Lecture 4
Reading Material

Reading:
Chapter 6 Solymar and Walsh
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

\[
i\hbar \frac{d(\omega_1(t))}{dt} = H_{11}\omega_1(t) + H_{12}\omega_2(t)\]

\[
i\hbar \frac{d(\omega_2(t))}{dt} = H_{21}\omega_1(t) + H_{22}\omega_2(t)\]

Coupling Term

$H_{12}\omega_2(t)$

$H_{21}\omega_1(t)$

$H_{22}\omega_2(t)$
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).

\[
E = \frac{\hbar^2 k^2}{2m}
\]

\[
E_{\text{Potential Well } V=\infty} = \frac{\hbar^2 n^2}{8m L}, \quad n = 1, 2, 3, \ldots
\]

E vs. k is quadratic with curvature given by the carrier effective mass \( m \) (Semiconductor)
Now let's look at a cube with sides $L$ that contains the electrons. The electron energy can be written as

$$E = \frac{\hbar^2}{2m} (\kappa_x^2 + \kappa_y^2 + \kappa_z^2)$$

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

$n_x, n_y, n_z = 1, 2, 3 \ldots$
Energy Level Differences vs. $n$

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

Let $n^2 = n_x^2 + n_y^2 + n_z^2$

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

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

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

$\Delta E$ 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
$$\frac{4n^3 \pi}{3}$$
states

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

The number of states with energy less than $E$ are
$$\frac{4\pi}{3} \left( \frac{8mL^2}{\hbar^2}E \right)^{3/2} = \frac{4\pi}{3} \left( \frac{8mL^2}{\hbar^2} \right)^{3/2} E^{3/2}$$

and the number of states with energy less than $E + dE$ are
$$\frac{4\pi}{3} \left( \frac{8mL^2}{\hbar^2} \right)^{3/2} (E + dE)^{3/2}$$

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

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

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

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

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

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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

\[
f(E) = \frac{1}{e^{\frac{(E-E_F)}{\kappa_B T}} + 1}
\]
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 $T=0$
  \[
  NL^3 = \frac{\pi}{2} (8m)^{3/2} \left(\frac{L}{\hbar}\right)^3 \int_0^{E_F} E^{1/2}dE = \frac{\pi}{2} (8m)^{3/2} \left(\frac{L}{\hbar}\right)^3 \left[ 2 \right] = 4 \left(8m\right)^{3/2} \left(\frac{L}{\hbar}\right)^3 E_F^{3/2}
  \]
  \[
  E_F = \left( \frac{3}{8} \frac{Nh^3}{\pi \left(8m\right)^{3/2}} \right)^{2/3} = \frac{h^2}{2m} \left( \frac{3N}{8\pi} \right)^{2/5}
  \]
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

<table>
<thead>
<tr>
<th>Metal</th>
<th>E_F (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>4.72</td>
</tr>
<tr>
<td>Na</td>
<td>3.12</td>
</tr>
<tr>
<td>K</td>
<td>2.14</td>
</tr>
<tr>
<td>Rb</td>
<td>1.82</td>
</tr>
<tr>
<td>Cs</td>
<td>1.53</td>
</tr>
<tr>
<td>Cu</td>
<td>7.04</td>
</tr>
<tr>
<td>Ag</td>
<td>5.51</td>
</tr>
<tr>
<td>Al</td>
<td>11.70</td>
</tr>
</tbody>
</table>
Fermi-Dirac Statistics

Region I: $E_F - E >> k_B T$

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

Approximately Unity

Region II: $E_F - E >> k_B T$

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

Slope is function of $T$

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

Region III: $E_F - E >> k_B T$

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

Maxwell - Boltzman distribution tail

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