PHYS 487: Lecture # 5

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Lecture Span

- Free electron gas and band structure

The free electron gas

Imagine some box of matter, and filling it with electrons. With dimensions $L_x, L_y, \& \ L_z$. 3D infinite well. Independent, non-interacting electrons.

$$V(x,y,z) = \begin{cases} 0 & \text{inside} \\ \infty & \text{outside} \end{cases} \tag{1}$$

This is a good model for a metal. We first start with

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

$$\psi(x,y,z) = X(x)Y(y)Z(z) \tag{3}$$

Then, we get

$$E = E_x + E_y + E_z \tag{4}$$

Define wavenumbers: $k_i = \sqrt{2mE_i}/\hbar$. Boundary conditions:

$$k_i L_i = n_i \pi \tag{5}$$

Therefore, the wavefunction is

$$\psi_{n_x,n_y,n_z} n = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(n_x \pi / L_x x\right) \dots \tag{6}$$

With energies:

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) = \frac{\hbar^2 k^2}{2m} \tag{7}$$

Find the highest energy (fermi energy): Note that $|E| \sim |k|^2$. Consider a coordinate system with axis k_x, k_y, k_z. Then the distance between each k vector is π/L_i. Therefore, the volume per state is

$$V \sim \frac{\pi^3}{L_z L_y L_z} \tag{8}$$

Here, we find

$$\frac{1}{8}\left(\frac{4}{3}\pi k_f^3\right) = \frac{N_e}{2}\frac{pi^3}{V} \tag{9}$$

Then, we get

$$k_F = (3\rho\pi^2)^{1/3} \tag{10}$$

With

$$E_f = \frac{\hbar^2}{2m}\left(3\rho\pi^2\right)^{2/3} \tag{11}$$

Physically, the energy levels depend on the magnitude of k, which can be interpreted as a sphere in k space, where all the surface has the same k and therefore the same energy. Since we have a finite number of electrons, we find the maximal energy of the system. Here, using this volume approximation, we find that the maximal volume of the vector in k space of just one eight of the vector is $N_e/2 \times \pi^3/V$. Doing some algebra, where 1/8 represents just 1/8 of the volume, we can find k.

Electron Shell

Consider a shell in k space. But how many states are in between $[k_i, k_i + dk]$. Consider a shell

$$V_{shell} = \frac{1}{8}\left(4\pi k^2\right) dk \tag{12}$$

Then, the number of energy states in this shell is (dividing this shell by the volume differential)

$$dN = \frac{\frac{1}{2}\pi k^2}{\pi^3/V} dk \tag{13}$$

Then, accounting for the pauli exclusion principle

$$dN = \frac{Vk^2}{\pi^2} dk \tag{14}$$

Then

$$dE = \frac{\hbar^2 k^2}{2m} dN \tag{15}$$

It follows that

$$dE = \frac{\hbar^2 k^2}{2m}\frac{V}{\pi^2} k^2 dk \tag{16}$$

We can then integrate this in k space:

$$\int_{E_f}^{0} dE = \int_0^{k_f} dk \frac{\hbar^2 k^2}{2m}\frac{V}{\pi^2} k^2 \tag{17}$$

$$= \frac{\hbar^2 (3\pi^2 N_e)^{5/3}}{10\pi^2 m} V^{-2/3} \tag{18}$$

Note, although the electrons are discrete with k, if $N_e \to \infty$, then we can approximate this with an integral. Consider

$$dE = -\frac{2}{3}\hbar^2 \frac{(2\pi^2 N_e)^{5/3}}{10\pi^2 m} V^{-5/3} dV = -\frac{2}{3} E_{tot}\frac{dV}{V} \tag{19}$$

Thermodynamics connection: $dW = PdV$, here $P = (2/3)E_{tot}/V$, this means that particles tend to stay escape (pressure pushes out).

Simple model of a crystal

Dirac comb

$$V(x) = \alpha \sum_{j=0}^{N} \delta(x - ja) \tag{20}$$

Then, we use Bloch's theorem which states that the wavefunction should be

$$\psi(x) = \exp(iqx)u(x) \tag{21}$$

and

$$\psi(x - a) = \exp(-iqa)\psi(x) \tag{22}$$

If we do a cyclical boundary condition,

$$\psi(x) = \exp(iNqa)\psi(x) \tag{23}$$

Therefore,

$$q = \frac{2\pi n}{Na} \tag{24}$$

In $(0, a)$,

$$\frac{\hbar^2}{2m}\psi'' = E\psi'' \iff \psi'' = -k^2\psi \tag{25}$$

Then

$$\psi(x) = A\sin(kx) + B\cos(kx) \tag{26}$$

And using bloch's theorem, from $(-a, 0)$

$$\psi(x) = \exp(-iqa)(A\sin(kx) + B\cos(kx)) \tag{27}$$

Boundary condition at $x = 0$: ψ is continuous but not necessarily ψ'. Then, the boundary condition states that the constant B must be:

$$B = \exp(-iqa)(A\sin(kx) + B\cos(ka)) = \psi(0) \tag{28}$$

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{\epsilon}\psi''(x)dx + \int_{-\epsilon}^{\epsilon}V(x)\psi(x)dx = E\int_{-\epsilon}^{\epsilon}\psi(x)dx \tag{29}$$

Take the limit as $\epsilon \to 0$

$$-\frac{\hbar^2}{2m}\Delta\psi' + \psi(0) = 0 \tag{30}$$

Then given $\psi'_R(0)$ and $\psi'_L(0)$, we get that $\psi'(0)$ is

$$KA - \exp(-iqa)k(A\cos(ka) - B\sin(ka)) = \frac{2m\alpha}{\hbar^2}B \tag{31}$$

Then, we can obtain

$$\cos(qa) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka) \tag{32}$$

Note that because of the LHS, we have that

$$|\cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka)| \leq 1 \tag{33}$$

This forms bands on the ψ, ka space.