Solids

Lecture 30

Physics 342 Quantum Mechanics I

Friday, April 18th, 2008

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

30.1 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:

$$V(x, y, z) = \begin{cases} 0 & 0 < x < \ell_x, 0 < y < \ell_y \text{ and } 0 < z < \ell_z \\ \infty & \text{otherwise} \end{cases}$$
(30.1)

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:

$$X(x) = A \sin(k_x x) \quad Y(y) = B \sin(k_y y) \quad Z(z) = C \sin(k_z z).$$
(30.2)

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:

$$k_x = \frac{n_x \pi}{\ell_x} \quad k_y = \frac{n_y \pi}{\ell_y} \quad k_z = \frac{n_z \pi}{\ell_z} \tag{30.3}$$

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{n_x,n_y,n_z} = E\,\psi_{n_x,n_y,n_z} \longrightarrow E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right).$$
 (30.4)

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 $E = \frac{\hbar^2 k^2}{2m}$. 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 30.1.



Figure 30.1: 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

k-volume per state =
$$\frac{\pi^3}{\ell_x \, \ell_y \, \ell_z} = \frac{\pi^3}{V} \longrightarrow \rho_{\text{states}} = \frac{V}{\pi^3}$$
 (30.5)

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

30.1.1 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 atoms 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 demands¹. Our current goal is to calculate the total energy associated with Nq 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 consider 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 Nq electrons represent $\frac{1}{2}Nq$ total states (since there can be two electrons per state). The radius of the sphere in k-space that allows all Nq electrons to exist, two per state can be found from:

$$\frac{1}{8} \left(\frac{4}{3} \pi k_f^3\right) \rho_{\text{states}} = \frac{N q}{2}.$$
(30.6)

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

$$k_f = \left(\frac{3\,\pi^2\,N\,q}{V}\right)^{1/3}.$$
(30.7)

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:

$$dV_k = \frac{1}{8} 4\pi k^2 dk, \qquad (30.8)$$

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

$$ds = \rho_{\text{states}} \, dV_k = \frac{V}{\pi^3} \, \frac{\pi \, k^2}{2} \, dk.$$
 (30.9)

¹You 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 $\frac{\hbar^2 k^2}{2m}$ and can hold two electrons, so the energy associated with the infinitesimal volume dV_k is

$$dE = \frac{\hbar^2 k^2}{m} ds = \frac{V k^4 \hbar^2}{2 \pi^2 m} dk.$$
 (30.10)

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

$$E = \frac{V \hbar^2}{2 \pi^2 m} \frac{1}{5} k_f^5 = \frac{\hbar^2 \pi^{4/3} (3 N q)^{5/3}}{10 m V^{2/3}}.$$
 (30.11)

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

$$P = -\frac{dE}{dV} = \frac{2}{3}E/V.$$
 (30.12)

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.

30.2 Lattice Potential

A refinement of the free electron gas introduces fixed nuclei – we imagine that the electrons move around under the attractive influence of the atomic nuclei fixed on some grid. To understand the basic physics of the model (originally introduced by Kronig-Penney), we can take a simple one-dimensional, periodic train of delta spikes.

Consider a set of equally spaced delta spikes, separated by a distance ℓ , and given some scale α , so that each contributes $V_{\delta} = \alpha \, \delta(x - j \, \ell)$ to the potential $(j \in \mathbb{Z})$. We assume that the potential continues "forever" (i.e. that there are a large number of nuclei), and that the wave-function must be bounded in magnitude (not going to infinity at spatial infinity). The potential is shown in Figure 30.2.

The wave function can be thought of as a piecewise function – in between each spike, we must satisfy $-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x)$, and we know the solution



Figure 30.2: An infinite string of Dirac spikes separated by equal distance $\ell.$

for the j^{th} wave function (the one defined for $j \ell \le x \le (j+1)x$):

$$\psi_j = A_j \cos(kx) + B_j \sin(kx) \quad k^2 \equiv \frac{2 m E}{\hbar^2}$$
 (30.13)

From the boundary conditions appropriate to the delta spike, we can relate the solution ψ_{j+1} to ψ_j :

$$\psi_j((j+1)\,\ell) = \psi_{j+1}((j+1)\,\ell) \qquad \psi'_{j+1}((j+1)\,\ell) - \psi'_j((j+1)\,\ell) = \frac{2\,m\,\alpha}{\hbar^2}\,\psi_j((j+1)\,\ell) \tag{30.14}$$

If we think of a local $x_j = x - j \ell$ that goes, in each "cell" from $0 \to \ell$, then we can write the connection between any two cells as:

$$\psi_j(x_j = \ell) = \psi_{j+1}(x_{j+1} = 0)$$

$$\psi'_{j+1}(x_{j+1} = 0) - \psi'_j(x_j = \ell) = \frac{2 m \alpha}{\hbar^2} \psi_{j+1}(x_{j+1} = 0).$$
 (30.15)

In terms of the coefficients, we have:

$$A_{j+1} = A_j \cos(k\,\ell) + B_j \sin(k\,\ell)$$

$$k\,B_{j+1} - k\,B_j \cos(k\,\ell) + k\,A_j \sin(k\,\ell) = \frac{2\,m\,\alpha}{\hbar^2}\,A_{j+1}$$
(30.16)

and we can write this in terms of the transfer matrix:

$$\begin{pmatrix} A_{j+1} \\ B_{j+1} \end{pmatrix} = \underbrace{\begin{pmatrix} \cos(k\,\ell) & \sin(k\,\ell) \\ \frac{2\,m\,\alpha}{\hbar^2\,k}\,\cos(k\,\ell) - \sin(k\,\ell) & \frac{2\,m\,\alpha}{\hbar^2\,k}\sin(k\,\ell) + \cos(k\,\ell) \\ \equiv \mathbb{M} & (30.17) \end{pmatrix}}_{\equiv \mathbb{M}}$$

Now we can move directly to the solution ψ_{j+1} by multiplication:

$$\begin{pmatrix} A_{j+1} \\ B_{j+1} \end{pmatrix} = \mathbb{M}^{j} \begin{pmatrix} A_{0} \\ B_{0} \end{pmatrix}, \qquad (30.18)$$

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and this multiplication is dominated by the behavior of the eigenvalues of \mathbb{M} – if the eigenvalues have magnitude > 1, it will diverge from some initial set of coefficients, to infinity. So to get a well-behaved wave-function, we must have both of the eigenvalues of \mathbb{M} bounded in magnitude by 1.

The eigenvalues of this two-by-two matrix are easy to write out:

$$\lambda_{\pm} = \cos(k\,\ell) + \frac{m\,\alpha}{\hbar^2\,k}\sin(k\,\ell) \pm \sqrt{\sin(k\,\ell) \left(\frac{2\,m\,\alpha}{\hbar^2\,k}\cos(k\,\ell) + \left(\frac{m^2\,\alpha^2}{\hbar^4k^2} - 1\right)\sin(k\,\ell)\right)} \tag{30.19}$$

Without worrying about the complex magnitude, suppose we set each of these separately equal to a function of k, $f_{\pm}(k)$ – then we can solve for $f_{+}(x) + f_{-}(x)$ by substitution

$$f_{+}(x) + f_{-}(x) = 2 \cos(k \,\ell) + \frac{2 \,m \,\alpha}{\hbar^2 \,k} \sin(k \,\ell). \tag{30.20}$$

Our requirement is that the functions $f_{\pm}(k)$ be, individually, less than or equal to one in absolute value, so that the infinite matrix multiplication converges (to ± 1 or 0), and this gives us a constraint on the energy $k = \frac{\sqrt{2mE}}{\hbar^2}$ – we have admissable solutions only when

$$\left|\cos(k\,\ell) + \frac{m\,\alpha}{\hbar^2\,k}\,\sin(k\,\ell)\right| \le 1. \tag{30.21}$$

Defining the unitless constants $\frac{m \alpha \ell}{\hbar^2 k} \equiv \beta$, and $k \ell = z$, our requirement is

$$\left|\cos(z) + \frac{\beta}{z}\sin(z)\right| \le 1.$$
(30.22)

Now for the physical point – looking at the solutions to this inequality for various β (delta strengths), we see that there are "gaps" in the energy, where there is no valid solution for k, and "bands" where k varies continuously. As an example, take $\beta = 2$ – we show the value of the left-hand side of (30.22), together with a function that is 1 when there are allowed solutions, 0 otherwise in Figure 30.3.

While this is a simple one-dimensional picture, the idea carries over to two and three dimensions. In our electron gas model, there was a continuum of energies allowed, but when we introduce a periodic potential (due to whatever mechanism), we find that there are "continuum" regions, where electrons can gain energy (filling the band), and then gaps, where we need



Figure 30.3: The left-hand side of (30.22) and a step function to show the allowed regimes for $\beta = 2, 8$.

to add some amount of energy to get an electron through to the next band. Materials with significant gap structure are insulators, difficult to get electrons moving (you have to input energy in a filled band to get the electron to cross it) – materials where a band is relatively unfilled are conductors – it takes very little energy to move an electron (since there is a local continuum of energies for it to exist in).



in the presence of a magnetic field (but no electrostatic field):

$$H = \frac{1}{2m} \left(\mathbf{p} - q \, \mathbf{A} \right) \cdot \left(\mathbf{p} - q \, \mathbf{A} \right) \tag{30.23}$$

where \mathbf{A} is the magnetic vector potential.

a. For $\mathbf{B} = B_0 \hat{\mathbf{z}}$, find an appropriate vector potential \mathbf{A} with $\nabla \cdot \mathbf{A} = 0$ – use cylindrical coordinates.

b. Write (but do not solve) the time-independent Schrödinger equation for this Hamiltonian, using the usual identification $\mathbf{p} \longrightarrow \frac{\hbar}{i} \nabla$. Expand out all terms, assuming $\psi = \psi(s, \phi)$ in cylindrical coordinates to get a second order PDE in s and ϕ .

Problem 30.3

For the following polynomial:

$$x^2 + \epsilon x - c = 0. \tag{30.24}$$

a. Find the roots using the quadratic equation. Expand the two roots, assuming ϵ is small ($\epsilon \ll 1$ and $c \sim 1$) through first order in ϵ .

b. Go back to the polynomial, and input the ansatz: $x = x_0 + \epsilon x_1$. Expand the polynomial and collect terms of order ϵ^0 and ϵ^1 . Set each of the resulting expressions equal to zero separately to find x_0 and x_1 (the argument here is that for ϵ small, we cannot have cancellation of terms of different order in ϵ – so each order in ϵ must be zero separately). Compare with your expansion from part a.