Free Electron Theory of a Metal

Readings: Hill, pp. 441-444

We know how to think about the electronic structure of a molecule — we know the orbitals, their energies, their occupancies — but with a metal, which we treat as one giant molecule of N atoms, how do we handle the large number of orbitals and electrons? Need to invent new ideas like the density of electronic states which is # of states/unit quantum number or # of states/unit energy.

FREE ELECTRON MODEL

Many metals (Na, K, Rb, Li, Au, Ag, Cu) have one unpaired s electron per atom that acts “free.” The interaction with the ion core and other electrons is sufficiently weak to justify building a model in which these interactions are ignored. The potential energy is zero everywhere except $\infty$ potential at the ends of the box.

Equation of motion for particle in a box

$$-\frac{h^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = E \psi(x, y, z)$$

Solutions for cubic box of length L

$$\psi(x, y, z) = \left( \frac{8}{L^3} \right)^{1/2} \sin \left( \frac{n_x \pi x}{L} \right) \sin \left( \frac{n_y \pi y}{L} \right) \sin \left( \frac{n_z \pi z}{L} \right)$$

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

Define wavevectors in terms of quantum #’s (because, in the solid state, wavevectors are more convenient for counting states than quantum numbers).

$$k_x = \frac{\pi}{L} n_x \quad k_y = \frac{\pi}{L} n_y \quad k_z = \frac{\pi}{L} n_z$$

$$k^2 = k_x^2 + k_y^2 + k_z^2$$

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

Now, $a$ is the lattice constant

$$E = \frac{\hbar^2}{2ma^2} (ka)^2$$

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and

\[(ka)^2 = n_x^2 \pi^2 \left( \frac{a}{L} \right)^2 + n_y^2 \pi^2 \left( \frac{a}{L} \right)^2 + n_z^2 \pi^2 \left( \frac{a}{L} \right)^2 \]

Now, it is easy to see that because \(a/L \ll 1\), \(ka\) can be treated as a quasi-continuous variable, thus the allowed values of \(E\) also vary continuously.

Large degeneracy — all states with same value of \((ka)^2\) or same value of \(n_x^2 + n_y^2 + n_z^2\) will have the same energy. For small values of \(n_x, n_y, n_z\), it is possible to enumerate the degeneracy, but not so for large values — and we will need large values because \(e^-'s\) are fermions and each state may be occupied by at most one fermion. So the answer is to calculate the density of states.

**DENSITY OF STATES** (# of states per unit wavevector)

Surface area of sphere with radius \(k\) is \(4\pi k^2\)
Each state on the surface has same value of \(k\) or \(E\)
Spherical shell of radius \(k\) and thickness \(dk\) has volume \(4\pi k^2 dk\)
How many different wavevector states are there in this volume?

\((\pi/L)^3 = \text{volume of one state because each } k \text{ has length } \pi/L. \text{ [Where does this k-space volume come from? There must be N half wavelengths per L in order to satisfy boundary conditions: } L = N(\lambda/2). \text{ But } k_N = 2\pi/\lambda_N. \text{ Thus } k_N = N(\pi/L). \text{ k changes in steps of } \pi/L, \text{ thus the k-space volume associated with each allowed value of } k_{l,m,n} \text{ is } (\pi/L)^3.\]
Number of states with range of k between k and k + dk is

\[ dN = \frac{4\pi k^2 dk}{8(\pi/L)^3} = \frac{L^3}{2\pi^2} k^2 dk \]

divide by 8 to include only the positive octant of spherical shell because \( k_x, k_y, \) and \( k_z \) must all be positive.

**DENSITY OF STATES** (# of states per unit energy)

replace \( k^2 \) and \( dk \) in above equation for \( dN \):

\[
E = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \left( \frac{2mE}{\hbar^2} \right)^{1/2}
\]

\[
\frac{dk}{dE} = \frac{1}{2} \left( \frac{2m}{\hbar^2} \right)^{1/2} E^{-1/2} \Rightarrow dk = \frac{1}{2} \left( \frac{2m}{\hbar^2} \right)^{1/2} E^{-1/2} dE
\]

\[
dN = \frac{L^3}{2\pi^2} k^2 dk = \frac{L^3}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{1/2} E^{1/2} dE
\]

\[
V = L^3
\]

\[
dN = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} dE
\]

This is the number of states with \( E \) in the range between \( E \) and \( E + dE \).