Topic 8-1: Free Electron Model
Kittel Pages: 133-138

Summary: In this set of notes we introduce the free electron model. We proceed to solve this model with fixed and periodic boundary conditions.

- Begin with the free electron model developed by Summerfield in 1933
- Assumptions of the free electron model
  - No interactions between electrons and nuclei or electrons with other electrons
  - Effectively we have a one electron system
  - Potential is flat within the box and is infinite everywhere else
- Start with the time independent Schrodinger equation (TISE)

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E'\psi(\vec{r}) \quad [1]$$

- $V(\vec{r})$ is the system potential, the potential inside our infinite well
  - Let $V(\vec{r}) = V_o$ within the solid and infinity everywhere else
- Let $E = E' - V_o$ so we have:

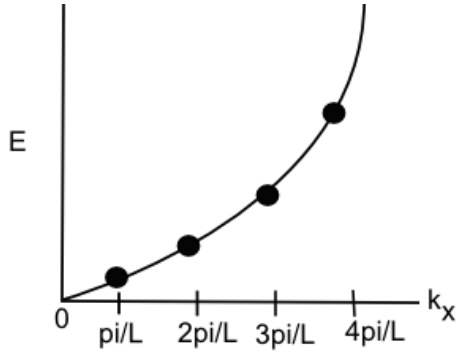
$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = E'\psi(\vec{r}) - V_o\psi(\vec{r}) = E\psi(\vec{r}) \quad [2]$$

- Now we have a differential equation that will give a standing wave solution within the box
- Still need boundary conditions to get a function

Standing wave approach w/ fixed boundary conditions

- Assume the electron never leaves the box so our wavefunction is zero at the box edges
- This means we need a sine wave so $\psi(x) = Asin(k_x x)$ where A comes from normalizing the integral using $\int_{solid} \psi^* \psi \, d\vec{r} = 1$
- Can put limits on k_x such that $k_x = \frac{\pi}{L} n_i$ where n_i is an integer
- If $n_i = 0$ $\psi(x) = 0$ which is not normalizable so we don't want to include that
- Negative n_i would give the same effective wavefunction as a positive one so that is unnecessary as well
- This means we only have positive integer values for n_i with no upper bound as our potential walls are infinitely high

- Plugging $\psi(\vec{r})$ into the TISE we get $E = \frac{\hbar^2}{2m}|k|^2$ which is the dispersion relation for electrons, E(k)
- Since we defined k in terms of an integer, our k space is **discrete**, just as it was for phonons!!



- Spacing is now $\frac{\pi}{L}$ for the standing wave description, unlike phonons where it was $\frac{2\pi}{L}$
- Now in 3D:

$$\psi(\vec{r}) = (\tfrac{2}{L})^{3/2} sin(k_x x) sin(k_y y) sin(k_z z) \quad [3]$$

$$E = \frac{\hbar^2}{2m}\left(k_x{}^2 + k_y{}^2 + k_z{}^2\right) = \frac{\hbar^2}{2m}\left|\vec{k}\right|^2 \quad [4]$$

- Can construct a constant energy surface with $\left|\vec{k}\right|$ as the radius in k space
  - Will result in 1/8 of a sphere (first octant) because of our limits on k
- That is about all for fixed boundary conditions

Periodic boundary conditions approach

- What is different for periodic boundary conditions
  - $\psi(x) = \psi(x + L)$ where L is the length of our box
  - Use a traveling wave solution:

$$\psi(\vec{r}) = Ae^{i\vec{k}\cdot\vec{r}} \quad [5]$$

    - $A = \frac{1}{L}^{3/2}$ in 3D
- No limits on $\vec{k}$
  - $\vec{k} = 0$ gives $\psi(\vec{r}) = Ae^0 = 1$ which is normalizable

- $\psi(k) \neq \psi(-k)$ waves travel in opposite direction

- In this case, (just like in phonons) the spacing in k space for periodic boundary conditions will be $\frac{2\pi}{L}$.
- **Concept check:** The spacing in periodic vs fixed boundary conditions is different, is this ok?
  - Should be okay if the number of k points up to a certain energy level are equal in both cases
- Total number of points = total volume of k space considered times the number of k points per unit volume
- For fixed boundaries this is $\frac{1}{8} V_{sphere} \frac{1\ k\ point}{(\frac{\pi}{L})^3}$
- For periodic boundaries this is $V_{sphere} \frac{1\ k\ point}{(\frac{2\pi}{L})^3} = \frac{1}{8} V_{sphere} \frac{1\ k\ point}{(\frac{\pi}{L})^3}$ which means both cases come out to be equal!
- While the k space looks different for each case, they are consistent in the total number of electronic states $N_k(E)$
- This means that the density of states, D(E), is also the same for both cases

Questions to Ponder

1. This model has no potential at the bottom of the well. When is this appropriate and why?