Chapter 3 Intro. to the Quantum Theory of Solids

3.1 Allowed and Forbidden Energy Bands

In Chapter 2, we looked at the single proton & 1 electron atom, i.e., isolated hydrogen atom. However, hydrogen gas/molecules are H_2 (why? Trying to fill 1s shell.)

3.1.1 Formation of Energy Bands

* As shown in Fig. 3.1, we see the probability density function for an electron for a single H in lowest (n=1) energy state E_1.

* what happens if we have H_2?

⇒ The probability density functions for the electrons for the <u>two</u> atoms overlap. As a consequence, the electrons interact.

⇒ Pauli exclusion principle says that both electrons can <u>NOT</u> have the same quantum state. ($s=+\frac{1}{2}$ & $s=-\frac{1}{2}$)

⇒ E_1 splits into 2 energy levels! (They are still close, but distinct.)

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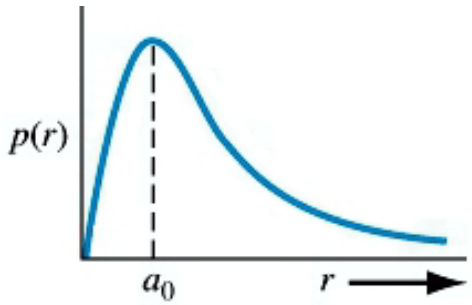

Figure 3.1 | (a) Probability density function of an isolated hydrogen atom.

- Remember that the Bohr radius $a_0 = 0.529$ Å.
- Next look at what happens when two hydrogen atoms (and their electrons) are put with in ~8 Å of one another.

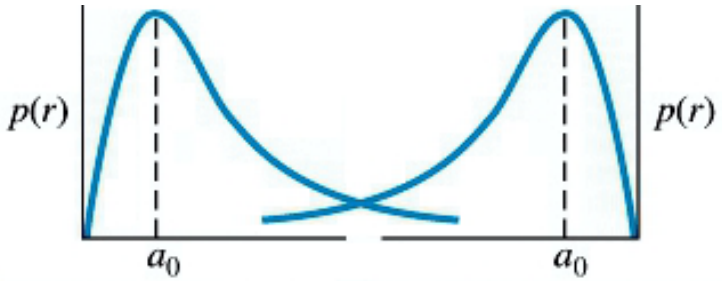

Figure 3.1 | (b) Overlapping probability density functions of two adjacent hydrogen atoms.

- Per Pauli exclusion principle, both electrons can not have the same quantum state ⇒ the E_1 energy state splits into two (very close) discrete energy states.

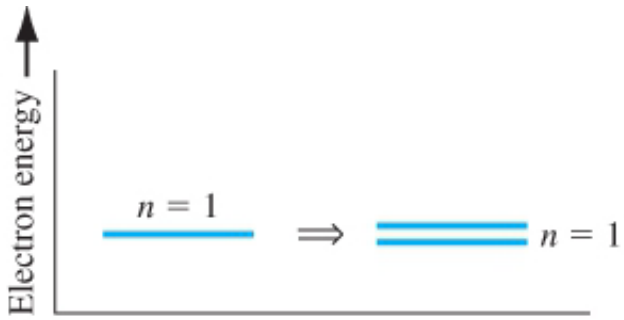

Figure 3.1 | (c) The splitting of the $n = 1$ state.

3.1.1 cont.

Pushing this concept further - what happens in materials like silicon (diamond lattice) where we have ~ $5 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3}$?

⇒ As shown in Fig. 3.2, each quantized energy level for the electrons w/ an isolated atom divide into a huge # of closely spaced energy levels (~ 5×10^{22}). Though these levels are technically still quantized/discrete, they are much (by orders of magnitude) closer together than those of the isolated atom.

⇒ 'energy bands' are formed as the atoms spacing reaches a distance $r \leq r_0$ (equilibrium interatomic distance of crystal)

(See Fig. 3.3 & Fig. 3.4)

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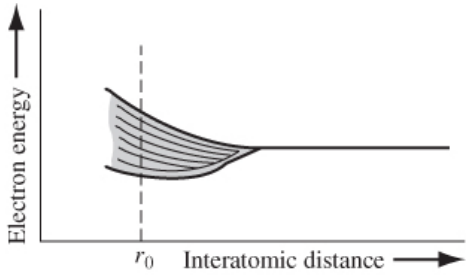

Figure 3.2 | The splitting of an energy state into a band of allowed energies.

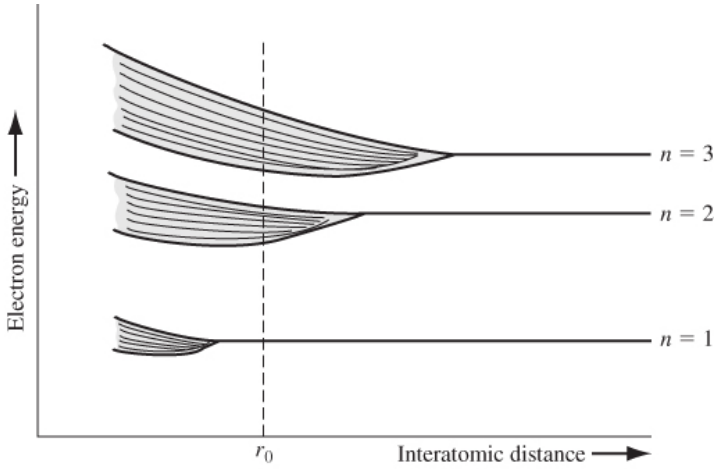

Figure 3.3 | Schematic showing the splitting of three energy states into allowed bands of energies.

- Energy states split as atoms get close enough for probability density functions of electrons to overlap, i.e., E_3 first, then E_2, …

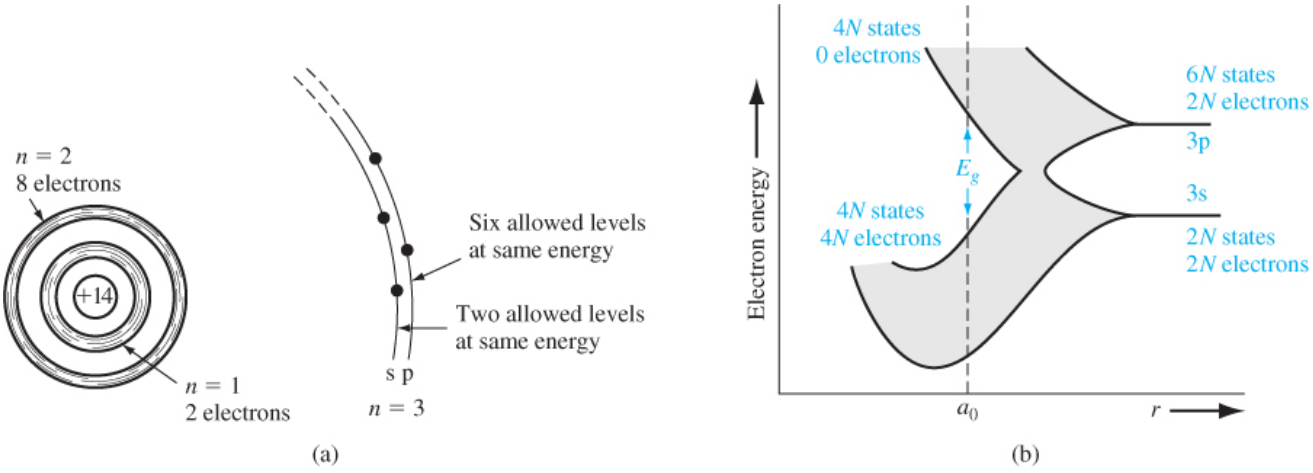

Figure 3.4 | (a) Schematic of an isolated silicon atom. (b) The splitting of the 3s and 3p states of silicon into the allowed and forbidden energy bands.
(From Shockley [6].)

- Splitting occurs for electrons in <u>outermost</u> energy level (quantum number $n = 3$).

3.1.2 The Kronig-Penney Model

→ Fig. 3.5 looks at what happens if we put like one-electron atoms in a row (1D problem). Results in overlapping potential functions

→ Fig 3.6 shows the 1-D Kronig-Penney model that approximates the overlapped potential functions w/ periodic (period a+b where a is width where V=0 and b is width where V=V0) potential barriers.

→ Using a math thm by Felix Bloch (Swiss phys.) the solution to the time-indep. Schrodinger wave function is of the form

$$\psi(x) = u(x)\, e^{jkx} \qquad k \equiv \text{wave number}$$

where u(x) is periodic function (period a+b)

→ For E<V0 (true for electrons in a crystal), we have a situation similar to the previous chapter when we had an electron encountering a finite height & width barrier (tunneling).

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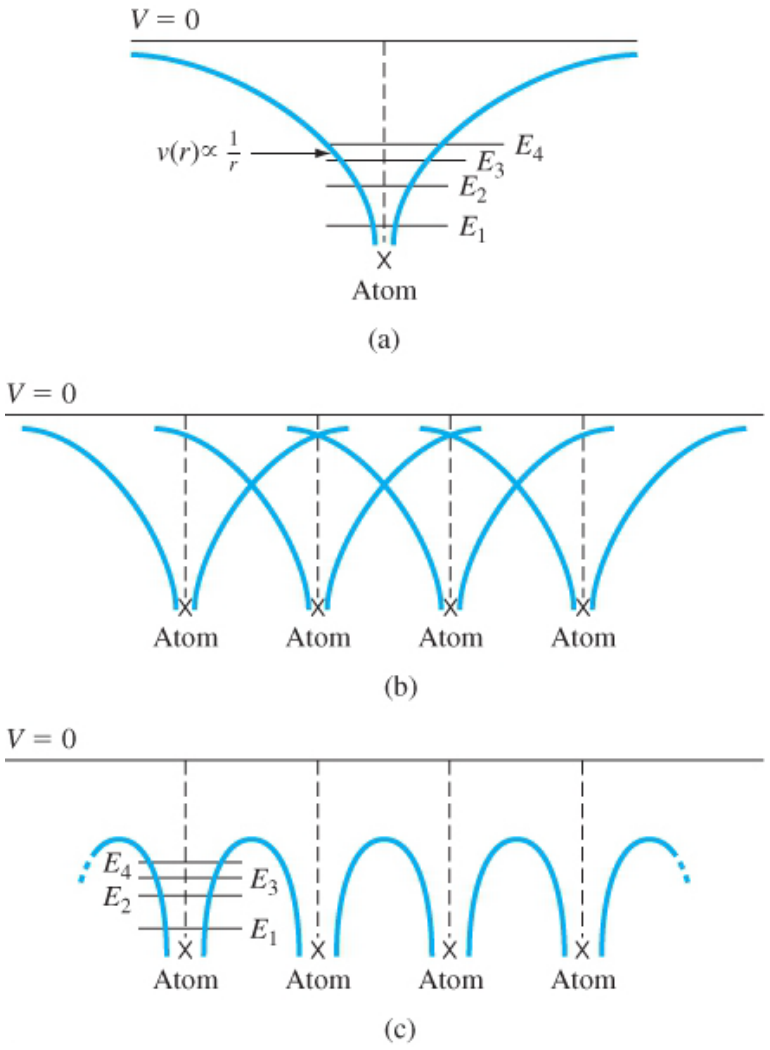

Figure 3.5 | (a) Potential function of a single isolated atom. (b) Overlapping potential functions of adjacent atoms. (c) Net potential function of a one-dimensional single crystal.

- Approximate as a series of periodic potential barriers, i.e., Kronig-Penney model.

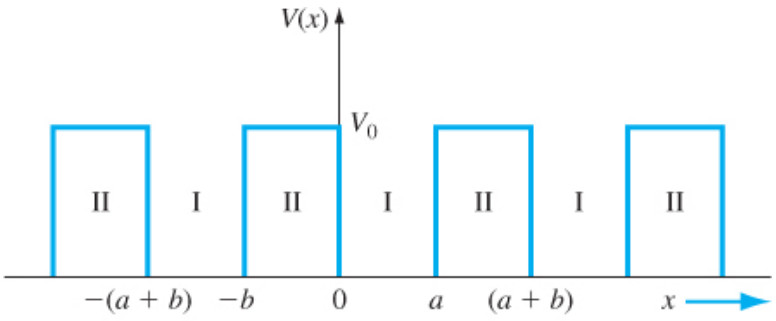

Figure 3.6 | The one-dimensional periodic potential function of the Kronig–Penney model.

3.1.2 cont.

$$\psi(x,t) = \psi(x)\phi(t) = u(x)e^{jkx}e^{-j(E/\hbar)t} \quad (3.2)$$

For Region I where $V=0$ $(0<x<a)$, we get a time-independent Schrodinger's eqn

$$\frac{d^2u_1(x)}{dx^2} + 2jk\frac{du_1(x)}{dx} - (k^2-\alpha^2)u_1(x) = 0 \quad (3.4)$$

where $u_1(x)$ is the amplitude of $\psi_1(x)$

and $$\alpha^2 = \frac{2mE}{\hbar^2} \quad (3.5)$$

For Region II where $V=V_0$ $(-b<x<0)$, we get

$$\frac{d^2u_2(x)}{dx^2} + 2jk\frac{du_2(x)}{dx} - \left(k^2-\alpha^2+\frac{2mV_0}{\hbar^2}\right)u_2(x) = 0$$

defining $$\beta^2 = \alpha^2 - \frac{2mV_0}{\hbar^2} = \frac{2m}{\hbar^2}(E-V_0)$$

this becomes

$$\frac{d^2u_2(x)}{dx^2} + 2jk\frac{du_2(x)}{dx} - (k^2-\beta^2)u_2(x) = 0 \quad (3.8)$$

$\Rightarrow$ For $E>V_0$, β is real.

$\Rightarrow$ For $E<V_0$, β imaginary. $\beta = j\gamma$

3.1.2 cont.

Solving these 2nd order ODEs yields

Region I $u_1(x) = A e^{j(\alpha - k)x} + B e^{-j(\alpha + k)x}$ $\quad 0 < x < a$

Region II $u_2(x) = C e^{j(\beta - k)x} + D e^{-j(\beta + k)x}$ $\quad -b < x < 0$

Apply boundary conditions @ $x = 0$

$$u_1(0) = A + B = C + D = u_2(0)$$

$$\left.\frac{du_1}{dx}\right|_{x=0} = (\alpha - k)A - (\alpha + k)B = (\beta - k)C - (\beta + k)D = \left.\frac{du_2}{dx}\right|_{x=0}$$

Apply boundary condition @ $x = a$ & $x = -b$ (using periodicity) to get

$$u_1(a) = A e^{j(\alpha - k)a} + B e^{-j(\alpha + k)a} = C e^{j(\beta - k)b} + D e^{-j(\beta + k)b} = u_2(-b)$$

$$\left.\frac{du_1}{dx}\right|_{x=a} = (\alpha - k)A e^{j(\alpha - k)a} - (\alpha + k)B e^{-j(\alpha - k)a}$$

$$= (\beta - k)C e^{-j(\beta - k)b} - (\beta + k)D e^{j(\beta + k)b} = \left.\frac{du_2}{dx}\right|_{x=-b}$$

⇓ lots of work

$$-\frac{(\alpha^2 + \beta^2)}{2\alpha\beta}\sin(\alpha a)\sin(\beta b) + \cos(\alpha a)\cos(\beta b) = \cos[k(a+b)] \quad (3.15)$$

3.1.2 cont.

For the case $E < V_0$ where

$$\beta^2 = -\frac{2m}{\hbar^2}(V_0 - E) \Rightarrow \beta = j\gamma = j\sqrt{\frac{2m(V_0-E)}{\hbar^2}},$$

this becomes

$$\frac{\gamma^2-\alpha^2}{2\alpha\gamma}\sin(\alpha a)\sinh(\gamma b) + \cos(\alpha a)\cosh(\gamma b) = \cos[k(a+b)] \quad (3.21)$$

↳ Not easy to solve. Must use numerical or graphical techniques. However, there are only certain values of αa (LHS) that give real values for k (RHS).

Letting $b \to 0$ (width of V_0 regions) and $V_0 \to \infty$ (height), but keep product bV_0 finite.

This yields - $\left(\frac{mV_0 ba}{\hbar^2}\right)\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka$

where we define $P' = \frac{mV_0 ba}{\hbar^2}$, yielding

$$P'\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka \quad (3.24)$$

↑ sinc()

Remember α depends on E

3.1.3 The K-Space Diagram

* Define some function $f(\alpha a) = P' \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$ for the LHS and plot the terms (Fig. 3.8)

* Since $f(\alpha a) = \cos ka$, we must have $-1 \leq f(\alpha a) \leq 1$ to get real solns to k via ka in the cos ka term, i.e. $f(\alpha a) = 1 \Rightarrow ka = 0$, $f(\alpha a) = -1 \Rightarrow ka = \pi$

* Remember $\alpha^2 = \frac{2mE}{\hbar^2}$, so for Fig 3.8 c) the horizontal axis is related to energy E whereas the vertical axis is related to k_0.

* Using only the shaded areas of Fig 3.8c), a plot of E versus k is generated Fig 3.9. Note that there are allowed energy ranges (bands) and forbidden energy bands

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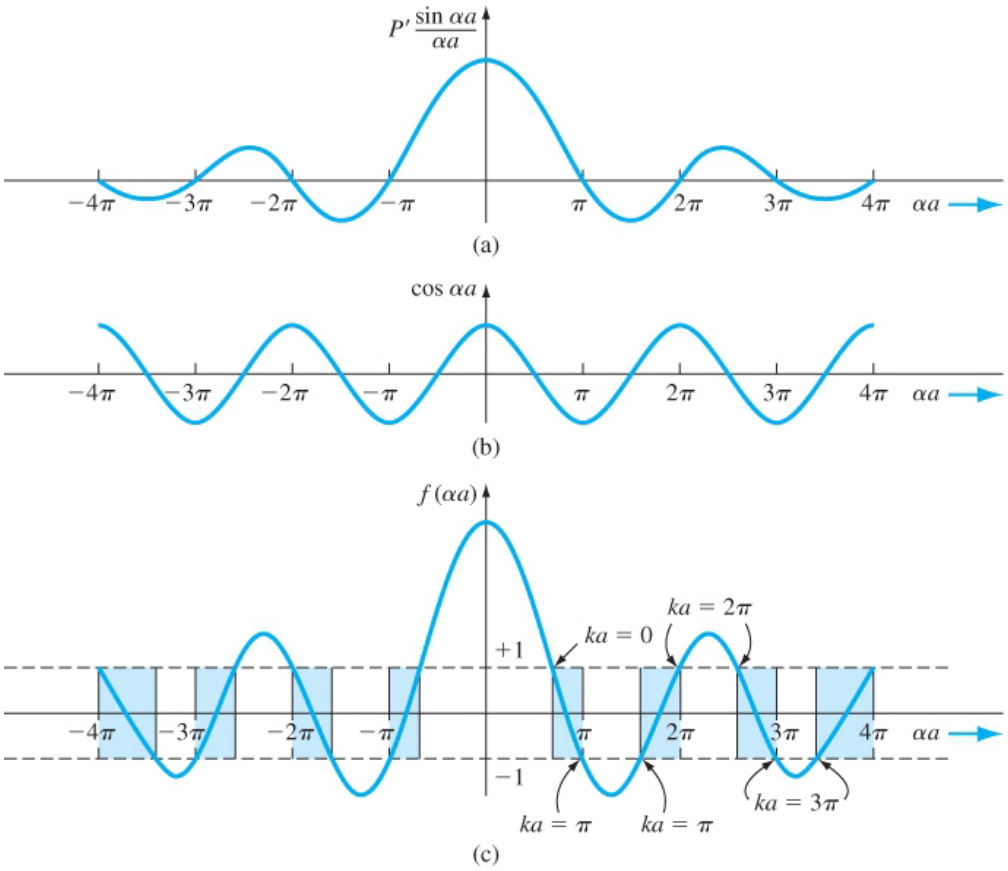

Figure 3.8 | A plot of (a) the first term in Equation (3.29), (b) the second term in Equation (3.29), and (c) the entire $f(\alpha a)$ function. The shaded areas show the allowed values of (αa) corresponding to real values of k.

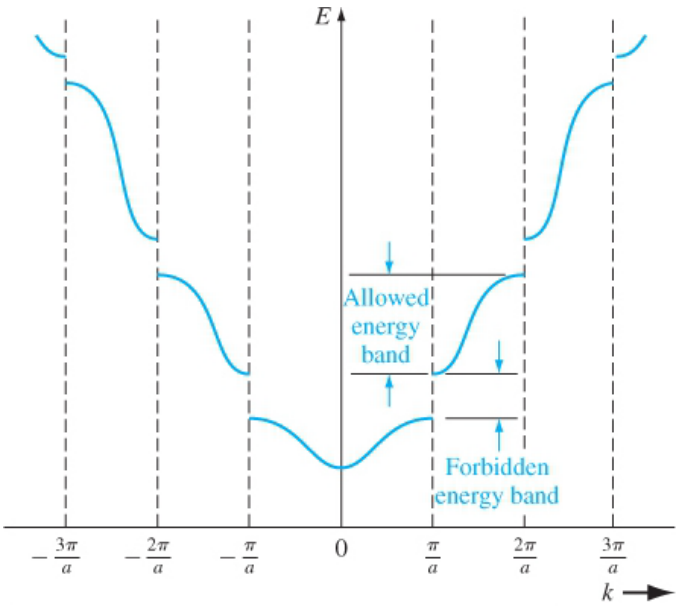

Figure 3.9 | The E versus k diagram generated from Figure 3.8. The allowed energy bands and forbidden energy bandgaps are indicated.

- Taking advantage of the fact that the cosine function is periodic, i.e.,

$$\cos(ka) = \cos(ka + 2n\pi) = \cos(ka - 2n\pi),$$

we can shift parts of the plot in Figure 3.9 to create a plot of E versus k in a reduced k-space. This is shown in Figures 3.10 and 3.11 and serves to clearly show the **allowed** and forbidden energy bands.

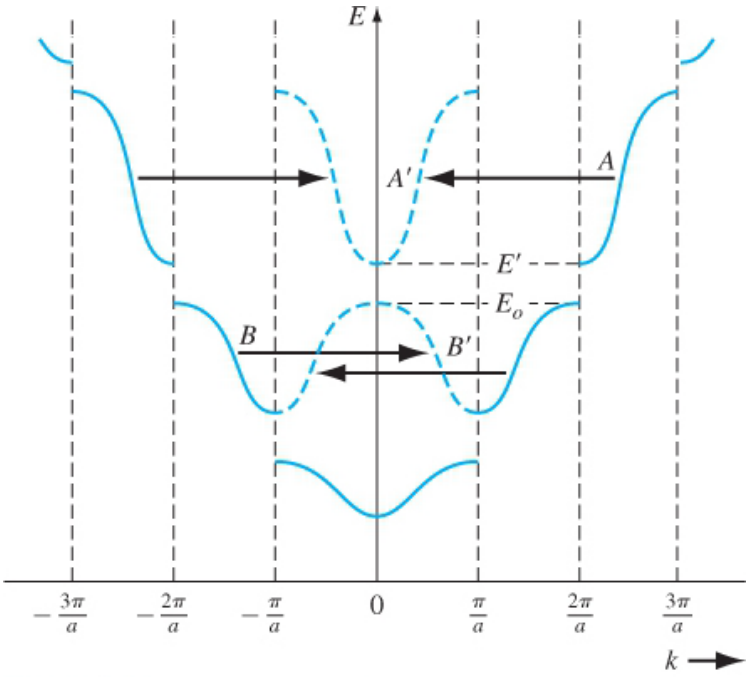

Figure 3.10 | The E versus k diagram showing 2π displacements of several sections of allowed energy bands.

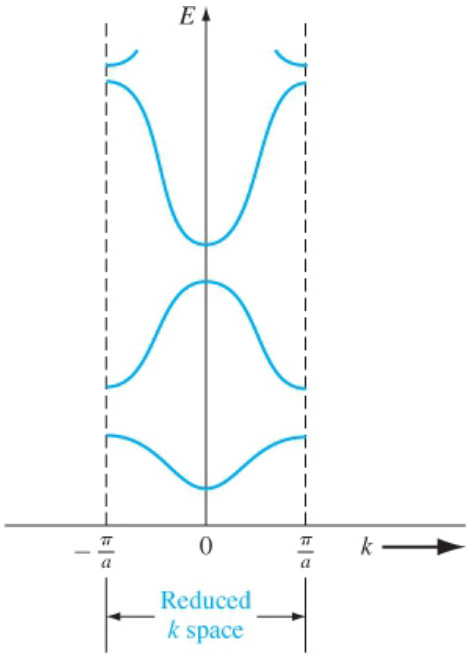

Figure 3.11 | The E versus k diagram in the reduced-zone representation.

3.2 Electrical Conduction in Solids

* At absolute zero, $K.E. = T = 0$, and all electrons in a crystal lattice are at their lowest energy state.
* This means the electrons fill the lowest energy bands in an orderly fashion starting w/ $n=1$, then $n=2$, ... (see Fig 3.12). The outermost band filled w/ electrons @ $T=0$ is the valence band. (See Fig 3.12)
* As the temperature of the material increases, some of the valence electrons will gain enough thermal energy ($T>0$) to go to the next higher energy band, called the conduction band.

⇒ See Fig 3.13 & Fig 3.4b (Si. l. con)

→ some empty covalent bonds (+)

→ some electrons free to roam about in crystal lattice See Fig 3.14

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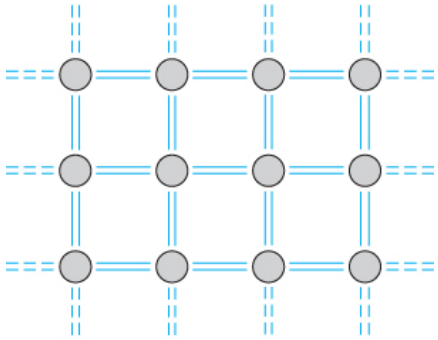


Figure 3.12 | Two-dimensional representation of the covalent bonding in a semiconductor at $T = 0$ K.

- Now, let temperature increase so that K.E. = $T > 0$

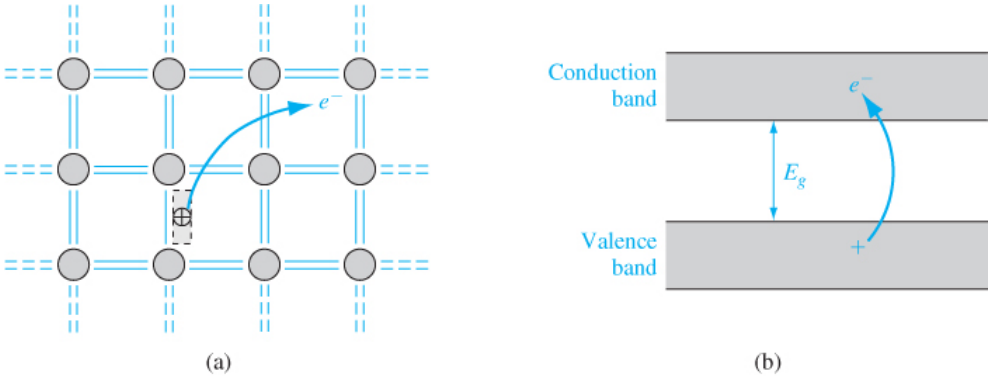


Figure 3.13 | (a) Two-dimensional representation of the breaking of a covalent bond. (b) Corresponding line representation of the energy band and the generation of a negative and positive charge with the breaking of a covalent bond.

- For silicon, we might see

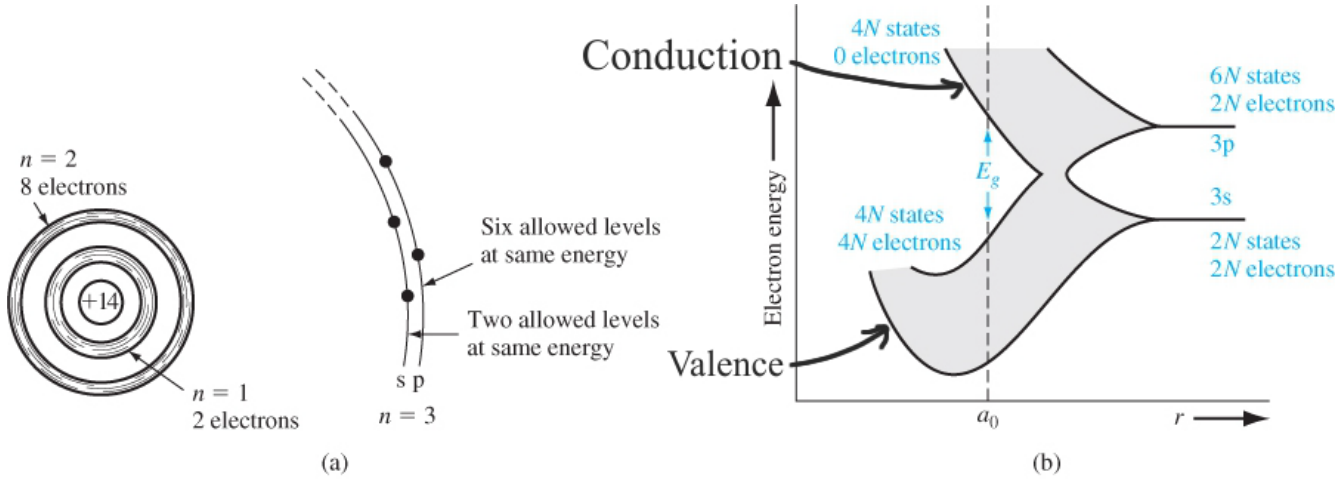


Figure 3.4 | (a) Schematic of an isolated silicon atom. (b) The splitting of the 3s and 3p states of silicon into the allowed and forbidden energy bands.
(From Shockley [6].)

- Looking at energy E versus k bands at a) 0 K and b) > 0 K, we see that some of the valence electrons in the highest energy states move to some of the lowest energy conduction states when there is thermal energy.

- Note the distribution is shown as symmetric as we are assuming there is no externally applied forces or fields.

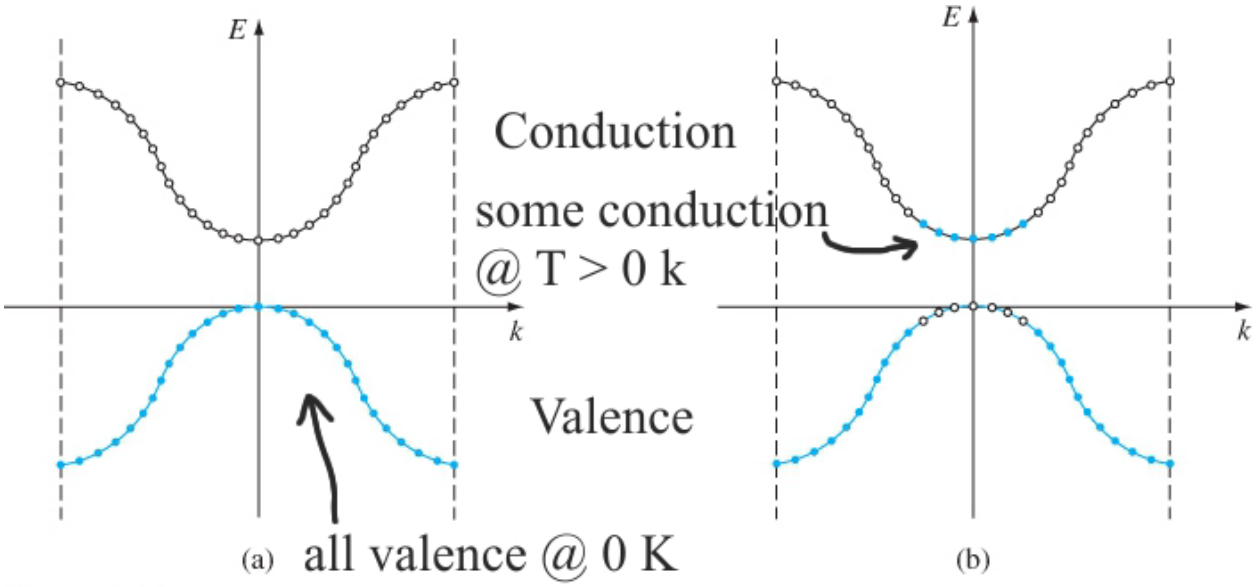


Figure 3.14 | The E versus k diagram of the conduction and valence bands of a semiconductor at (a) $T = 0$ K and (b) $T > 0$ K.

3.2.2 Drift Current

What if a voltage / electric field is applied externally?

Now some of the conduction electrons begin to move in response to Coulomb force $\bar{F} = q\bar{E}$.

Going back to EE 381, we have some current density $J = qNv_d$ (A/m^2 or A/cm^2)

where q = charge (of e^-), N = vol. density ($\#/m^3$ or $\#/cm^3$),

and v_d = drift velocity (m/s or cm/s).

If we look @ single electrons & add up

$$J = q\sum_{i=1}^{N} v_i$$

v_i ← velocity of i^{th} charge

N ← # electrons/unit vol.

$$= -e\sum_{i=1}^{N} v_i$$

How is this velocity related to the external force?

3.2.2 cont.

energy gain $= dE = F\,dx = F\,v\,dt$

F: force; dx: distance moved; $v\,dt$: distance @ velocity for Δt

3.2.3 Electron Effective Mass

The net force on an electron in a lattice is the sum of internal and external forces $F_{TOT} = F_{ext} + F_{int} = m a$

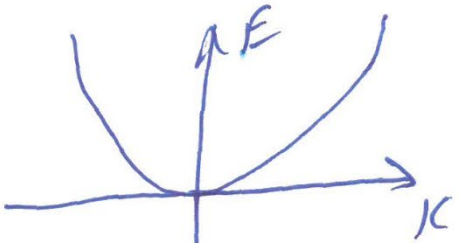
m: mass; a: acceleration

We can't measure F_{int}, so we define

$F_{ext} = m^* a$ where $m^* \equiv$ effective mass

Let's start w/ an electron in free space. Here

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



parabola

3.2.3 cont.

Take derivative wrt k

$$\frac{dE}{dk} = \frac{d}{dk}\left(\frac{\hbar^2}{2m}k^2\right) = \frac{\hbar^2}{m}k$$

Per (2.25b) $p = \hbar k$, so

$$\frac{dE}{dk} = \frac{\hbar p}{m} = \frac{\hbar m v}{m} = \hbar v$$

$$\hookrightarrow \quad v = \frac{1}{\hbar}\frac{dE}{dk} \qquad (3.39)$$

velocity related to slope of E vs k

What about $\frac{d^2E}{dk^2}$?

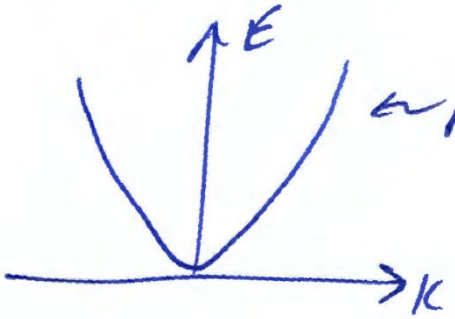
$$\frac{d^2E}{dk^2} = \frac{d}{dk}\left(\frac{\hbar^2}{m}k\right) = \frac{\hbar^2}{m}$$

$$\hookrightarrow \quad \frac{1}{m} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2} \qquad (3.41)$$

free space

$\Rightarrow$ Mass of electron is inversely proportional to 2nd derivative of E wrt k

$\Rightarrow$ From



← parabola

we see that $m > 0$ as $\frac{d^2E}{dk^2} > 0$

3.2.3 cont.

Looking at the two lower curves of Fig 3.11, we see in Fig 3.16a that we can approximate the E vs k curves for electrons in our 1D lattice w/ parabolas.

for Fig 3.16a, near bottom of conduction band

$$E - E_c \simeq C_1 k^2 \quad \text{where } C_1 \text{ is some positive constant}$$

(E_c: constant (minimum conduction band energy))

$$\frac{d^2(E-E_c)}{dk^2} = \frac{d^2E}{dk^2} = 2C_1$$

Mult. by $\frac{1}{\hbar^2}$ to get

$$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} = \frac{2C_1}{\hbar^2} = \frac{1}{m^*}$$ ← effective mass of conduction electron

Since $C_1 > 0 \Rightarrow m^* > 0$

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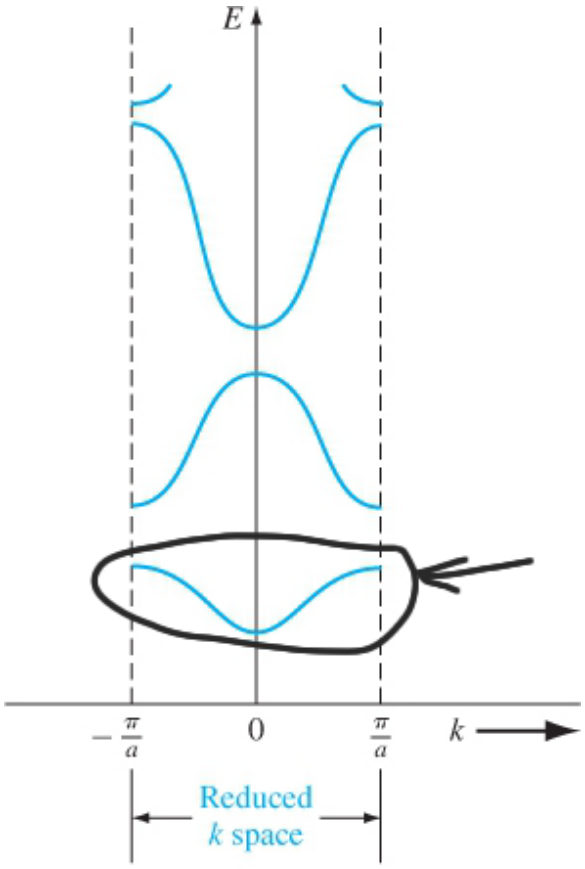
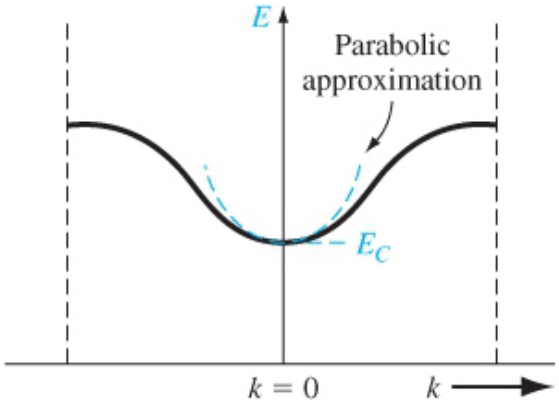


Figure 3.11 | The E versus k diagram in the reduced-zone representation.



(a)

Figure 3.16 | (a) The conduction band in reduced k space, and the parabolic approximation.

- E_C is the energy at the bottom of the conduction band (constant).

3.2.4 Concept of the Hole

So, what is going on in valence band when we have an applied voltage or $\bar{E}$ field?

As shown in Fig 3.17, the valence electrons now that the temp > 0K could change locations to fill the empty spots left by electrons going to the conduction band. Even though it is actually electrons moving, effectively it looks like a 'positive' charge called a 'hole' moving.

As shown in Fig 3.18, looking at the valence band, minus the electrons that went to the conduction band, it 'looks' as if the empty spots are filled w/ positive charges.

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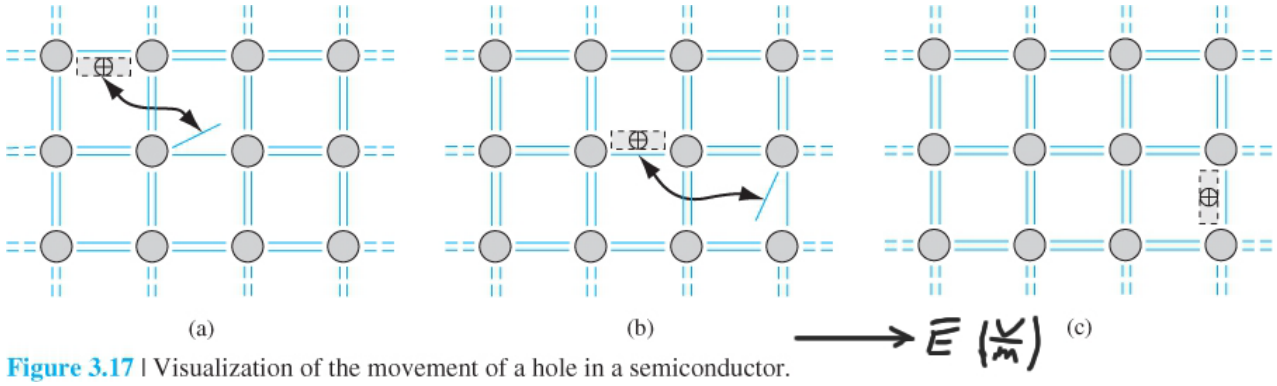


Figure 3.17 | Visualization of the movement of a hole in a semiconductor.

- The electrons are moving right to left while the holes are moving left to right.
- Looking at the valence energy bands-

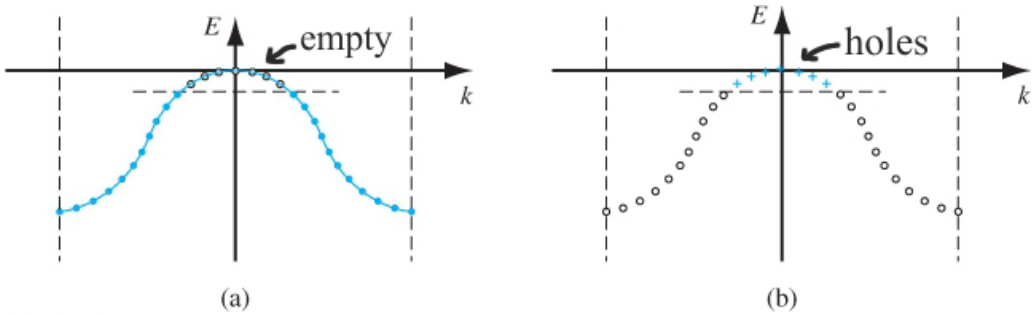


Figure 3.18 | (a) Valence band with conventional electron-filled states and empty states. (b) Concept of positive charges occupying the original empty states.

- Compare this with earlier energy versus *k* plots.

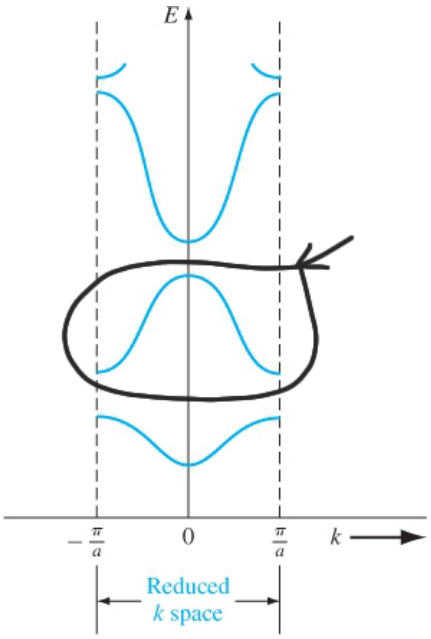


Figure 3.11 | The *E* versus *k* diagram in the reduced-zone representation.

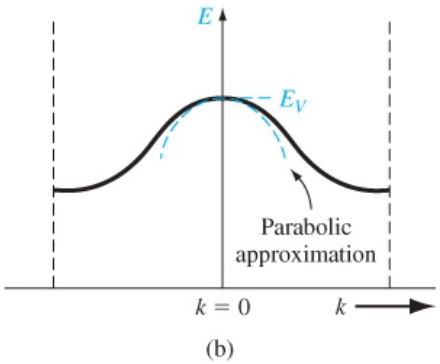


Figure 3.16 | (b) The valence band in reduced *k* space, and the parabolic approximation.

3.2.4 cont.

Now let's look at drift current in valence band.

$$J = -e \sum_{i(\text{filled})} v_i \quad \leftarrow \text{Not too useful}$$

$$= -e \sum_{i(\text{total})} v_i + e \sum_{i(\text{empty})} v_i$$

$\sum_{i(\text{total})}$: all filled (No net current)

$\sum_{i(\text{empty})}$: holes

$$J = 0 + e \sum v_i$$

$$\hookrightarrow v_i = v(E) = \frac{1}{\hbar}\frac{dE}{dk} \leftarrow \text{velocity of empty states (holes)}$$

Looking @ Fig. 3.16 b, we have

$$E = E_V - C_2 k^2$$

negative parabola $C_2 > 0$

$$\frac{d^2}{dk^2}\left(\right.$$

$$\frac{d^2E}{dk^2} = -2C_2$$

and $$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} = -\frac{2C_2}{\hbar^2} = \frac{1}{m^*}$$

$\Rightarrow m^*$ in this case is negative!

3.2.4 cont.

So electrons near top of valence band appear to have negative mass,

From $F = m^* a = e^- E$

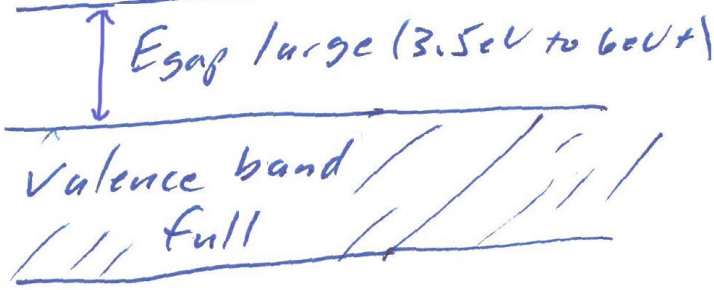
$\hookrightarrow a = \frac{-eE}{-|m^*|} = \frac{+eE}{|m^*|}$ or They go in same direction as applied $\bar{E}$ field (weird)

Rather than deal w/ this counterintuitive behavior. We'll instead consider these as holes (positive charge and positive mass m_p^*) going in the direction of applied $\bar{E}$. This makes much more sense :).

3.2.5 Metals, Insulators, & Semiconductors

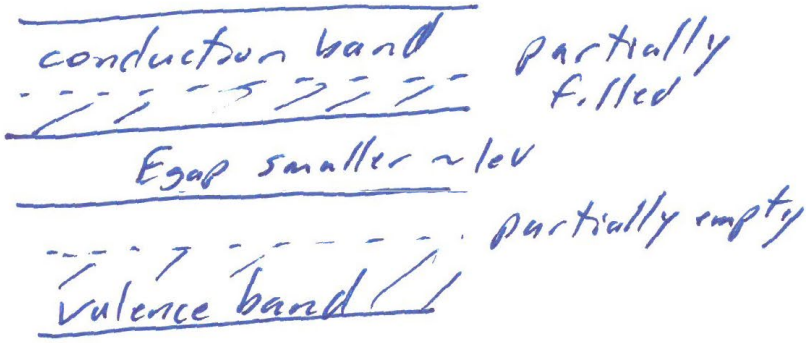
Insulators

σ low



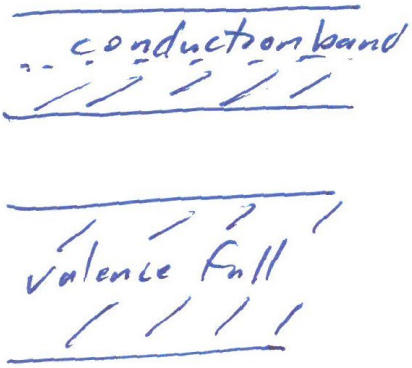
Semiconductors

σ moderate

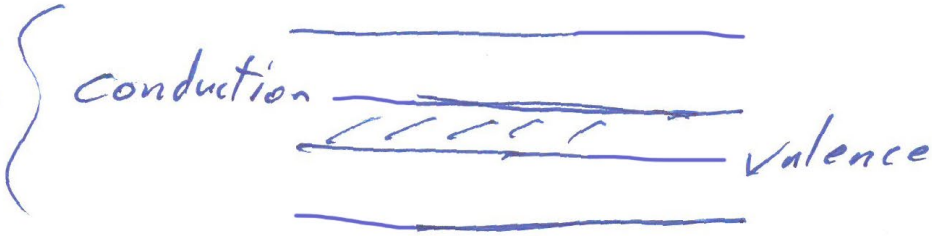


Metals

σ high



Overlap!



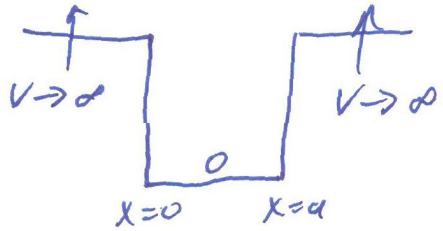
3.3 skip (Ext. to 3D)

3.4 Density of States Function

→ In semiconductors above OK, some electrons are going to jump up to the conduction band. We want to figure out how many free electrons are there, available to conduct current.

→ Our first step is to find the number of quantum states available at a particular energy level or band by the Density of States Function.

Back in Chap 2, we had the 1D Infinite Potential Well (2.3.2)



where the wave eqn was

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \qquad n = 1, 2, 3, \ldots$$

$$\hookrightarrow k_n = \frac{n\pi}{a} = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\hookrightarrow E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2}$$

3.4.1 Mathematical Derivation

Consider a free electron confined to a 3D infinite potential well.

Here, $V(x,y,z) = 0$ for $\left.\begin{array}{l} 0 < x < a \\ 0 < y < a \\ 0 < z < a \end{array}\right\}$ cubic crystal

$$V(x,y,z) \to \infty \text{ elsewhere}$$

Extrapolating our prior results and assuming separation of variables

$$k^2 = \frac{2mE}{\hbar^2} = k_x^2 + k_y^2 + k_z^2$$

$$= n_x^2 \frac{\pi^2}{a^2} + n_y^2 \frac{\pi^2}{a^2} + n_z^2 \pi^2/a^2$$

$$= \left(n_x^2 + n_y^2 + n_z^2\right) \frac{\pi^2}{a^2}$$

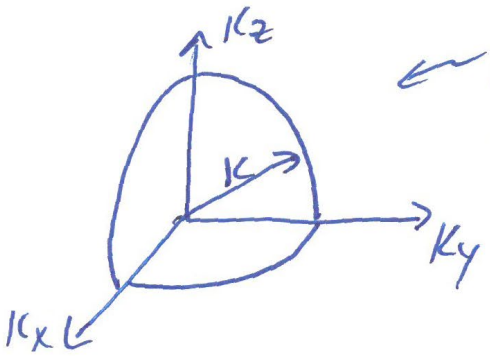
$n_x = 1, 2, \ldots$
$n_y = 1, 2, \ldots$
$n_z = 1, 2, \ldots$

In k-space, adjacent quantum steps are separated by π/a

e.g., $k_{x+1} - k_x = (n_x + 1)\pi/a - n_x \pi/a = \pi/a$.

Therefore, we can say the volume V_k of a single state is $V_k = (\pi/a)^3$

3.4.1 cont.



← positive octant radius k

→ differential change in volume of a sphere in k-space $\Delta Vol = \underbrace{4\pi k^2}_{\text{area}} \underbrace{dk}_{\text{increase in radius}}$

→ Then, the differential density of quantum states can be found by dividing ΔVol by V_k (vol. of single quantum state) w/ a couple tweaks. Tweak #1 - multiply by 2 to allow for + spin & - spin. Tweak #2 - multiply by $1/8$ since we are only doing positive octant.

$$\text{diff. density of quantum states} \equiv g_T(k)\,dk = 2\left(\frac{1}{8}\right)\frac{4\pi k^2 dk}{(\pi/a)^3}$$

$$= \frac{\pi k^2 dk}{\pi^3} a^3$$

Now $k^2 = \frac{2mE}{\hbar^2} \rightarrow k = \frac{\sqrt{2mE}}{\hbar} \rightarrow \frac{dk}{dE} = \frac{1}{\hbar}\sqrt{\frac{m}{2E}}$

3.4.1 cont.

Substituting for k^2 & dk yields

$$g_T(E)\,dE = \frac{\pi a^3}{\pi^3}\left(\frac{2mE}{\hbar^2}\right)\frac{1}{\hbar}\sqrt{\frac{m}{2E}}\,dE \quad (3.67)$$

which is the # of energy states between E & $E+dE$. Using $\hbar = h/2\pi$, we can get

$$g_T(E)\,dE = \frac{4\pi a^3}{h^3}(2m)^{3/2}\sqrt{E}\,dE \quad (3.68)$$

which is the # of energy states between E and $E+dE$ in the crystal volume a^3.

We divide by $a^3 dE$ to get the quantum states per unit volume & per unit energy

$$g(E) = \frac{4\pi(2m)^{3/2}}{h^2}\sqrt{E} \quad (3.69)$$

Obviously, $g(E)$ increases/decreases w/ $\sqrt{E}$, the energy of the electron.

3.4.2 Extension to Semiconductors

In section 3.2, we introduced parabolic approx. to the conduction & valence bands as well as effective masses.

For the conduction band, we have

$$E - E_c = \frac{\hbar^2 k^2}{2 m_n^*} \quad \text{upward parabola} \quad (3.71)$$

subscript $n \equiv$ negative

where m_n^* is the effective mass of the electrons for its electron density of states. Using this in conjunction w/ our 3D infinite quantum well results gives

$$g_c(E) = \frac{4\pi (2m_n^*)^{3/2}}{h^3} \sqrt{E - E_c} \quad (3.72)$$

as the density of allowed electronic energy states in the conduction band.

Note: $E \geq E_c$ for this to be valid.

$g_c(E = E_c) = 0$ (No states available for electrons)

$g_c(E)$ increases w/ E increasing.

3.4.2 cont.

In the valence band, we are using 'holes' w/ effective masses of m_p^* ($p \equiv$ positive) as our 'free' particles. Here

$$E_v - E = \frac{\hbar^2 k^2}{2 m_p^*} \qquad \text{downward parabola} \qquad (3.74)$$

which leads to

$$g_v(E) = \frac{4\pi (2 m_p^*)^{3/2}}{h^3} \sqrt{E_v - E} \qquad (3.75)$$

that is valid for $E \leq E_v$.

Notes: $g_v(E = E_v) = 0$ (No states available for holes)

$g_v(E)$ increases as E for holes decreases.

Also $g(E) = 0$ for $E_v < E < E_c$

$\Rightarrow$ No states available for holes or electrons in forbidden energy band

See Fig 3.27 & Table 4.1

From *Semiconductor Physics and Devices: Basic Principles* (4th Edition), Donald A. Neamen, McGraw Hill, 2012, ISBN 978-0-07-352958-5.

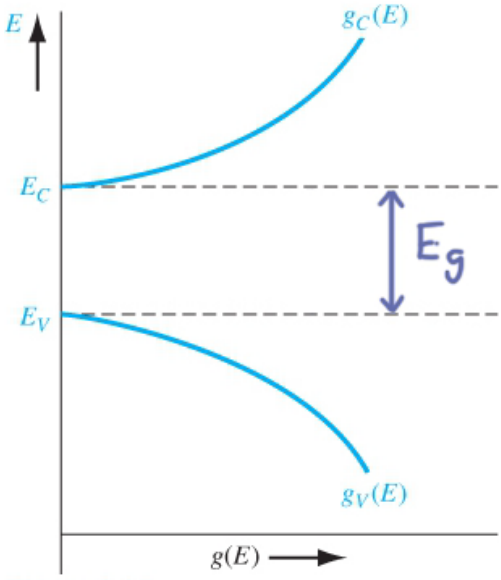


Figure 3.27 | The density of energy states in the conduction band and the density of energy states in the valence band as a function of energy.

➢ Looking ahead to Chapter 4, Table 4.1 gives some typical values (@ 300 K?).

Table 4.1 | Effective density of states function and density of states effective mass values

	N_c (cm^{-3})	N_v (cm^{-3})	m_n^*/m_0	m_p^*/m_0
Silicon	2.8×10^{19}	1.04×10^{19}	1.08	0.56
Gallium arsenide	4.7×10^{17}	7.0×10^{18}	0.067	0.48
Germanium	1.04×10^{19}	6.0×10^{18}	0.55	0.37

http://apachepersonal.miun.se/~gorthu/halvledare/Effective%20mass%20in%20semiconductors.htm

Effective mass and energy bandgap of Ge, Si and GaAs

Name	Symbol	Germanium	Silicon	Gallium Arsenide
Smallest energy bandgap at 300 K	E_g (eV)	0.66	1.12	1.424
Effective mass for density of states calculations				
Electrons	$m_e^*{}_{,dos}/m_0$	0.56	1.08	0.067
Holes	$m_h^*{}_{,dos}/m_0$	0.29	0.57/0.81[1]	0.47
Effective mass for conductivity calculations				
Electrons	$m_e^*{}_{,cond}/m_0$	0.12	0.26	0.067
Holes	$m_h^*{}_{,cond}/m_0$	0.21	0.36/0.386[1]	0.34

[1] Due to the fact that the heavy hole band does not have a spherical symmetry there is a discrepancy between the actual effective mass for density of states and conductivity calculations (number on the right) and the calculated value (number on the left) which is based on spherical constant-energy surfaces. The actual constant-energy surfaces in the heavy hole band are "warped", resembling a cube with rounded corners and dented-in faces.

3.4.2 cont.

ex. Find the number of quantum states for conduction electrons in germanium at 300K between E_c and $E_c + K_B T$ as well as the energy range (eV).

From the online info given:

$$E_g = 0.66\,eV, \quad m_n^* = 0.55\,m_0$$

$$K_B T = 1.380649 \times 10^{-23}\,J/K\,(300K)$$

$$= 4.14195 \times 10^{-21}\,J = 0.02585\,eV$$

$$N_{c,Ge} = \int g_c(E)\,dE = \int_{E_c}^{E_c + K_B T} \frac{4\pi (2m_n^*)^{3/2}}{h^3} \sqrt{E - E_c}\,dE$$

$$= \frac{4\pi (2m_n^*)^{3/2}}{h^3} \frac{2}{3} (E - E_c)^{3/2} \Big|_{E_c}^{E_c + K_B T}$$

$$= \frac{4\pi \left[2(0.55)9.1093837 \times 10^{-31}\right]^{3/2}}{(6.62607 \times 10^{-34})^3} 2/3 \left[K_B T - 0 \right]^{3/2}, \quad K_B T = 4.14195 \times 10^{-21}$$

$$N_{c,Ge} = 7.7 \times 10^{24}\,\frac{states}{m^3} = 7.7 \times 10^{18}\,\frac{states}{cm^3}$$

Similar to value of $N_c = 1.04 \times 10^{19}\,\frac{states}{cm^3}$ given in Table 4.1 (bit lower).

3.5 Statistical Mechanics

→ We are looking at overall behavior of extremely large numbers of particles (e.g., electrons &/or holes) rather than individual particles

3.5.1 Statistical Laws

→ We want to find the probability that the available quantum states are filled

Three distribution laws

1) Maxwell-Boltzmann probability function
   - particles are distinguishable
   - no limit to # per state
   e.g., gases in a container, low press.

2) Bose-Einstein function
   - particles are indistinguishable
   - no limit to # per state
   e.g., photons or black body rad.

★ 3) Fermi-Dirac probability function
   - particles are indistinguishable
   - 1 particle per state (Pauli exclusion principle)
   e.g., electrons or holes in a crystal

⇒ In each case, we assume particles do not interact.

3.5.2 The Fermi-Dirac Probability Function

Looking @ the i^{th} energy level w/ g_i quantum states in which to put N_i particles ($N_i \leq g_i$)

Initial $\underline{\quad}_1\ \underline{\quad}_2\ \underline{\quad}_3\ \cdots\ \underline{\quad}_{g_i}$ ← g_i spots altogether.

1st $\quad -\ -\ \underline{\bullet}\ \cdots\ \underline{\quad}_{g_i}$ ← g_i spots to choose from

2nd $\quad -\ \underline{\bullet}\ \underline{\bullet}\ \cdots\ \underline{\quad}_{g_i}$ ← $(g_i - 1)$ spots to choose from

⇓

Total number of ways to arrange N_i particles is then

$$g_i(g_i-1)(g_i-2)\cdots\left[g_i-(N_i-1)\right] = \frac{g_i!}{(g_i-N_i)!} \quad (3.76)$$

However, we must take into account that the particles are indistinguishable

e.g., $\quad -\ \underline{\overset{A}{\bullet}}\ \underline{\overset{B}{\bullet}} \quad = \quad -\ \underline{\overset{B}{\bullet}}\ \underline{\overset{A}{\bullet}}$

It turns out that there are $N_i!$ permutations that are duplicates if particles are indistinguishable.

3.5.2 cont.

Therefore, the # of independent ways to arrange/distribute particles @ the i^{th} energy level is:

$$W_i = \frac{g_i!}{N_i!(g_i - N_i)!} \qquad (3.77)$$

ex. Let's say we have 6 particles to fit in 9 states

$$W_i = \frac{9!}{6!(9-6)!} = \frac{9(8)(7)\,6!}{6!\,(3!)} = \frac{9(8)7}{3(2)(1)}$$

$$W_i = 84$$

Next, we need to extend this result to cover all $i = 1, \ldots, n$ energy levels

$$W = \prod_{i=1}^{n} \frac{g_i!}{N_i!(g_i - N_i)!} \qquad (3.79)$$

↑ product operator

This is the total number of ways that N electrons can be arranged

$$N = \sum_{i=1}^{n} N_i \qquad N_i = \#\text{ electrons at a particular level}$$

3.5.2 cont.

For a fixed number of particles w/ a constant total energy, we can find the most probable distribution function by varying N_i amongst the various levels as:

Fermi-Dirac distribution or prob. function

$$f_F(E) = \frac{N(E)}{g(E)}$$

$N(E)$ ← # density of particles (electrons) per unit volume & per unit energy

$g(E)$ ← # quantum states per unit volume & per unit energy

$$f_F(E) = \frac{1}{1 + e^{\left(\frac{E - E_F}{k_B T}\right)}} \quad (3.79)$$

where $E_F \equiv$ Fermi energy (eV or J)

$k_B \equiv$ Boltzmann's Constant ($\frac{eV}{K}$ or $\frac{J}{K}$)

$T \equiv$ temp. in Kelvin

$\Rightarrow f_F(E)$ gives the probability of a quantum energy state being filled at a particular energy E, i.e., ratio of filled to total # of quantum states

3.5.2 cont.

@ $T = 0\,K$

If $E < E_F$, $f_F(E) = \frac{1}{1+e^{-(E_F-E)}} = \frac{1}{1+e^{-\infty}}$

↳ $E - E_F < 0$

$= 1$ ⇐ 100% probability states are filled

If $E > E_F$, $f_F(E) = \frac{1}{1+e^{E-E_F/0}} = \frac{1}{1+e^{\infty}}$

↳ $E - E_F > 0$

$= 0$ ⇐ 0% probability states are filled

⇒ Makes sense. Valence energy bands (will be below E_F) are all full @ 0K, No conduction electrons.

Above absolute zero, $T > 0K$, $k_B T > 0$

Note: $f_F(E = E_F) = \frac{1}{1+e^{(E_F-E_F)/k_BT}} = \frac{1}{1+e^{0}}$

$= 1/2$ ⇐ Temp. independent!

50% probability energy level is filled.

Typically, $E_V < E_F \cong \frac{E_V + E_C}{2} < E_C$

usually small correction for temp

From *Semiconductor Physics and Devices: Basic Principles* (4th Edition), Donald A. Neamen, McGraw Hill, 2012, ISBN 978-0-07-352958-5.

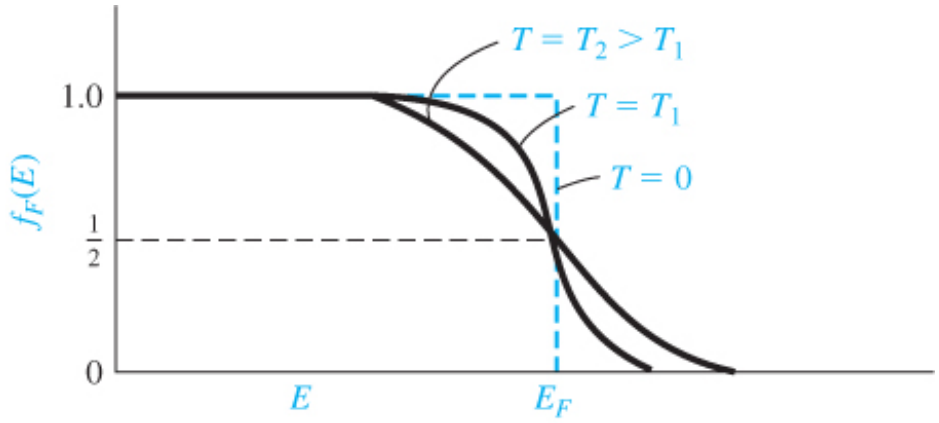
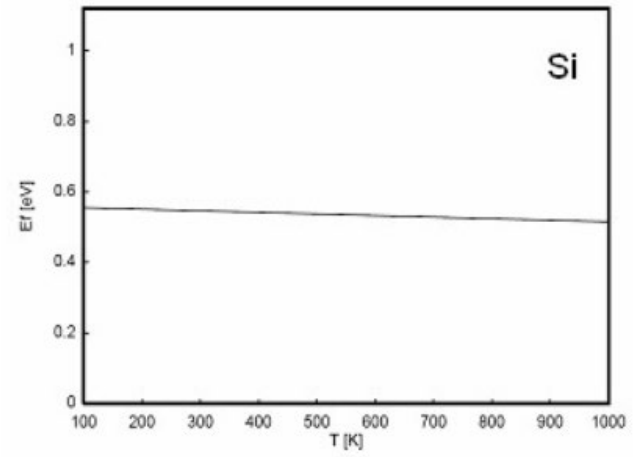
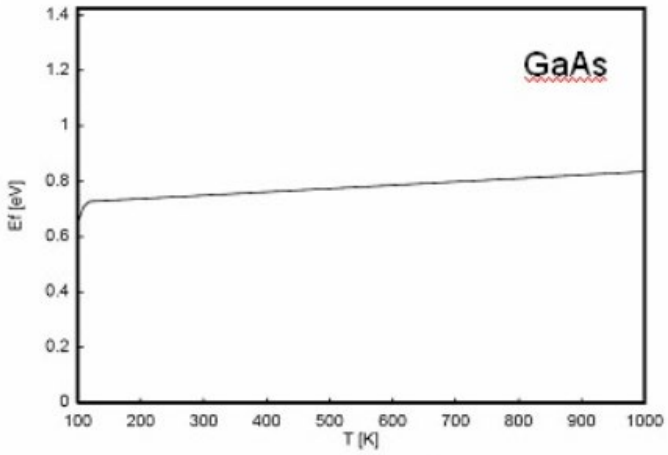


Figure 3.33 | The Fermi probability function versus energy for different temperatures.

- Note that $f_F(E)$ always passes through 0.5 at $E = E_F$.
- Note that $f_F(E)$ spreads out as temperature increases.

From https://lampx.tugraz.at/~hadley/psd/weblectures/Ef_intrinsic/index.php#:~:text=The%20Fermi%20energy%20is%20in,kBT%20~%200.025%20eV.

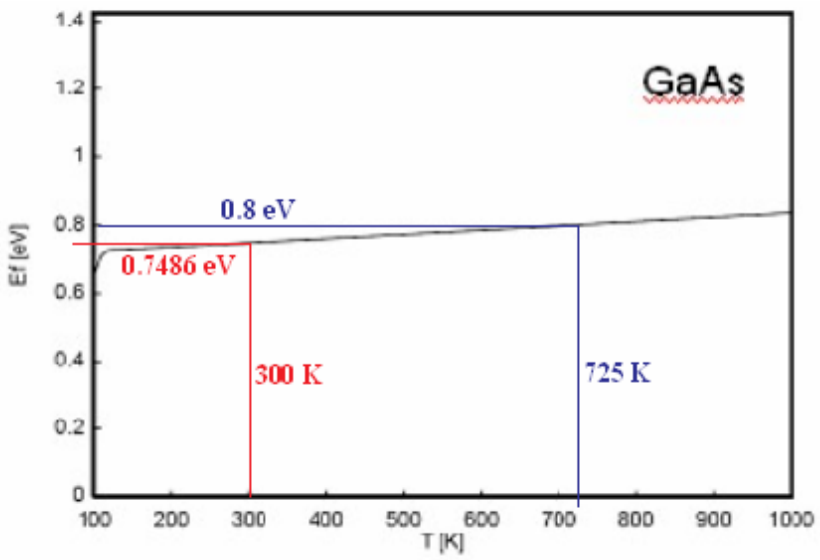




Properties	Si	Ge	GaAs
Bandgap E_g	1.12 eV	0.66 eV	1.424 eV
Effective density of states in conduction band (300 K) N_c	2.78×10^{25} m^{-3}	1.04×10^{25} m^{-3}	4.45×10^{23} m^{-3}
Effective density of states in valence band (300 K) N_v	9.84×10^{24} m^{-3}	6.0×10^{24} m^{-3}	7.72×10^{24} m^{-3}
Effective mass electrons m^*/m_0	$m_l^* = 0.98$ $m_t^* = 0.19$	$m_l^* = 1.64$ $m_t^* = 0.082$	$m^* = 0.067$
Effective mass holes m^*/m_0	$m_{lh}^* = 0.16$ $m_{hh}^* = 0.49$	$m_{lh}^* = 0.044$ $m_{hh}^* = 0.28$	$m_{lh}^* = 0.082$ $m_{hh}^* = 0.45$

Using MathCad

Example- Plot Fermi-Dirac probability function vs *E* (eV) at 300 K and 725 K for GaAs.



$kB\_eV := 8.617333 \cdot 10^{-5}$ eV/K

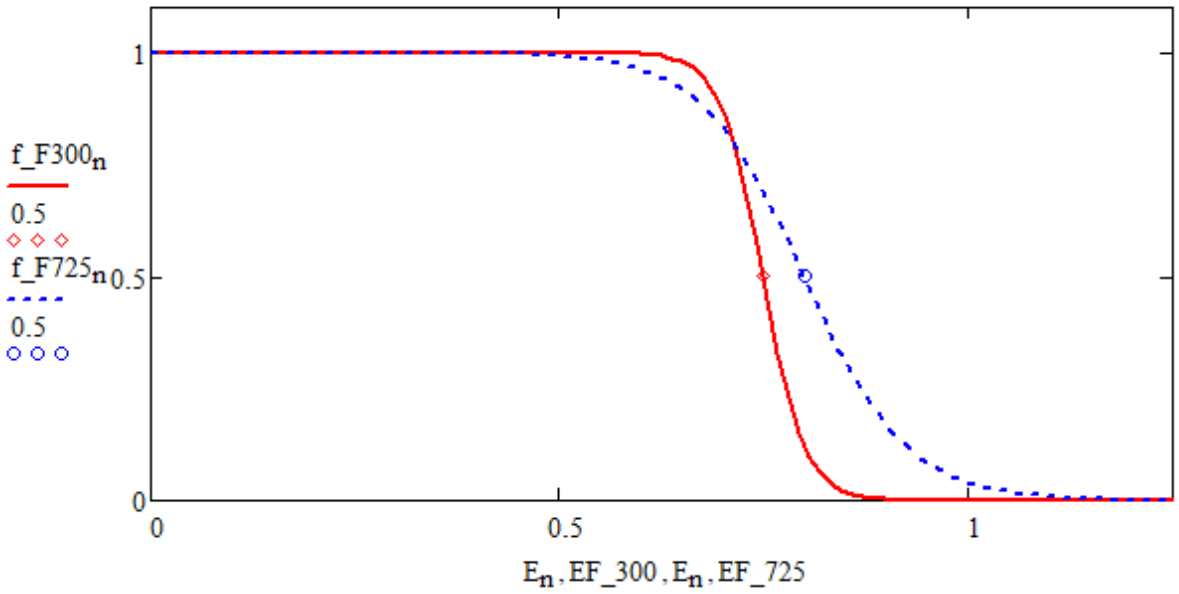
From graph, the Fermi energies for GaAs @ 300 K & 725 K are

$EF\_300 := 0.7486$ eV $\quad kB\_eV \cdot 300 = 0.025852$ eV

$EF\_725 := 0.8$ eV $\quad kB\_eV \cdot 725 = 0.062476$ eV

$n := 0 .. 100$

$E_n := \frac{n}{100} \cdot 1.3$ $\quad f\_F300_n := \frac{1}{1 + e^{\left(\frac{E_n - EF\_300}{kB\_eV \cdot 300}\right)}}$ $\quad f\_F725_n := \frac{1}{1 + e^{\left(\frac{E_n - EF\_725}{kB\_eV \cdot 725}\right)}}$



3.5.3 cont.

What about holes?

If/Since $f_F(E)$ gives the probability of an energy quantum state being filled w/ an electron, it makes sense that $1 - f_F(E)$ would be the probability of of a state NOT being filled w/ an electron (empty) ⇒ hole!

* As shown in next example, $f_F(E)$ and $1 - f_F(E)$ essentially are mirror images about E_F.

Maxwell-Boltzmann Approximation

When $(E - E_F) >> K_B T$, we can ignore factor of 1 in the denominator and get

$$f_F(E) \simeq e^{-\left(\frac{E - E_F}{K_B T}\right)}$$

How big is good enough? Using MathCad, when $E - E_F \simeq 4.6 K_B T$, the error is ~1%.

Using MathCad-

Example- Plot Fermi-Dirac electron and hole probability functions vs E (eV) at 725 K for GaAs. Also, plot Maxwell-Boltzmann approximation.

$kB\_eV := 8.617333 \cdot 10^{-5}$ eV/K

From graph (earlier)- $EF\_725 := 0.8$ eV $kB\_eV \cdot 725 = 0.062476$ eV

$n := 0 .. 100$ $E_n := \frac{n}{100} \cdot 1.6$ $E2_n := E_n + EF\_725$

$$f\_F725_n := \frac{1}{1 + e^{\left(\frac{E_n - EF\_725}{kB\_eV \cdot 725}\right)}} \qquad f\_FMB_n := e^{-\left(\frac{E2_n - EF\_725}{kB\_eV \cdot 725}\right)}$$