The 3-D quantum square well

In 3 dimensions the TISWE becomes:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

Where:

$$\vec{\nabla} = \frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j} + \frac{\partial}{\partial z}\hat{k} \text{ and } \nabla^2 = \vec{\nabla}\bullet\vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

in Cartesian coordinates.

This operator is also called the Laplacian operator.

Consider a free particle inside a box with lengths L_x, L_y, L_z along the x, y and z axes. The particle is constrained to be inside the box. Find the wave functions and the energies. Then find the ground energy and wave function and the first excited state energy for a cube of sides L.

Inside the box, the potential is zero. Thus, we have:

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

We solve this by assuming a solution of the form:

$$\psi = X(x)Y(y)Z(z)$$

We then operate on this with the Laplacian with the result:

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = -\frac{2mE}{\hbar^2} = -\left(k_x^2 + k_y^2 + k_z^2\right)$$

This allows separation into 3 independent equations:

$$\frac{d^2X}{dx^2} + k_x^2X = 0 : \frac{d^2Y}{dy^2} + k_y^2Y = 0 : \frac{d^2Z}{dz^2} + k_z^2 = 0$$

The solutions for each of the functions is a sine function. Thus we have the full solution to the problem given as:

$$\psi = A\sin(k_x x)\sin(k_y y)\sin(k_z z)$$

We apply the condition on the other boundary to set the wave numbers:

$$k_x = \frac{n_x\pi}{L_x} : k_y = \frac{n_y\pi}{L_y} : k_z = \frac{n_z\pi}{L_z}$$

Here's an important note: don't confuse this L with angular momentum which will soon appear!

We thus have the wave function:

$$\psi = A\sin\left(\frac{n_x\pi}{L_x}x\right)\sin\left(\frac{n_y\pi}{L_y}y\right)\sin\left(\frac{n_z\pi}{L_z}z\right)$$

Now we need to normalize this wave function. This is pretty straight-forward to do.

$$1 = \int_{\substack{\text{all}\\ \text{space}}} \psi^*\psi\, dx\, dy\, dz = A^2 \int_{x=0}^{x=L_x} \sin^2\left(\frac{n_x\pi}{L_x}x\right)dx \int_{y=0}^{y=L_y} \sin^2\left(\frac{n_y\pi}{L_y}y\right)dy \int_{z=0}^{z=L_z} \sin^2\left(\frac{n_z\pi}{L_z}z\right)dz$$

We know from the notes on the 1-D square well that each of these wave functions is normalized by multiplication by a term such as $\sqrt{\frac{2}{L}}$

We thus have the complete wave function given as:

$$\psi = \sqrt{\frac{8}{L_xL_yL_z}}\sin\left(\frac{n_x\pi}{L_x}x\right)\sin\left(\frac{n_y\pi}{L_y}y\right)\sin\left(\frac{n_z\pi}{L_z}z\right)$$

The energy of a particular eigenstate is thus given by:

$$E_{n_x,n_y,n_z} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2\pi^2}{2m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$

where the n's are 1,2,3,...

We don't permit n=0 here because the wave function would vanish.

Now an extremely important detail is this: what happens if we have a cube of side L?

In this case, we have:

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2mL^2}\left[n_x^2 + n_y^2 + n_z^2\right]$$

We might as well now get rid of the x,y,z notation and replace it by 1,2,3 to prevent confusion in the future. In this notation we have:

$$E_{n_1,n_2,n_3} = \frac{\hbar^2\pi^2}{2mL^2}\left[n_1^2 + n_2^2 + n_3^2\right]$$

Now let's start building up the energy states and counting the number of ways to do each state. I'm going to define the dimensionless energy as:

$$\varepsilon_{1,2,3} \equiv \frac{E_{n_1,n_2,n_3}}{\frac{\hbar^2\pi^2}{2mL^2}} = \left[n_1^2 + n_2^2 + n_3^2\right]$$

I have produced a spreadsheet where the various energies are shown.
Included in this will be a discussion of accidental degeneracies

Now I want to show you immediately where this becomes very important.
Look at page 290 in your text for this discussion.
If we define the quantum number r as:

$$r^2 = n_1^2 + n_2^2 + n_3^2$$

We find that by filling successive electrons into a 3-D square well, the energy will be filled up from the lowest to the highest level. The allowed energies can be written as:

$$E = r^2 E_1; E_1 = \frac{h^2}{8mL^3}$$

r is a dimensionless quantity, not to be confused with a radius measuring distance.
The energy E1 here is, in fact, not the ground state of the 3D well ... rather it is 1/3 of this energy. This is ok and as it should be.

Now something that we have yet to discuss is this: electrons have spin which means that 2 electrons can have the same 3 n quantum numbers so long as the projection of their spins is in opposite directions. This will introduce a factor of 2 in the following calculations.

The "volume" of a sphere in "n" space will be given by:

$$V = \frac{4}{3}\pi r^3$$

but we only choose the one octant of this sphere which corresponds to positive n values.
Thus, the number of states up to r is given by:

$$N_r = (2)\left(\frac{1}{8}\right)\left[\frac{4}{3}\pi r^3\right]$$

But we know that

$$E = r^2 E_1; E_1 = \frac{h^2}{8mL^3} \Rightarrow r = \left(\frac{E}{E_1}\right)^{\frac{1}{2}}$$

So we can find the number of state to be given by:

$$N_r = \frac{1}{3}\pi\left(\frac{E}{E_1}\right)^{\frac{3}{2}}$$

At T=0, the Fermi Energy (E_F) is the energy of the highest occupied energy level. If there are N electrons total, then:

$$N = \frac{1}{3}\pi\left(\frac{E_F}{E_1}\right)^{\frac{3}{2}}$$

We can solve this for the Fermi energy:

$$E_F = E_1\left[\frac{3N}{\pi}\right]^{\frac{3}{2}} = \frac{h^2}{8m}\left[\frac{3N}{\pi L^3}\right]^{\frac{3}{2}}$$

The ratio N/L^3 is well known for most conductors: it is the number density of conduction electrons, a quantity easily measured using the Hall effect.

Here is a link to the Hall Effect from NIST

http://www.eeel.nist.gov/812/effe.htm

Essentially, if you direct a magnetic field at right angles to a current carrying metal, and the current is at right angles to the magnetic field, the charges respond to the Lorentz Force from the magnetic field:

$$F = ILB$$

where I is the current and L is the length of conductor in the magnetic field for each of the N total carriers in the conducting material. The material is assumed to have a thickness h, a width d and a length L.

This causes a drift in the N=n(Ldh) electrons towards the sides of the conductors until the electric field generated by this drift is equal to this force per unit charge, or:

$$n(Ldh)eE = ILB$$

where n is the number of carriers per unit volume.

This is related to the potential difference which develops across the strip by:

$$-\frac{\Delta V}{d} = E \Rightarrow -n(Lhd)e\frac{\Delta V}{d} = ILB \Rightarrow \Delta V = -\frac{IB}{nh}$$

Once you have the product nh, you can easily determine n by dividing by h, although it is sometimes useful to work with this quantity directly.

Back to the Fermi Energy, we had:

$$N_r = \frac{1}{3}\pi\left(\frac{E}{E_1}\right)^{\frac{3}{2}}$$

The density of states is obtained by differentiating this with respect to energy:

$$g(E) = \frac{dN_r}{dE} = \frac{\pi}{2}E_1^{-\frac{3}{2}}E^{\frac{1}{2}}$$

Now we can express this in terms of the Fermi energy as:

$$g(E) = \frac{3N}{2}E_F^{-\frac{3}{2}}E^{\frac{1}{2}}$$

This gives us directly the number of electrons as a function of energy:

$$n(E) = \begin{cases} g(E); E < E_F \\ 0; E > E_F \end{cases}$$

again, at absolute zero.

To find the average electronic energy, we then have:

$$\langle E \rangle = \frac{1}{N}\int_0^{\infty} En(E)dE = \frac{1}{N}\int_0^{E_F} Eg(E)dE$$

$$= \frac{1}{N}\int_0^{E_F} \left(\frac{3N}{2}\right) E_F^{-\frac{3}{2}} E^{\frac{3}{2}} dE = \frac{3}{5}E_F$$

Later, I hope to show you how this becomes involved with electrical conduction. For now, be aware that with the average electron energy, you can obtain the thermodynamics of a system consisting of an electron gas since the internal energy of the electron gas is given by:

$$U = N\langle E \rangle$$

More on this when we talk about the theory of electron conduction.