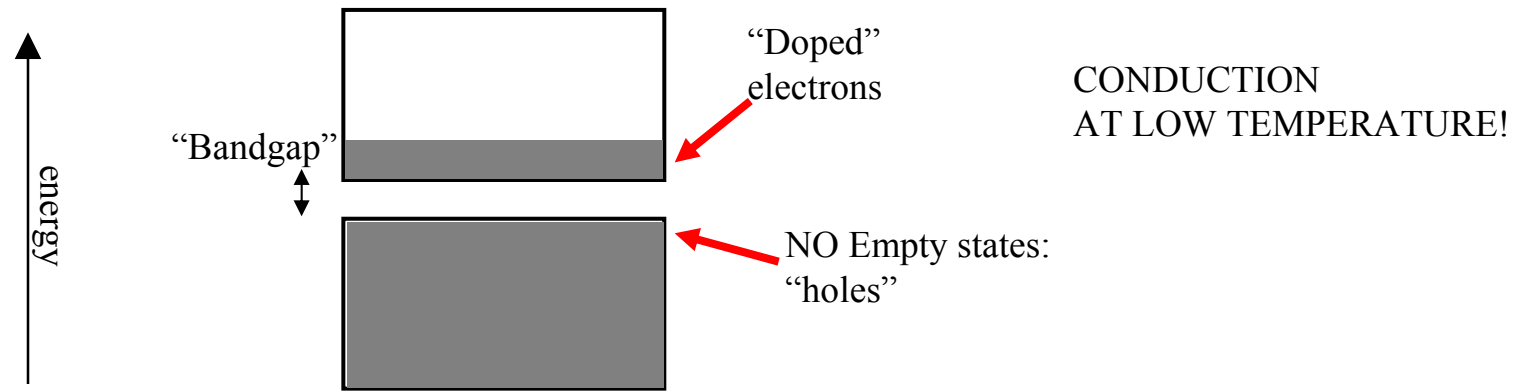


# N-type doped semiconductors:

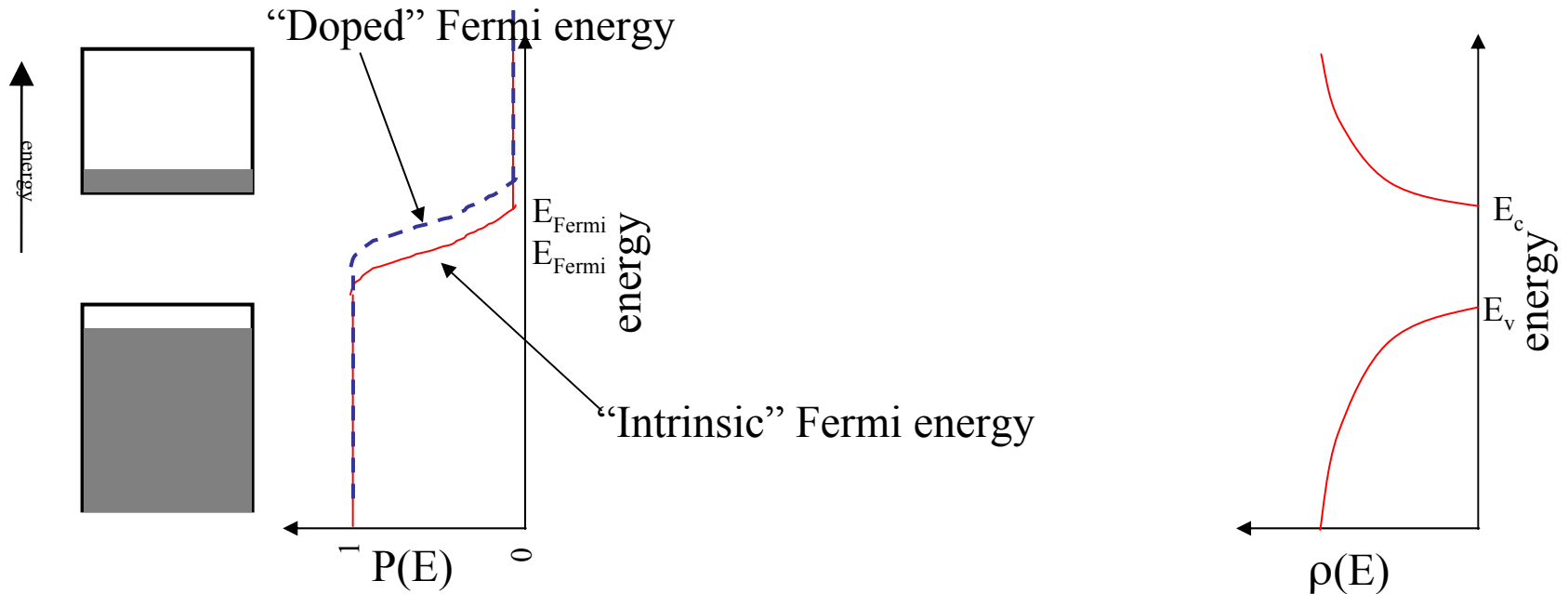
## Finite temperature:



## "Low" temperature:



# How many electrons in conduction band?



$$n_{total} = n_i + N_{donors} = 2 \left( \frac{m_e^* kT}{2\pi\hbar^2} \right) e^{(E_{Fermi (intrinsic)} - E_c)/kT} + N_{donors}$$

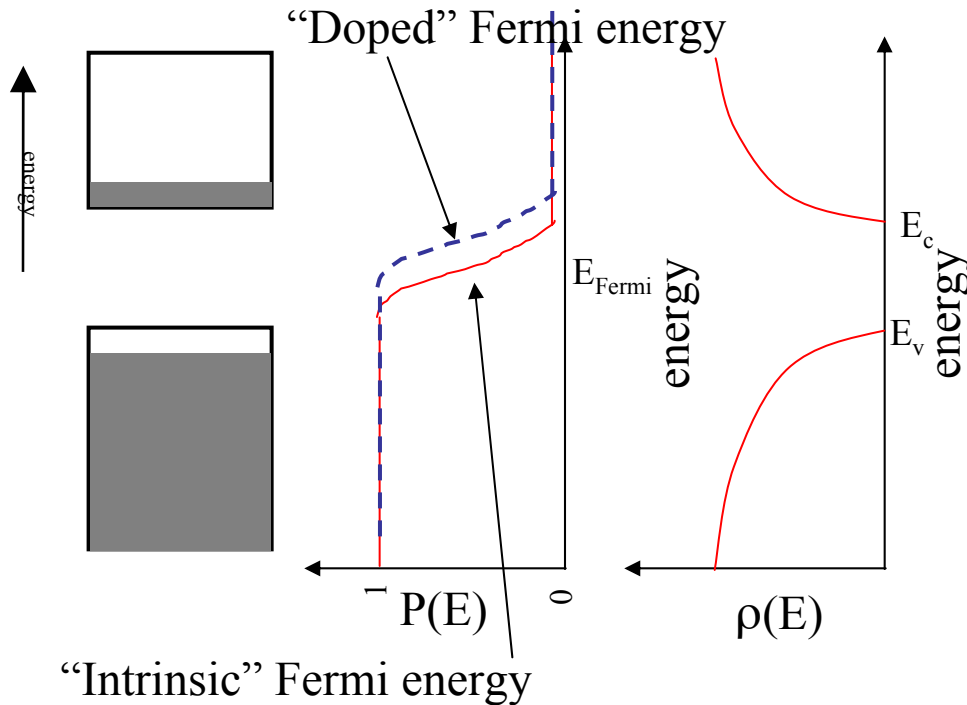
We can determine the new Fermi level by the relationship:

$$n_{total} = n_i + N_{donors} = 2 \left( \frac{m_e^* kT}{2\pi\hbar^2} \right) e^{(E_{Fermi new} - E_c)/kT}$$

HW will calculate what has to be  $E_{Fermi new}$  for a given dopant density  $N$  for this formula to come out right..

# How many electrons in conduction band?

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



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

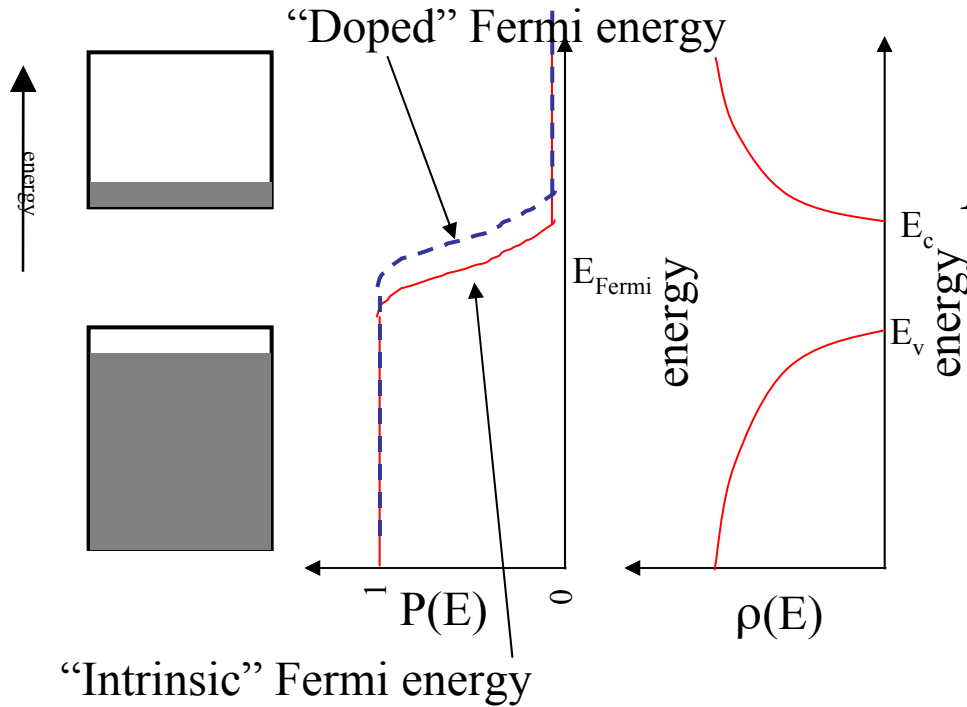
$$\rho_{\text{electrons}}(E) dE = \frac{2^{1/2} m^{3/2}}{\pi^2 \hbar^3} \cdot (E - E_c)^{1/2} dE$$

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

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

# How many holes in valence band?

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



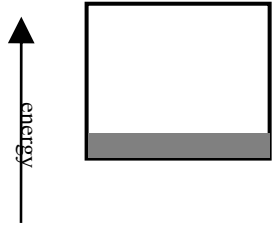
$$p_i = \int_{E_c}^{-\infty} [1 - P(E)] \rho(E) dE$$

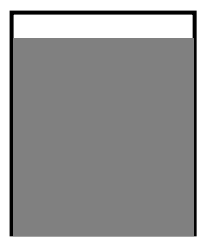
$$\rho_{\text{electrons}}(E) dE = \frac{2^{1/2} m^{3/2}}{\pi^2 \hbar^3} \cdot (E - E_c)^{1/2} dE$$

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

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

# Holes and electrons 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  $E_f - E_c \neq (1/2) E_{\text{gap}}$  and  $E_v - E_f \neq (1/2) E_{\text{gap}}$ !

$$n > p$$

We can do the whole exercise  
again with HOLES.


Group\*\*

Period

# Silicon

## p-type (hole) dopants

### “acceptors”



Period	1 IA 1A	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A	
1	1 <u>H</u> 1.008																		2 <u>He</u> 4.003
2	3 <u>Li</u> 6.941	4 <u>Be</u> 9.012											5 <u>B</u> 10.81	6 <u>C</u> 12.01	7 <u>N</u> 14.01	8 <u>O</u> 16.00	9 <u>F</u> 19.00	10 <u>Ne</u> 20.18	
3	11 <u>Na</u> 22.99	12 <u>Mg</u> 24.31	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IIB 2B	13 <u>Al</u> 26.98	14 <u>Si</u> 28.09	15 <u>P</u> 30.97	16 <u>S</u> 32.07	17 <u>Cl</u> 35.45	18 <u>Ar</u> 39.95		
4	19 <u>K</u> 39.10	20 <u>Ca</u> 40.08	21 <u>Sc</u> 44.96	22 <u>Ti</u> 47.88	23 <u>V</u> 50.94	24 <u>Cr</u> 52.00	25 <u>Mn</u> 54.94	26 <u>Fe</u> 55.85	27 <u>Co</u> 58.47	28 <u>Ni</u> 58.69	29 <u>Cu</u> 63.55	30 <u>Zn</u> 65.39	31 <u>Ga</u> 69.72	32 <u>Ge</u> 72.59	33 <u>As</u> 74.92	34 <u>Se</u> 78.96	35 <u>Br</u> 79.90	36 <u>Kr</u> 83.80	
5	37 <u>Rb</u> 85.47	38 <u>Sr</u> 87.62	39 <u>Y</u> 88.91	40 <u>Zr</u> 91.22	41 <u>Nb</u> 92.91	42 <u>Mo</u> 95.94	43 <u>Tc</u> (98)	44 <u>Ru</u> 101.1	45 <u>Rh</u> 102.9	46 <u>Pd</u> 106.4	47 <u>Ag</u> 107.9	48 <u>Cd</u> 112.4	49 <u>In</u> 114.8	50 <u>Sn</u> 118.7	51 <u>Sb</u> 121.8	52 <u>Te</u> 127.6	53 <u>I</u> 126.9	54 <u>Xe</u> 131.3	
6	55 <u>Cs</u> 132.9	56 <u>Ba</u> 137.3	57 <u>La*</u> 138.9	72 <u>Hf</u> 178.5	73 <u>Ta</u> 180.9	74 <u>W</u> 183.9	75 <u>Re</u> 186.2	76 <u>Os</u> 190.2	77 <u>Ir</u> 190.2	78 <u>Pt</u> 195.1	79 <u>Au</u> 197.0	80 <u>Hg</u> 200.5	81 <u>Tl</u> 204.4	82 <u>Pb</u> 207.2	83 <u>Bi</u> 209.0	84 <u>Po</u> (210)	85 <u>At</u> (210)	86 <u>Rn</u> (222)	
7	87 <u>Fr</u> (223)	88 <u>Ra</u> (226)	89 <u>Ac~</u> (227)	104 <u>Rf</u> (257)	105 <u>Db</u> (260)	106 <u>Sg</u> (263)	107 <u>Bh</u> (262)	108 <u>Hs</u> (265)	109 <u>Mt</u> (266)	110 ---	111 ---	112 ---	114 ---	116 ---	118 ---				

Lanthanide Series\*

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

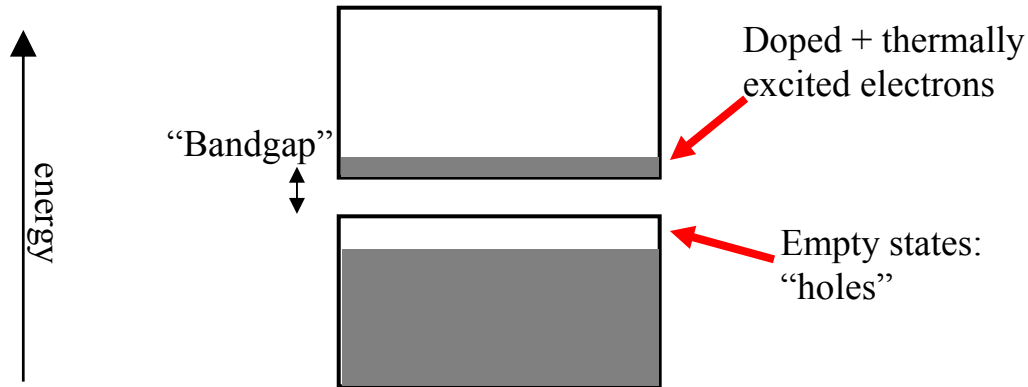
58 <u>Ce</u> 140.1	59 <u>Pr</u> 140.9	60 <u>Nd</u> 144.2	61 <u>Pm</u> (147)	62 <u>Sm</u> 150.4	63 <u>Eu</u> 152.0	64 <u>Gd</u> 157.3	65 <u>Tb</u> 158.9	66 <u>Dy</u> 162.5	67 <u>Ho</u> 164.9	68 <u>Er</u> 167.3	69 <u>Tm</u> 168.9	70 <u>Yb</u> 173.0	71 <u>Lu</u> 175.0
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Actinide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

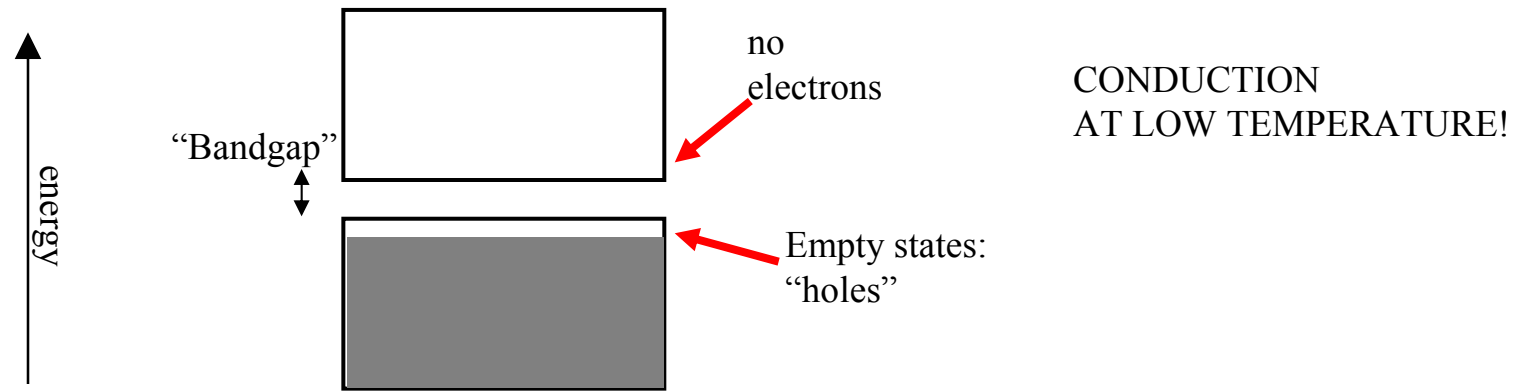
90 <u>Th</u> 232.0	91 <u>Pa</u> (231)	92 <u>U</u> (238)	93 <u>Np</u> (237)	94 <u>Pu</u> (242)	95 <u>Am</u> (243)	96 <u>Cm</u> (247)	97 <u>Bk</u> (247)	98 <u>Cf</u> (249)	99 <u>Es</u> (254)	100 <u>Fm</u> (253)	101 <u>Md</u> (256)	102 <u>No</u> (254)	103 <u>Lr</u> (257)
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# P-type doped semiconductors:

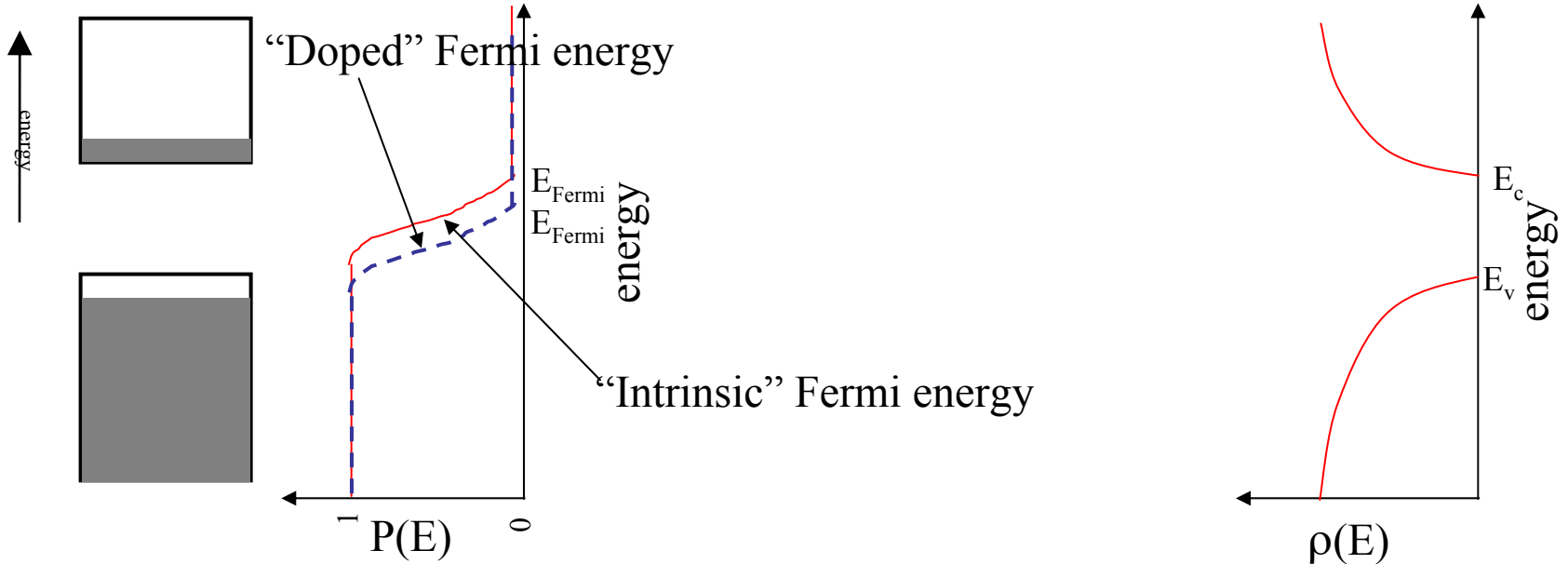
## Finite temperature:



## “Low” temperature:



# How many holes in valence band?



$$p_{total} = p_i + N_{acceptors} = 2 \left( \frac{m_h^* kT}{2\pi\hbar^2} \right) e^{(E_v - E_{Fermi (intrinsic)})/kT} + N_{acceptors}$$

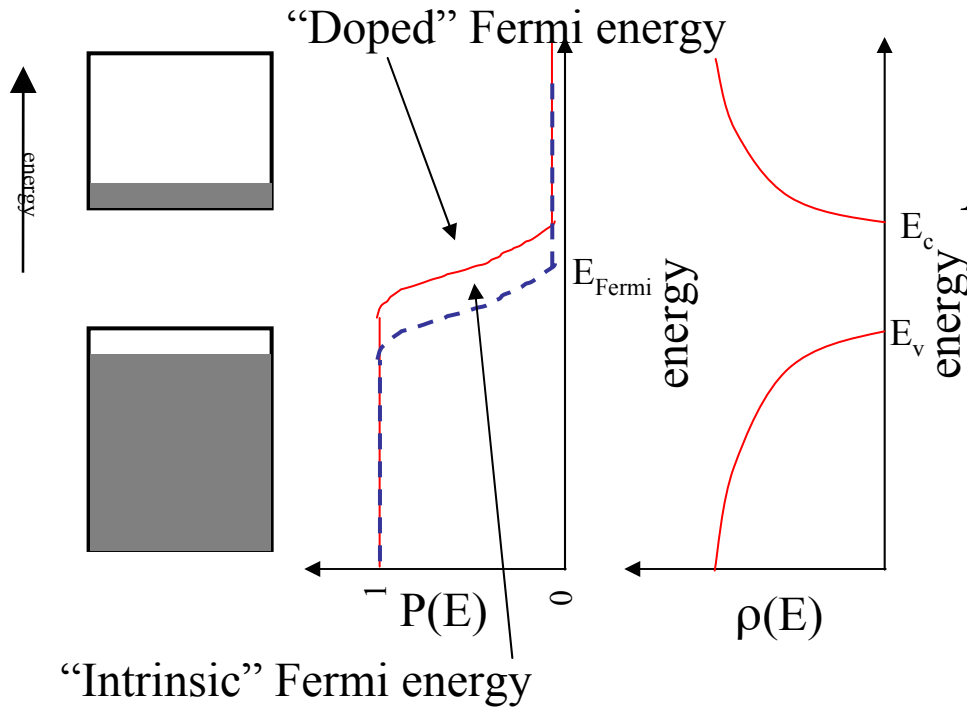
We can determine the new Fermi level by the relationship:

$$p_{total} = p_i + N_{acceptors} = 2 \left( \frac{m_h^* kT}{2\pi\hbar^2} \right) e^{(E_v - E_{Fermi new})/kT}$$

HW will calculate what has to be  $E_{Fermi new}$  for a given dopant density  $N$  for this formula to come out right..

# How many holes in valence band?

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



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

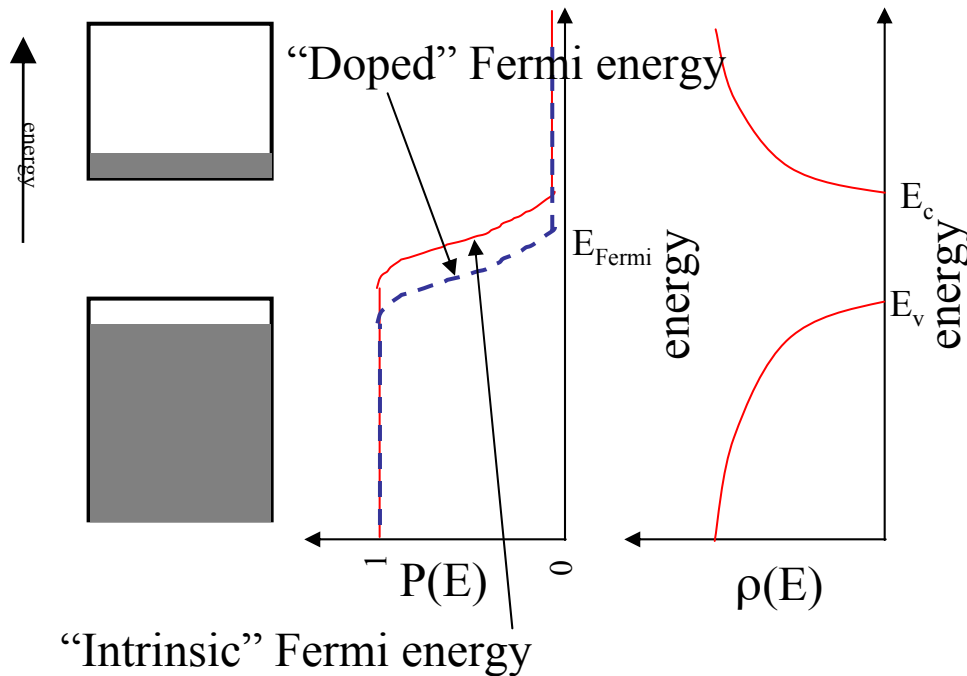
$$\rho_{\text{electrons}}(E) dE = \frac{2^{1/2} m^{3/2}}{\pi^2 \hbar^3} \cdot (E - E_c)^{1/2} dE$$

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

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

# How many electrons in conduction band?

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



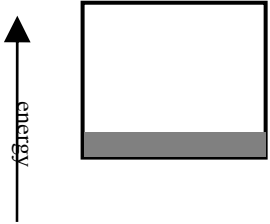
$$n_i = \int_{E_c}^{\infty} P(E) \rho(E) dE$$

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

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

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

# Holes and electrons when doped


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

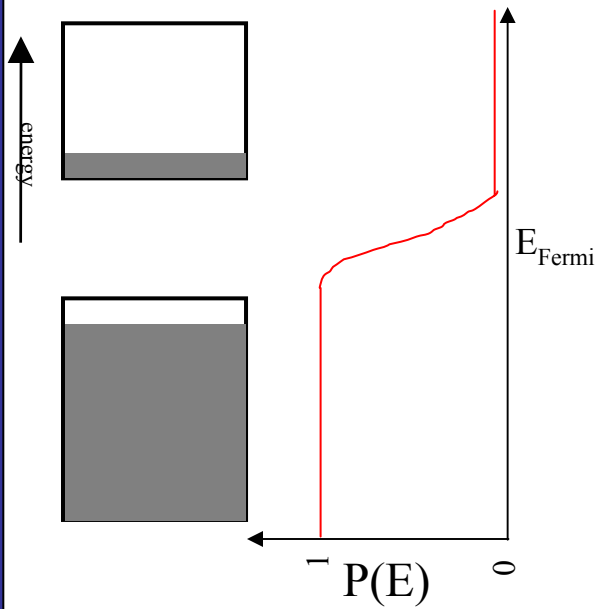

$$n = 2 \left( \frac{m_e^* kT}{2\pi\hbar^2} \right)^{3/2} e^{(E_f - E_c)/kT}$$

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

$$n < p$$

# In conclusion:

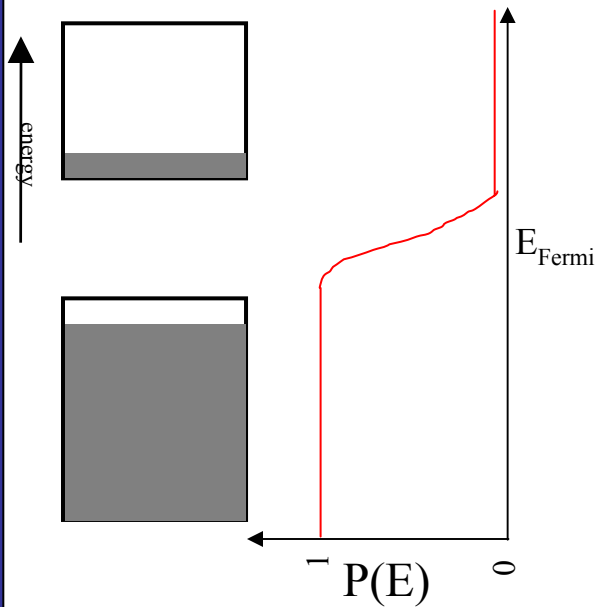
Intrinsic:



$$n = p$$

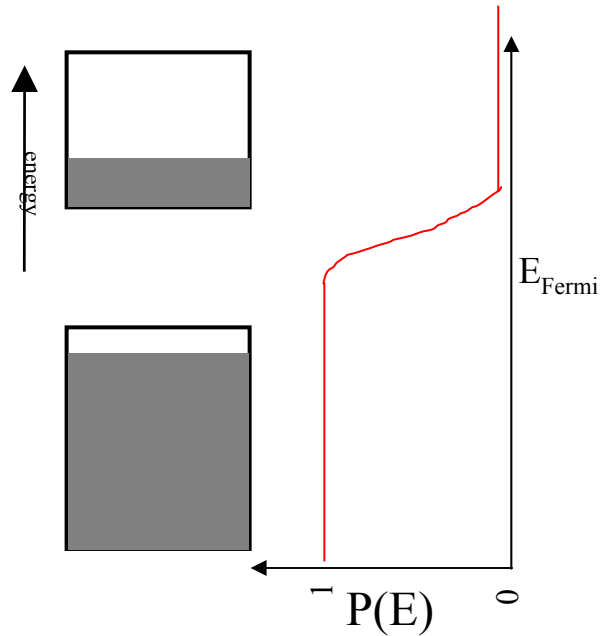
# In conclusion:

## Intrinsic:



$$n = p$$

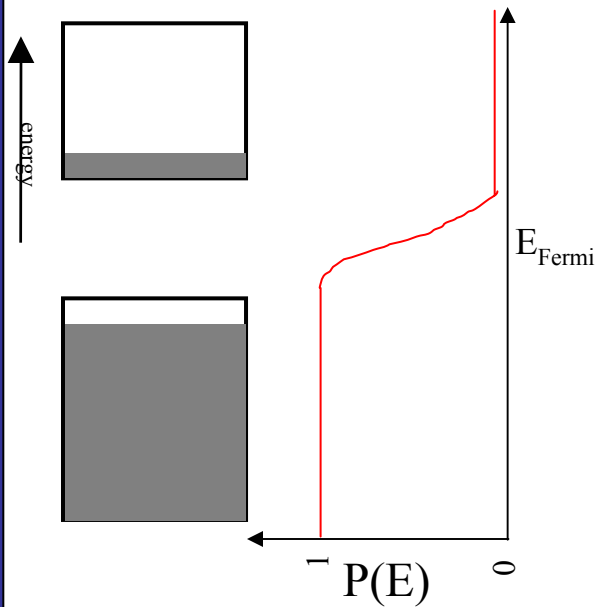
## n-type:



$$n > p$$

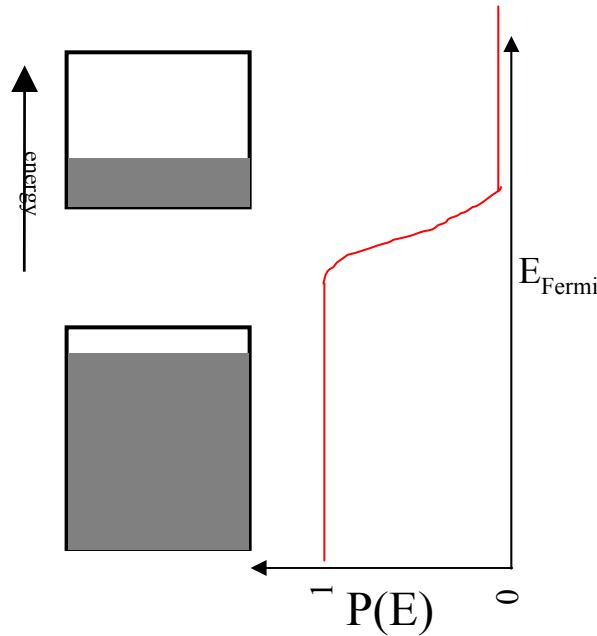
# In conclusion:

Intrinsic:



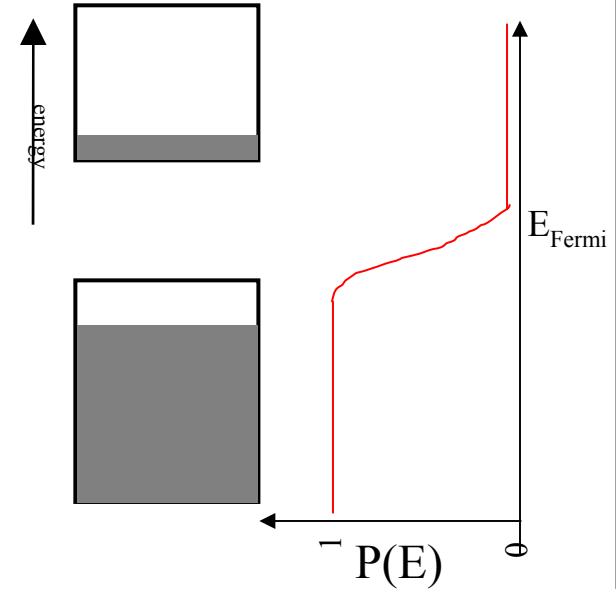
$$n = p$$

n-type:



$$n > p$$

p-type:



$$n < p$$

# What we've done:

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