5.62 Physical Chemistry II
Spring 2008

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 ∞ potential at the ends of the box.

Equation of motion for particle in a box

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

Solutions for cubic box of length L

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

$$E=\frac{\hbar^2}{2m}\frac{\pi^2}{L^2}\left(n_x^2+n_y^2+n_z^2\right)$$

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

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

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

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

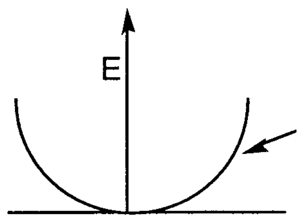
Now, a is the lattice constant

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

and

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

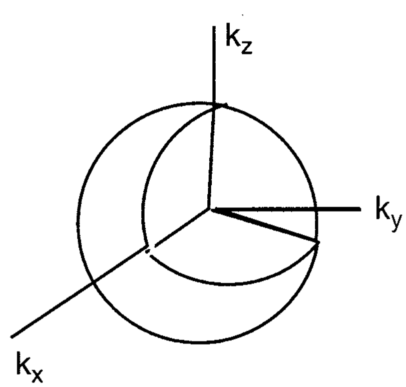
Now, it is easy to see that because $a/L \ll 1$, ka can be treated as a quasi-continuous variable, thus the allowed values of E also vary continuously.



Really a <u>very</u> large number of points but allowed values of ka and E are very closely spaced.

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.

<u>DENSITY OF STATES</u> (# 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?

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

Number of states with range of k between k and k + dk is

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

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

<u>DENSITY OF STATES</u> (# of states per unit energy)

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

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

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

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

$$V = L^3$$

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

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