Solids I

Lecture 33

Physics 342
Quantum Mechanics I

Wednesday, April 21st, 2010

We can consider simple models of solids – these highlight some special techniques.

33.1 An Electron in a Box

We begin our discussion of solids by considering a single electron confined to a box – the three-dimensional infinite square well potential:

$$V(x, y, z) = \begin{cases} 0 & 0 < x < \ell_x, 0 < y < \ell_y \text{ and } 0 < z < \ell_z \\ \infty & \text{otherwise} \end{cases} \quad (33.1)$$

This is just three copies of the one-dimensional problem, and we quote the result – it is, as an aside, very similar to the cavity EM modes from electrodynamics. All three directions are periodic (under a separation ansatz $\psi(x, y, z) = X(x) Y(y) Z(z)$, and the boundary conditions at $x = 0$, $y = 0$, $z = 0$ give us the following:

$$X(x) = A \sin(k_x x) \quad Y(y) = B \sin(k_y y) \quad Z(z) = C \sin(k_z z). \quad (33.2)$$

The requirement that the wavefunction vanish outside the box, together with continuity at the boundary also imposes $X(\ell_x) = Y(\ell_y) = Z(\ell_z) = 0$, which, as usual, leads to quantization of the allowed modes:

$$k_x = \frac{n_x \pi}{\ell_x} \quad k_y = \frac{n_y \pi}{\ell_y} \quad k_z = \frac{n_z \pi}{\ell_z} \quad (33.3)$$

for independent integers (n_x, n_y, n_z). Now, the total energy of the configuration, from Schrödinger's equation, is

$$-\frac{\hbar^2}{2 m} \nabla^2 \psi_{n_x, n_y, n_z} = E \psi_{n_x, n_y, n_z} \longrightarrow E = \frac{\hbar^2}{2 m} \left(k_x^2 + k_y^2 + k_z^2 \right). \quad (33.4)$$

So if we think of a vector $\mathbf{k} = k_x\,\hat{\mathbf{x}} + k_y\,\hat{\mathbf{y}} + k_z\,\hat{\mathbf{z}}$, the energy is just $E = \frac{\hbar^2\,k^2}{2\,m}$. In this setting (as a Fourier transform type of object), the vector $\mathbf{k}$ is known as a "wave-vector".

The actual values for the wave-vector are restricted since they must satisfy the boundary conditions from above. For a grid of points in the vector space defined by the axes k_x, k_y and k_z, each integer vertex represents an allowed single-electron state – but the vertices are equivalent to the cubes of which they are one corner. This is easiest to see in two-dimensions as in Figure 33.1.
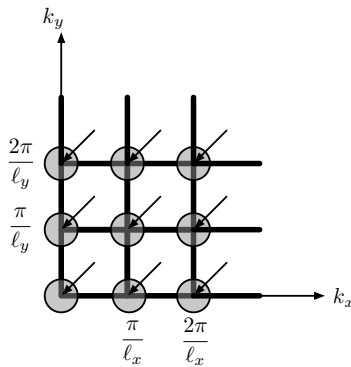

Figure 33.1: A two-dimensional lattice in k-space. We have integer spacings in x: $\frac{\pi}{\ell_x}$ and in y: $\frac{\pi}{\ell_y}$. The arrow from each box points to its associated vertex, showing a one-to-one correspondence between vertices and boxes.

In three dimensions, we can also associate the cubical boxes (now) with a single vertex. Hence the density of states is 1 per box of volume $\frac{\pi}{\ell_x}\,\frac{\pi}{\ell_y}\,\frac{\pi}{\ell_z}$, or

$$\text{k-volume per state} = \frac{\pi^3}{\ell_x\,\ell_y\,\ell_z} = \frac{\pi^3}{V} \longrightarrow \rho_{\text{states}} = \frac{V}{\pi^3} \qquad (33.5)$$

in k-space, with $V \equiv \ell_x\,\ell_y\,\ell_z$.

33.1.1   Multiple Electrons

Now in a solid, there are typically a few electrons associated with each atom that are "free to roam", contributing a sea of electrons that could, potentially, be bound up in our box. If we have N atoms, each contributing q electrons, then we have a *huge* number of electrons that can be in our box.

Electrons are fermions, so in any particular state, we can have (at most) two electrons paired in either a singlet or triplet state – this is a manifestation of the Pauli exclusion principle, and comes, mathematically, from the antisymmetrized wave function of fermions: For two electron wavefunctions occupying the same spatial state, $\psi_1 = \psi_{1,1,1}$ and $\psi_2 = \psi_{1,1,1}$, we must have an antisymmetric spin state (singlet) to make the total wavefunction antisymmetric, as nature demands[1]. Our current goal is to calculate the total energy associated with $N\,q$ electrons. Keep in mind that in k-space, a radius corresponds to an energy, and all states at a particular radius have the same energy.

Consider a sphere in k-space – we need only take the k_x, k_y, $k_z > 0$ octant of that sphere since our solutions are all for positive integer constants. For a sphere of radius k_f, the volume of our positive octant is $V_+ = \frac{1}{8}\left(\frac{4}{3}\pi\,k_f^3\right)$. The energy density of states is $\frac{V}{\pi^3}$ from above, and $N\,q$ electrons represent $\frac{1}{2}N\,q$ total states (since there can be two electrons per state). The radius of the sphere in k-space that allows all $N\,q$ electrons to exist, two per state can be found from:

$$\frac{1}{8}\left(\frac{4}{3}\pi\,k_f^3\right)\rho_{\text{states}} = \frac{N\,q}{2}. \tag{33.6}$$

This serves to define the sphere of radius k_f (and hence energy) taken up by Nq electrons, the so-called "Fermi surface" with radius:

$$k_f = \left(\frac{3\,\pi^2\,N\,q}{V}\right)^{1/3}. \tag{33.7}$$

We are imagining a large number of atoms contributing at least one electron (N is on the order of Avogadro's number, for example), and then even though the "boundary" at the Fermi surface is not truly spherical, we can approximate it as spherical in order to calculate the total energy of the configuration. A small shell dk at radius k (one octant) has infinitesimal volume:

$$dV_k = \frac{1}{8}\,4\,\pi\,k^2\,dk, \tag{33.8}$$

and the total number of electron states lying within this shell is

$$ds = \rho_{\text{states}}\,dV_k = \frac{V}{\pi^3}\,\frac{\pi\,k^2}{2}\,dk. \tag{33.9}$$

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[1]You might ask whether it is possible to have, say, three electrons in the same spatial state – then we just need a totally antisymmetric spin state for them to occupy – does such a state exist?

Each state has energy $\frac{\hbar^2 k^2}{2\,m}$ and can hold two electrons, so the energy associated with the infinitesimal volume dV_k is

$$dE = \frac{\hbar^2\,k^2}{m}\,ds = \frac{V\,k^4\,\hbar^2}{2\,\pi^2\,m}\,dk. \tag{33.10}$$

To find the total energy of the free electron gas, we integrate the energy in each shell from $k = 0 \to k_f$:

$$E = \frac{V\,\hbar^2}{2\,\pi^2\,m}\,\frac{1}{5}\,k_f^5 = \frac{\hbar^2\,\pi^{4/3}\,(3\,N\,q)^{5/3}}{10\,m\,V^{2/3}}. \tag{33.11}$$

This energy is calculated in k space, but the final result depends on the volume of our (spherical) box – we can ask, for example, what the electron gas pressure on the walls of the box is. For an ideal gas, $dW = P\,dV$, so we can take the energy change associated with a volume change and find the effective pressure

$$P = -\frac{dE}{dV} = \frac{2}{3}\,E/V. \tag{33.12}$$

We have here a force (per unit area) not associated with any fundamental force of nature, there is nothing in this calculation but non-interacting electrons confined to a box. Nevertheless, it is a real measurable effect.

Homework

Reading: Griffiths, pp. 214–224.

Problem 33.1

Griffiths 5.7. Three particle wave functions.

Problem 33.2

Griffiths 5.16. Calculation of "exclusion pressure" for copper.

Problem 33.3

Griffiths 5.34. Free electron gas in two dimensions.