



Lecture 4

Reading Material



Reading:

Chapter 6 Solymar and Walsh

Last Lecture



- ✓ Coupled States:

- ✓ If there is no coupling, $E=E_0$

- ✓ If there is coupling, the energy level is split into two new levels E_0+A and E_0-A

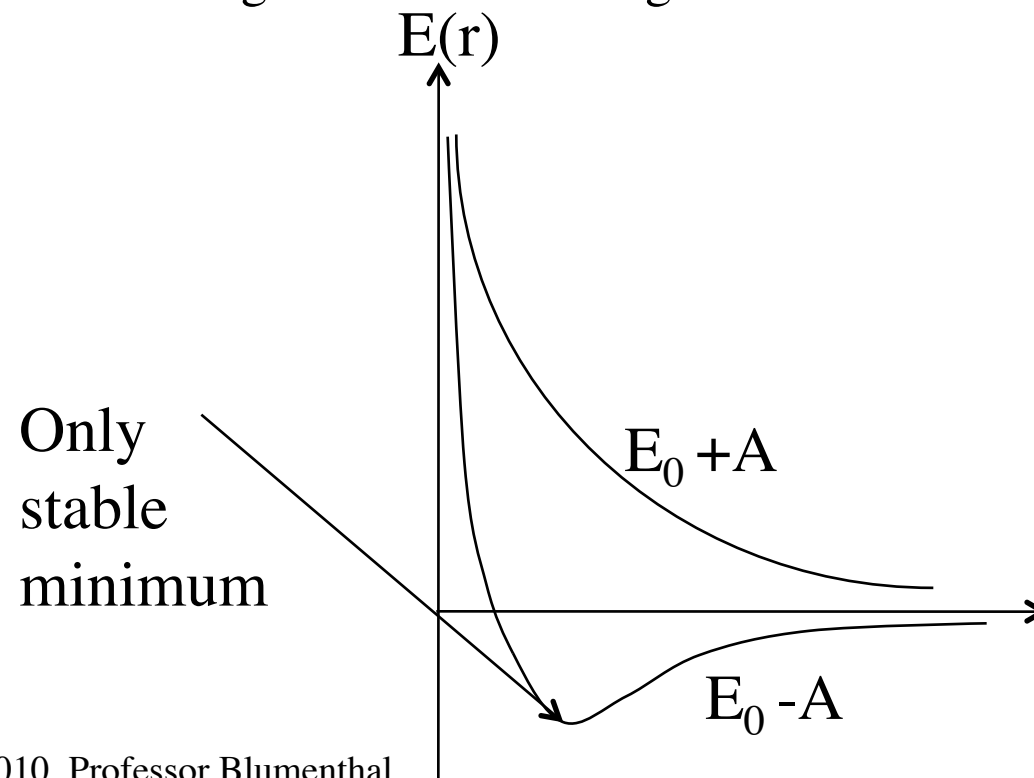
Coupled Schrodinger's Equations

- Lets consider the simplest case where there are two solutions $j=1$ and $j=2$.
- Our two Diff. equations will look like

$$\begin{aligned} i\hbar \frac{d(\omega_1(t))}{dt} &= H_{11}\omega_1(t) + \boxed{\text{Coupling Term}} \\ i\hbar \frac{d(\omega_2(t))}{dt} &= \boxed{\text{Coupling Term}} + H_{22}\omega_2(t) \end{aligned}$$

Coupled States

- As the two are brought together from infinity, only one solution has attractive and repulsive forces balance out to a stable solution.
- In the time dynamic solution, the electron can jump from one nucleus to the other and a sharing can occur forming a bond.



Chapter 6 – Free Electron Theory of Metals



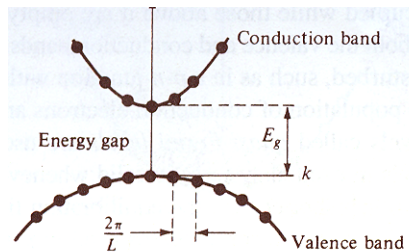
- ⇒ What do we know about metals?
 - ⇒ Conducts electricity – low resistance
 - ⇒ Good thermal conductor
- ⇒ What can we guess about metals?
 - ⇒ Electrons are free to flow and with net current zero the motion is random
 - ⇒ There are atoms inside the metal but most valence electrons (if not all) are free to move
 - ⇒ The electrons are bounded by the surface of the metal – it does not appear easy for them to escape the metal without connecting the metal to a circuit – it may be as if there is an infinite potential boundary at the surface.
 - ⇒ The potential (and kinetic) energy of the electron should be affected by the presence of all the other electrons and nuclei.

The Free Electron Model of Metals

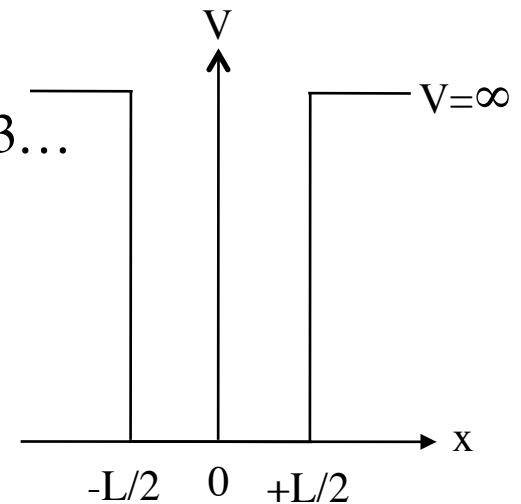
- Assume all electrons have the same potential energy – Sommerfeld (1928).
- Consider first the model of a potential well of width (L) with infinite walls, an energy (E) of a state the electron can occupy, the electrons momentum (k) and its effective mass (m).

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

$$E|_{\text{Potential Well } V=\infty} = \frac{\hbar^2}{8m} \frac{n^2}{L}, n = 1, 2, 3, \dots$$



E vs. k is quadratic with curvature given by the carrier effective mass m (*Semiconductor*)



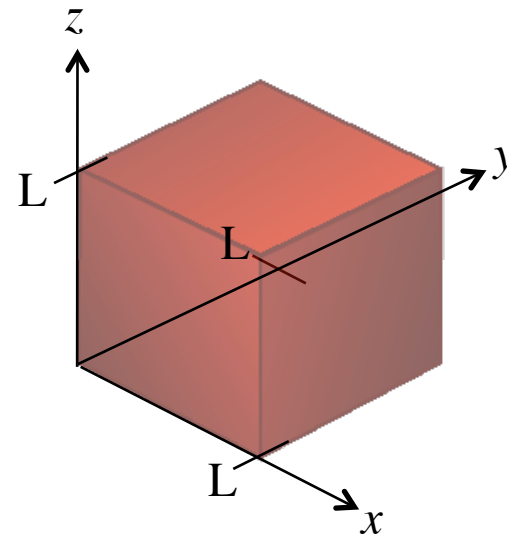
The Free Electron Model of Metals

- Now let's look at a cube with sides L that contains the electrons. The electron energy can be written as

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

$$= \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

$$n_x, n_y, n_z = 1, 2, 3, \dots$$



Energy Level Differences vs. n

- Note that the difference between each adjacent energy level is dependent on the square of the energy level number (n).

$$\text{Let } n^2 = n_x^2 + n_y^2 + n_z^2$$

$$E_n = \frac{\hbar^2}{8mL^2} n^2$$

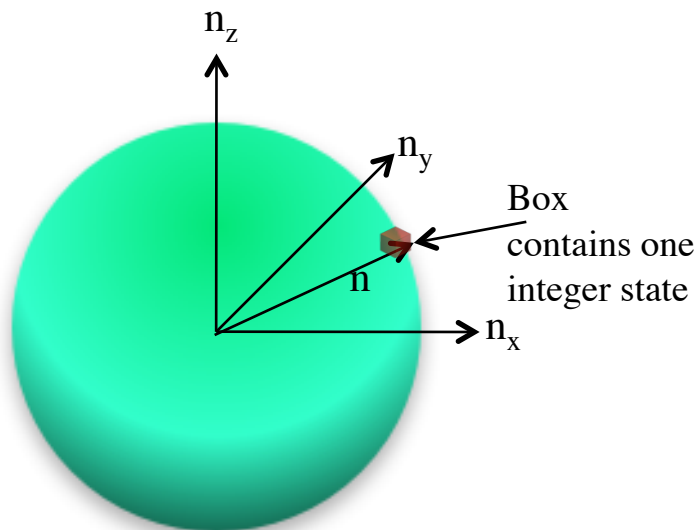
$$E_{n-1} = \frac{\hbar^2}{8mL^2} (n-1)^2$$

$$\Delta E = E_n - E_{n-1} = \frac{\hbar^2}{8mL^2} [n^2 - (n-1)^2] = -\frac{3\hbar^2}{8mL^2} [2n + 1]$$

- ΔE increases with increasing n !

Density of States

- How many energy states are there between energy levels E and $E+dE$?



In a sphere of radius n there are

$$\frac{4n^3\pi}{3} \text{ states}$$

Since

$$n = \left(\frac{8mL^2}{h^2} E \right)^{1/2}$$

The number of states with energy less than E are

$$\frac{4\pi}{3} \left(\frac{8mL^2}{h^2} E \right)^{3/2} = \frac{4\pi}{3} \left(\frac{8mL^2}{h^2} \right)^{3/2} E^{3/2}$$

and the number of states with energy less than $E + dE$ are

$$\frac{4\pi}{3} \left(\frac{8mL^2}{h^2} \right)^{3/2} (E + dE)^{3/2}$$

The number of states between E and $E + dE$ is

$$Z(E)dE = \frac{4\pi}{3} \left(\frac{8mL^2}{h^2} \right)^{3/2} (E + dE)^{3/2} - \frac{4\pi}{3} \left(\frac{8mL^2}{h^2} \right)^{3/2} E^{3/2} = \frac{4\pi}{3} \left(\frac{8mL^2}{h^2} \right)^{3/2} [(E + dE)^{3/2} - E^{3/2}]$$

$$Z(E)dE \approx 2\pi \left(\frac{8mL^2}{h^2} \right)^{3/2} E^{1/2} dE$$

Accounting for positive integer values for n only and 2 spin states per energy level

$$Z(E)dE \approx \frac{2}{8} 2\pi \left(\frac{8mL^2}{h^2} \right)^{3/2} E^{1/2} dE = \frac{\pi}{2} (8m)^{3/2} \left(\frac{L}{h} \right)^3 E^{1/2} dE$$

Fermi-Dirac Statistics



- Electrons are Fermions.
- No two Fermions can occupy the same state in the same incrementally small volume – Pauli Exclusion Principle
- Populating the lowest states first and adding electrons while maintaining the Pauli Exclusion Principle, and letting the number of electrons approach infinity
- The probability that a state at energy (E) is occupied by an electron is given by the Fermi-Dirac function

$$f(E) = \frac{1}{e^{(E-E_F)/\kappa_B T} + 1}$$

Fermi-Dirac Statistics

- The probability of an electron having energy at E_F (the Fermi level) is $\frac{1}{2}$.
- At $T=0$, there will be no electrons at energies above the Fermi level and all electrons will have energies below the Fermi level.

$$F(E)|_{E=E_F} = \frac{1}{2}$$
$$F(E)|_{T=0} = \begin{cases} 1, & E < E_F \\ 0, & E > E_F \end{cases}$$

- The total number of energy states below E_F that electrons can occupy is equal to the total number of electrons in a cube of sides length L and electron volume density N

$$NL^3 = \int_0^{E_F} Z(E) dE$$

- Using our previous results for $Z(E)$, we can solve for E_F at $T=0$

$$NL^3 = \frac{\pi}{2} (8m)^{3/2} \left(\frac{L}{h}\right)^3 \int_0^{E_F} E^{1/2} dE = \frac{\pi}{2} (8m)^{3/2} \left(\frac{L}{h}\right)^3 \left[\frac{2}{3} E_F^{3/2} \right] = \frac{4}{3} \frac{\pi}{2} (8m)^{3/2} \left(\frac{L}{h}\right)^3 E_F^{3/2}$$

$$E_F = \left(\frac{3}{8} \frac{Nh^3}{\pi(8m)^{3/2}} \right)^{2/3} = \frac{h^2}{2m} \left(\frac{3N}{8\pi} \right)^{2/3}$$

Fermi-Dirac Statistics

- Counter-intuitive to a classical model where all electrons would be at zero energy @zero temperature, the Paul exclusion principle and the distribution of allowed energy levels tells us that there is a distribution of electron energies even at $T = 0$ and that all these electrons lie at energies less than E_F .

Examples of E_F for various metals

Metal	E_F (eV)
Li	4.72
Na	3.12
K	2.14
Rb	1.82
Cs	1.53
Cu	7.04
Ag	5.51
Al	11.70

Fermi-Dirac Statistics

Region I: $E_F - E \gg k_B T$

$$F(E) \approx 1 - \exp\left[-\frac{E - E_F}{k_B T}\right] \approx 1$$

Approximately Unity

Region II: $E_F - E \gg k_B T$

$$0 \leq F(E) \leq 1$$

Slope is function of T

10% - 90% Width $\approx 4.4 k_B T$

Region III: $E_F - E \gg k_B T$

$$F(E) \approx \exp\left[-\frac{E - E_F}{k_B T}\right]$$

Maxwell - Boltzman distribution tail

