Lecture 3: Electron statistics in a solid

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1 Density of states

In the band theory of the solid, developed earlier, $N$ atoms with $N$ atomic orbitals formed $N$ molecular orbitals. Each MO can take 2 electrons (opposite spin) so that there are a total of $2N$ energy states. These are discrete states but for large values of $N$ the spacing between them are so small that they can be considered to be continuous, forming an energy band. Density of states (DOS) is defined as the number of available energy states per unit energy per unit volume. The units are $J^{-1}m^{-3}$ or $eV^{-1}cm^{-3}$ and it provides information on how the energy states are distributed in a given solid. It is typically denoted as $g(E)$. The experimental density of states of a material can be measured by photo electron spectroscopy or Scanning Tunneling Microscopy (STM) or Electron Energy Loss spectroscopy (EELS). These techniques probe the density of empty or filled states around the Fermi energy, called Local DOS (LDOS). Density functional calculations can also be used to calculate the density of states. These model the electron density distribution in a solid and also model the atomic potential within the solid. Figure 1 shows the calculated DOS for Cu around the Fermi energy.
Figure 1: Calculated DOS of Cu around the Fermi level. The filled states lie below $E_F$ while the empty states lie above $E_F$. The broad peak below $E_F$ corresponds to the filled 3d states.
The density of states can be used to calculate the total number of electron in a band. If \( g(E) \) is the DOS, then the total number of electrons in a band, \( S(E) \) is given by

\[
S(E) = \int_E g(E) dE
\]

where the integration is performed over the entire energy band. This equation assumes that the probability of occupation of the state is 1. This is not always true when we look at the conduction band of a semiconductor, where the occupation probability is defined by a Fermi function. An energy expression for the density of states, \( g(E) \), will be useful for evaluation of the integral in equation 1.
1.1 DOS in a 3D uniform solid

To simplify the calculation for \( g(E) \) consider a 3D solid with uniform potential. This is a simplification of a real solid but is a good approximation of the valence band of metals where the electrons are loosely bound to the atom and are delocalized. We will also use this approximation for electrons and holes near the edge of the band. For simplicity the uniform potential can be taken to be zero. For this solid the electron is defined by 3 quantum numbers \((n_1, n_2, n_3)\) and its energy is given by

\[
E = \frac{\hbar^2}{8m_eL^2}(n_1^2 + n_2^2 + n_3^2) \quad (2)
\]

Equation 2 is for a cubic solid of length \( L \) with the 3 quantum numbers for the 3 axes. \( m_e \) is the free electron mass. We can replace the 3 quantum numbers by a single value \( n \) so that equation 2 is modified into

\[
E = \frac{\hbar^2n^2}{8m_eL^2} \quad (3)
\]

For small values of \( n \) these energy levels are quantized, but for large values of \( n \) the spacing between them are close so that the energy levels can be considered to be continuous. So \( n \) represents the radius of a sphere, where
the total number of states within the sphere is given by its volume. This is shown schematically in figure 2. Since the quantum numbers can only be positive (the quantum numbers represent the electron wavefunction and it can be shown that to avoid exponential increasing functions the quantum numbers have to be non-zero positive integers) we can only take the first quadrant of the sphere.

Figure 2: Energy states in a solid with uniform potential. The portion of the sphere corresponds to the constant energy surface. Only the first quadrant is to be considered since the quantum numbers are non-zero positive integers.

Each state, or electron wavefunction ($\Psi$) in the crystal, can be represented by a unit volume at $n_1$, $n_2$, and $n_3$. 

\[ n_1^2 + n_2^2 + n_3^2 \leq n^2 \]

Volume \( V = \frac{1}{8} \pi n^3 \)
Hence the total number of ‘orbitals’ (energy states), $S_{orb}(n)$, is given by the volume of the sphere in the first quadrant

$$S_{orb}(n) = \frac{1}{8} \left( \frac{4}{3} \pi n^3 \right) = \frac{1}{6} \pi n^3$$

(4)

Since each orbital can take two electrons of opposite spin, the total number of energy states (including spin), $S(n)$, is given by

$$S(n) = 2S_{orb}(n) = \frac{1}{3} \pi n^3$$

(5)

We can relate $n$ (quantum number of the electron in the solid) to the energy $E$ using equation 3 to write the total number of states in terms of energy, $S(E)$. This is given by

$$S(E) = \frac{1}{3} \pi (8m_eE)^{\frac{3}{2}} \frac{L^3}{h^3}$$

(6)

Dividing by the volume of the cube will give total number of states per unit volume, $S_v(E)$. The density of states is the differential of the total number of states, so that $g(E)$ is given by

$$dS_v/dE = g(E) \quad \longrightarrow \quad g(E) = 8\pi \sqrt{2} \left( \frac{m_e}{h^2} \right)^{\frac{3}{2}} \sqrt{E}$$

(7)
Equation 7 gives the DOS in a solid with a uniform potential. At the bottom of the band, which is normally chosen as the reference so energy is set to 0, DOS is zero. As the energy increases $g(E)$ also increases. The functional form is shown schematically in figure 3. $g(E)$ represents the density of available states. It does not provide information whether those states are occupied or not. The occupation is given by the Fermi function and is usually a function of temperature.

Figure 3: Plot of DOS vs. E for a 3D solid using free electron mass. This is a plot of equation 7 using MATLAB.
1.2 DOS for a 2D solid

The density of states function will change upon changing the dimensionality of the solid. Consider the case of a 2D solid with a uniform potential. There are 2 quantum numbers, $n_1$ and $n_2$, which are related to the energy, similar to equation 2.

$$E = \frac{\hbar^2}{8m_eL^2} (n_1^2 + n_2^2) = \frac{\hbar^2 n^2}{8m_eL^2}$$  \hspace{1cm} (8)

For a 2D case, $n$, represents the radius of a circle, shown in figure 4, and only the first quadrant can be considered since the quantum numbers should be positive.

Figure 4: Energy states in a 2D solid with uniform potential. Instead of a sphere states of constant energy form a circle and only the first quadrant is relevant

Each state, or electron wavefunction in the crystal, can be represented by a box at $n_1$, $n_2$. 

<table>
<thead>
<tr>
<th>$n_1$</th>
<th>$n_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
</tr>
</tbody>
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$n_1^2 + n_2^2 \leq n^2$
It is possible to calculate the density of states per unit area, $S_{area}(n)$, including spin

$$S_{area}(n) = \frac{\pi n^2}{2}$$  \hspace{1cm} (9)

Using equation 8 it is possible to calculate the DOS in terms of energy, $S_{area}(E)$

$$S_{area}(E) = \frac{4\pi m_e}{\hbar^2} E$$  \hspace{1cm} (10)

Differentiating equation 10 gives the density of states in two dimensions

$$g(E) = \frac{4\pi m_e}{\hbar^2}$$  \hspace{1cm} (11)

The density of states function is independent of energy, unlike 3D where $g(E)$ increases with energy. It is represented as a step function at different energy values.
1.3 DOS for a 1D solid

The calculation for a 1D solid is similar to the earlier calculations except that there is only one quantum number and spatially it is represented on a line (instead of circle in 2D and sphere in 3D). The total number of states, per unit length, $S(n)$, is just $2n$ and this is related to energy by equation 12.

$$n = \sqrt{\frac{8m_e}{h^2}} \quad E$$  \hspace{1cm} (12)

The density of states is given by

$$g(E) = \sqrt{\frac{8m_e}{h^2}} \frac{1}{\sqrt{E}}$$  \hspace{1cm} (13)

In a 1D solid the density of states decreases with energy. For a zero dimensional solid, energy states are only discrete. Solids with two, one, and zero dimensionality can be obtained by reducing the length in one or more dimensions. A thin film is an example of a two dimensional solid (or a single or bi layer of graphene), while a quantum wire is a one dimensional solid. A quantum dot is a zero dimensional solid. The density of states and hence the electronic properties of these materials are different from a bulk solid. The
**DENSITY OF STATES IN A BAND**  Given that the width of an energy band is typically $\sim 10$ eV, calculate the following, in per cm$^3$ and per eV units:

- **a.** The density of states at the center of the band.
- **b.** The number of states per unit volume within a small energy range $kT$ about the center.
- **c.** The density of states at $kT$ above the bottom of the band.
- **d.** The number of states per unit volume within a small energy range of $kT$ to $2kT$ from the bottom of the band.

**SOLUTION**

**a.** The density of states, or the number of states per unit energy range per unit volume $g(E)$, is given by

$$g(E) = (8\pi 2^{1/2}) \left(\frac{m_e}{\hbar^2}\right)^{3/2} E^{1/2}$$

which gives the number of states per cubic meter per Joule of energy. Substituting $E = 5$ eV, we have

$$g_{\text{center}} = (8\pi 2^{1/2}) \left[\frac{9.1 \times 10^{-31}}{(6.626 \times 10^{-34})^2}\right]^{3/2} (5 \times 1.6 \times 10^{-19})^{1/2} = 9.50 \times 10^{46} \text{ m}^{-3} \text{ J}^{-1}$$

Converting to cm$^{-3}$ and eV$^{-1}$, we get

$$g_{\text{center}} = (9.50 \times 10^{46} \text{ m}^{-3} \text{ J}^{-1})(10^{-6} \text{ m}^3 \text{ cm}^{-3})(1.6 \times 10^{-19} \text{ J eV}^{-1}) = 1.52 \times 10^{22} \text{ cm}^{-3} \text{ eV}^{-1}$$

**b.** If $\delta E$ is a small energy range (such as $kT$), then, by definition, $g(E) \delta E$ is the number of states per unit volume in $\delta E$. To find the number of states per unit volume within $kT$ at the center of the band, we multiply $g_{\text{center}}$ by $kT$ or $(1.52 \times 10^{22} \text{ cm}^{-3} \text{ eV}^{-1})(0.026 \text{ eV})$ to get $3.9 \times 10^{20} \text{ cm}^{-3}$. 
c. At $kT$ above the bottom of the band, at 300 K ($kT = 0.026$ eV), we have

$$g_{0.026} = (8\pi 2^{1/2}) \left[ \frac{9.1 \times 10^{-31}}{(6.626 \times 10^{-34})^2} \right]^{3/2} (0.026 \times 1.6 \times 10^{-19})^{1/2}$$

$$= 6.84 \times 10^{45} \text{ m}^{-3} \text{ J}^{-1}$$

Converting to cm$^{-3}$ and eV$^{-1}$ we get

$$g_{0.026} = (6.84 \times 10^{45} \text{ m}^{-3} \text{ J}^{-1})(10^{-6} \text{ m}^3 \text{ cm}^{-3})(1.6 \times 10^{-19} \text{ J eV}^{-1})$$

$$= 1.10 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$$

d. Within $kT$, the volume density of states is

$$(1.10 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1})(0.026 \text{ eV}) = 2.8 \times 10^{19} \text{ cm}^{-3}$$
2 Electron occupation probability

Density of states gives the number of available states for electrons to occupy. At absolute zero, electrons occupy the lowest energy state. Above 0 K, there is always some thermal energy for the electrons to occupy the unoccupied energy states. There are different statistics to describe the occupation of energy levels. The simplest statistics is the Boltzmann statistics which gives the probability of occupation, \( p(E) \), of a given energy state, \( E \),

\[
p(E) = A \exp\left(-\frac{E}{k_B T}\right)
\]

(14)

\( A \) is a constant. At 0 K all the particles have energy 0 and at any given \( T \), \( p(E) \) gives the probability of occupation. For a given temperature, \( p(E) \) reduces as \( E \) increases, as shown in figure 6.

Figure 6: Boltzmann probability distribution vs. energy at 1000 K. The probability drops steeply as energy increases due to the exponential nature of the function.
Boltzmann statistics works for a system of non-interacting particles but
electrons have a strong repulsive interaction. By Pauli’s exclusion principle
only 2 electrons can occupy a given energy state (of opposite spin). So all
electrons cannot occupy the same energy state, even at absolute zero. The
statistics obeyed by electrons is given by the Fermi-Dirac statistics.

2.1 Fermi-Dirac statistics

In Fermi-Dirac statistics, the probability of electron occupation of a given
energy state is represented by \( f(E) \) and given by

\[
f(E) = \frac{1}{1 + A \exp\left(\frac{E}{k_B T}\right)}
\]

(15)

\( A \) is a constant. \( f(E) \) is called the **Fermi function**. For solids \( A \) is related
to the Fermi energy \( (E_F) \) so that \( f(E) \) is given by

\[
f(E) = \frac{1}{1 + \exp\left[\frac{(E - E_F)}{k_B T}\right]}
\]

(16)

At absolute zero all energy levels below the Fermi level are occupied so that
the occupation probability is 1. Above \( E_F \) the levels are empty so that \( f(E) \)
is 0. Also, at any temperature \( f(E) \) at the Fermi level is 0.5. Figure 7
plots the Fermi function as a function of energy.
Figure 7: Fermi function $f(E)$ vs. energy at three different temperatures. The probability drops steeply as energy is increased from the Fermi function. To increase the probability the temperature has to be increased.

$f(E)$ is the probability of occupied energy states by electrons. While $[f(E)-1]$ is the probability of unoccupied (empty) energy states (if you draw $[f(E)-1]$ you will have the inverse drawing).
When the energy difference \((E - E_F)\) is much larger than \(k_B T\), the Fermi function behaves like Boltzmann function (similar to equation 14):

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

If \(g(E)\) is the density of states and \(f(E)\) gives the probability of occupation of those states at a given temperature, the number of occupied states, \(n(E)\), is given by

\[
n(E) = \int g(E)f(E)\,dE
\]  

Equation 17 can be used to calculate the concentration of electron and holes in semiconductors, which decides their conductivity.
Consider the energy band diagram for a metal. We know that the number of states $g(E)$ for an electron, per unit energy per unit volume, increases with energy as $g(E) \propto E^{1/2}$. We have also calculated that the probability of an electron being in a state with an energy $E$ is the Fermi–Dirac function $f(E)$. If we multiply $g(E)$ by $f(E)$, we obtain the number of electrons per unit energy per unit volume, or the electron concentration per unit energy. The area under the curve on the energy axis is the concentration of electrons in the band.

The figure shows:

(a) Above 0 K, due to thermal excitation, some of the electrons are at energies above $E_F$.
(b) The density of states, $g(E)$ versus $E$ in the band.
(c) The probability of occupancy of a state at an energy $E$ is $f(E)$.
(d) The product $g(E)f(E)$ is the number of electrons per unit energy per unit volume, or the electron concentration per unit energy. The area under the curve on the energy axis is the concentration of electrons in the band.
Density of states in silver

Consider an example to calculate the density of states in a metal, silver (Ag). Ag is a free electron metal, electrons in the outer shell are delocalized and are free to move in the material. Hence, valence electrons in Ag can be treated as electrons in an uniform potential. The atomic weight of Ag is 107.9 \( gmol^{-1} \) and the density (\( \rho \)) is 10.5 \( gcm^{-3} \). Hence the number of atoms per unit volume (\( n_V \)) can be calculated

\[
n_V = \frac{\rho N_A}{At.wt}
\]  

(18)

where \( N_A \) is Avogadro’s number. This gives \( n_V \) to be \( 5.85 \times 10^{22} \) atoms \( cm^{-3} \).

The Fermi energy (\( E_F \)) of Ag is at 5.5 eV. This is with reference to the bottom of the valence band (taken as zero). So the density of states, at the Fermi energy, for Ag can be calculated using equation 7 is given by

\[
g(E) = 8\pi\sqrt{2} \left( \frac{m_e}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E_F}
\]  

(19)

where \( E_F \) is 5.5 eV. This gives a number \( 9.95 \times 10^{46} \) \( m^{-3} \) \( J^{-1} \) or converting the units \( 1.59 \times 10^{22} \) \( cm^{-3} \) \( eV^{-1} \). This is of the same order of magnitude as the number of atoms per unit volume. Close to the bottom of the band the density of states is still a substantial quantity. Consider an energy \( k_B T \) above
the bottom of the band. At room temperature this energy is approximately 25 meV. Using equation 7 the density of states is $1.09 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$ which is still a substantial fraction of the number of atoms.

In order to calculate the total number of electrons in the band equation 17 can be integrated from the bottom of the band to $E_F$. The occupation probability, $f(E)$, is 1.

$$n(E) = \int_0^{E_F} g(E)dE$$  \hspace{1cm} (20)

The integral is

$$n(E) = 8\pi \sqrt{2} \left(\frac{m_e}{\hbar^2}\right)^{\frac{3}{2}} \frac{2}{3} E_F \sqrt{E_F}$$  \hspace{1cm} (21)

The calculated value of $n(E)$ is $5.08 \times 10^{22} \text{ cm}^{-3}$ which is very close to the number of atoms per cm$^{-3}$. Since each atom contributes one electron in Ag this is also the number of electrons and they fill all the states below $E_F$. Thus, a simple model of a solid with a uniform potential matches closely with reality. In silver, $E_F$ is in the middle of the band so that there are empty available states for the electrons to occupy. When an electric field electrons travel opposite to this field and they can occupy these empty states. This makes Ag a very good conductor of electricity.
4 Fermi function vs. Boltzmann function

We can compare the occupation probability using Fermi function and the Boltzmann function. This can be seen in figure

Figure 8: Comparison of the Fermi and Boltzmann probability distribution vs. normalized energy at constant temperature. Energy is plotted with reference to $E_F$ and normalized by temperature. At low $(E-E_F)$ Fermi function is accurate while at higher values Boltzmann function is a good approximation.