Lecture 3: electrons

- **Free electron gas**
- **Density of states**
- **Velocity and mass**
- **Metals, insulators, and semiconductors**
- **Introducing the lattice back in: Brillouin zones and Fermi surfaces**
- **Tight binding model**

Free electron gas in three dimensions

This toy problem turns out to be applicable to many simple metals such as sodium or copper, and it is a generalization of the infinite potential well to three dimensions. This model makes the following assumptions about electrons in a metal:

- Valence electrons are completely delocalized over the entire solid, such that they are treated as waves rather than particles
- The lattice is absent so we neglect interactions between electrons and lattice (the lattice will be put back in later)
- Electrons do not interact with each other at all, except via Pauli exclusion. In particular, coulomb repulsion is ignored

In three dimensions, the free particle Schrodinger equation is:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_k(r) = \epsilon_k \psi_k(r)$$

The wavefunctions are marked by k instead of by n, and we will see why in a moment.

At this point, it is helpful to start over with a different formalism.

We consider plane wave wavefunctions of the form

$$\psi_k(r) = e^{ik \cdot r}$$

Where k is a wavenumber or quantum mechanical momentum. It can be expressed as $k = \frac{2\pi}{\lambda}$ or $p = \hbar k$

And periodic boundary conditions of the form

$$\psi(x + L, y, z) = \psi(x, y, z)$$

$$\psi(x, y + L, z) = \psi(x, y, z)$$

$$\psi(x, y, z + L) = \psi(x, y, z)$$

Periodic boundary conditions better reproduce the fact that the solid looks infinite to the electrons. The formalism above also permits negative values of k as unique solutions, which makes more physical sense because of the connection between k and momentum. Finally, periodic boundary conditions are utilized in many modern computational techniques in condensed matter physics.

Plugging the first one into the wavefunction we get:

$$e^{i(k_x(x+L)+k_y y+k_z z)} = e^{i(k_x x+k_y y+k_z z)}$$

$$e^{ik_x L} = 1$$

$$k_x = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \dots$$

And similar for ky and kz.

Plugging the plane wave wavefunction into schrodinger's equation we get:

$$\frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \epsilon_k = \frac{\hbar^2 k^2}{2m}$$

As before, we take our N electrons and put them into the available states, filling lowest energy first. In 3D this is trickier because multiple states may have the same energy, even though they are marked by different k_x, k_y, k_z. In 3D, our rules for filling up electrons are:

- Every state is defined by a unique quantized value of (k_x, k_y, k_z)
- Every state can hold one spin up and one spin down electrons
- Fill low energy states first. In 3D, this corresponds to filling up a sphere in k space, one 'shell' at a time. Each shell is defined by a radius k, where $k^2 = k_x^2 + k_y^2 + k_z^2$, and every state in the shell has the same energy, although different combinations of k_x, k_y, k_z
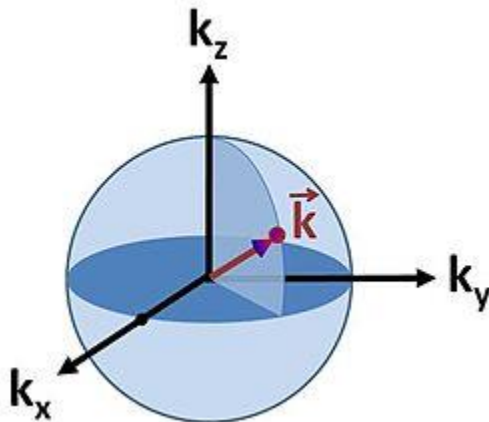
When we have used up all our electrons, we are left with a filled sphere in k space with radius k_F (called the Fermi momentum) such that

$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2$$

This sphere in k-space has a volume $\frac{4}{3}\pi k_F^3$ and it is divided into voxels of volume $\left(\frac{2\pi}{L}\right)^3$

If we divide the total volume of the sphere by the volume of each 'box' and account for the fact that each box holds 2 electrons, we get back how many electrons we put in:

$$2 * \frac{\frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3} = N = V k_F^3/3\pi^2$$

Here, $V = L^3$ is the volume of the solid. We can use this relationship to solve for k_F and show that it depends on electron density (N/V)

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

Plugging this back into the expression for ϵ_F we get:

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

At absolute zero, the Fermi sphere has a hard boundary between occupied and unoccupied states. At higher temperature, this boundary becomes fuzzier with increasing occupation permitted outside the initial boundary (think of a rocky planet like earth vs a gaseous planet like Jupiter). The width of this fuzziness is determined by the width of the Fermi-Dirac distribution at that temperature, and it is roughly proportional to $k_B T$. Notably, the vast majority of electrons in the Fermi gas are completely inert because they are buried deep inside the sphere. Only electrons close to the Fermi level are affected by temperature and participate in conduction. This is quite contrary to the conclusions of particle-like treatments of electrons in a metal which assume that all valence electrons participate in electronic properties.

Density of states

As with phonons, the density of states is a useful quantity for electrons.

I like to think of Density of States as a series of "boxes" where electrons can live. Each box is defined by the coordinates which distinguish one electron from another. In the case of a 3D free electron gas, each box is defined by unique k_x, k_y, k_z and spin. Where the density comes in is at each energy interval $d\epsilon$ we consider 'how many 'boxes' are there?'
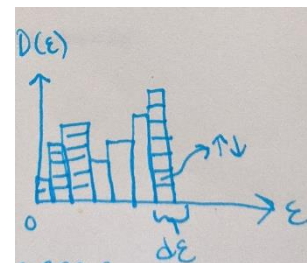
It is defined as:

$$D(\epsilon) \equiv \frac{d\widetilde{N}(\epsilon)}{d\epsilon}$$

Where $\widetilde{N}(\epsilon)$ is the number of states as a function of energy. We can find it by expressing $\widetilde{N}$ in terms of ϵ and taking a derivative. We begin by considering a sphere in k-space with an arbitrary radius k and asking how many electrons that will hold

$$N(k) = V k^3 / 3\pi^2$$

The relationship between energy and momentum in a free electron gas is pretty straightforward too (unlike with phonons):
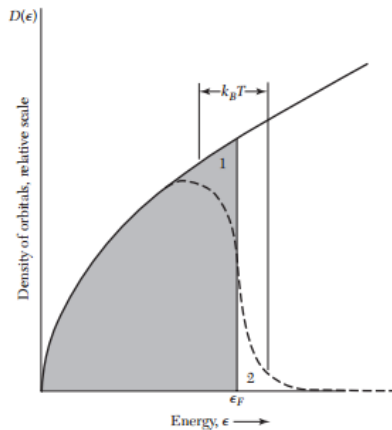
$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

Solving for k, and plugging in above we get

$$N(\epsilon) = \frac{V}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2}$$

Now we can just take the derivative with respect to energy and get:

$$D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\epsilon^{1/2}$$

Thus, the density of electron states in 3D is a function of energy. If you have more electrons, you will end up with a higher density of states **at the Fermi energy**.

Effect of temperature

Temperature introduces a 'cutoff' by the Fermi-dirac function

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_BT} + 1}$$

Such that some states with $\epsilon > \epsilon_F \sim \mu$ can be occupied and some states with $\epsilon < \epsilon_F \sim \mu$. Temperature only affects states roughly within k_BT of the Fermi energy. Another way to think of the effect of temperature is the fuzzing out of the boundary of the Fermi surface.

Electron velocity

There are two ways of extracting an electrons' velocity in a Fermi gas. These will be applicable even when electrons are modeled in a more sophisticated way.

- From the derivative of the energy vs k (equivalent to what we did for phonons): $v_g = \frac{1}{\hbar}\frac{\partial \epsilon_k}{\partial k} = \hbar k/m$. Note that this is an example of a very useful and measurable quantity derived directly from a materials' ϵ vs k relationship. This (ϵ vs k) is called a dispersion relation. For a free electron gas, it is quadratic, but it doe not have to be.
- By representing the linear momentum operator as $\boldsymbol{p} = -i\hbar\nabla$ and applying this to the plane-wave wavefunction to get $\boldsymbol{p} = \hbar\boldsymbol{k}$ and equating to m$\boldsymbol{v}$ to get $\boldsymbol{v} = \hbar\boldsymbol{k}/m$

The velocity of electrons at the fermi energy is called the Fermi velocity (v_F) and it is given by:

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

Effective mass

Electrons in a crystalline solid often exhibit properties that free electrons do not have. One of the most basic is that they may behave as if they have a different mass (either heavier or lighter) than the free electrons mass. The effective mass (usually written m* or m_{eff}) can also be derived from dispersion relations

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 \epsilon_k}{\partial k^2}$$

Electron-like vs hole-like bands

Charge carriers in a solid sometimes respond to electromagnetic fields as if they have positive charge, and this also originates from dispersion relations. Negative (electron-like) carriers have ϵ vs k which is
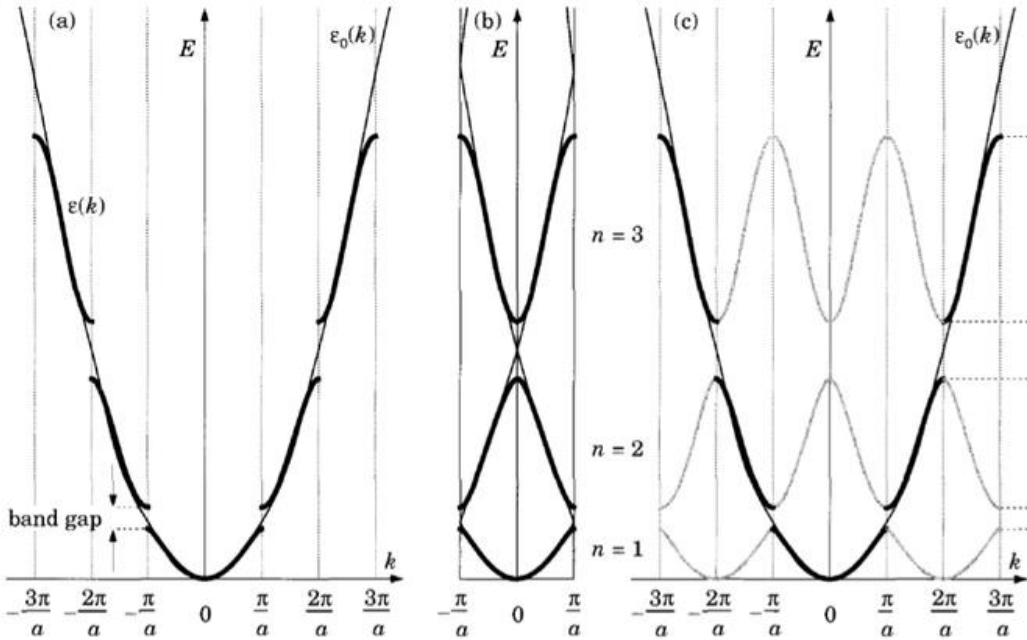
concave up and positive (hole-like) carriers have ϵ vs k which is concave down. The latter case can emerge from a free-*electron* gas once we turn on lattice interactions.
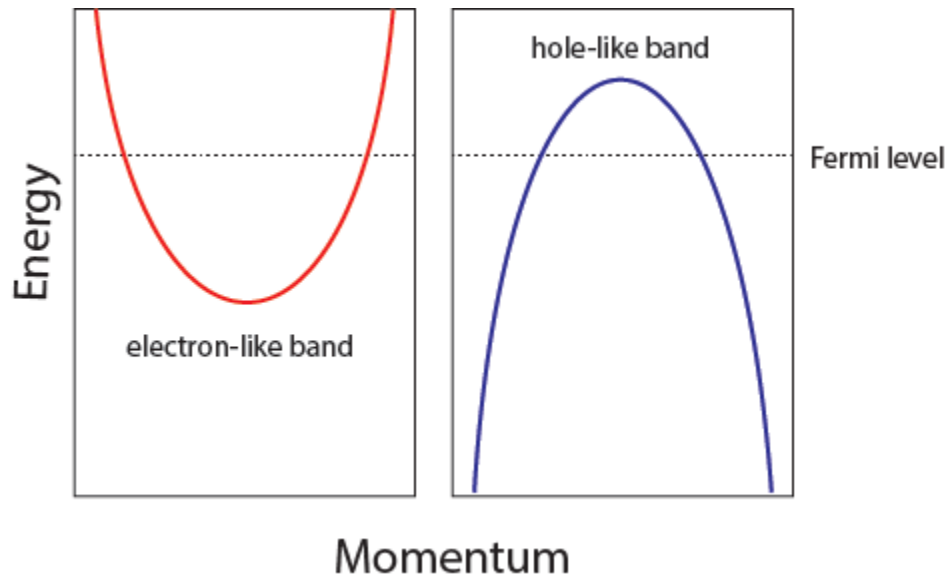
Turning the lattice potential back on: Brillouin zones and band gaps

So far, we have discussed electrons without the lattice, and now we turn the lattice back on. Since the electron gas originated from atoms giving up some electrons, the realistic lattice we turn on is a periodic array of positive charges. When we turn on the lattice potential, the following things happen. They are sketched below in 1D only, and generalizing to higher dimensions will be done later

1. The k-axis is divided up into 'Brillouin zones' of the same size. The length of each Brillouin zone is a reciprocal lattice vector, which in 1D is $\frac{2\pi}{a}$. This division reflects the periodicity of the lattice
2. Each Brillouin zone must contain the same information (reflecting periodicity in both real space and reciprocal space)
3. When dispersions cross, gaps open up, with the magnitude of these band gaps generally reflecting the strength of the lattice potential. There are several ways to think about this:
    a. Pauli exclusion: each point on the ϵ vs k graph can hold two electrons: one spin up, and one spin down. When two lines cross, you have 4 electrons trying to be in the same state, which won't fly
    b. Bragg reflection: each point where bands cross is related to an equivalent point via a reciprocal lattice vector, and these momenta can satisfy the Bragg condition introduced in lecture 2: $2\boldsymbol{k} \cdot \boldsymbol{G} = G^2 \rightarrow 1D\ case \rightarrow k = \pm\frac{1}{2}G = \pm\frac{n\pi}{a}$. Thus an electron that has those specific momenta will be Bragg reflected by the lattice, such that the electronic state at that momentum is comprised of a sum of two waves of the same wavelength moving in opposite directions. This is a standing wave with zero group velocity.

(a) ... (b) $n = 3$ ... $n = 2$ ... $n = 1$ ... (c)

E, $\varepsilon_0(k)$, $\varepsilon(k)$, band gap, k

$-\frac{3\pi}{a}$ $-\frac{2\pi}{a}$ $-\frac{\pi}{a}$ 0 $\frac{\pi}{a}$ $\frac{2\pi}{a}$ $\frac{3\pi}{a}$

Bloch functions

Bloch's theorem is one of the most important principles in solid state physics. It states that the solution to the Schrödinger equation with a periodic potential (i.e. a crystal) must have a specific form:

$$\psi_k(r) = u_k(r)e^{ik\cdot r}$$

Where $u_k(r)$ has the period of the lattice such that it is invariant under translation by a lattice vector (**T**): $u_k(r) = u_k(r + T)$

Eigenfunctions of this form are called Bloch functions. They consist of a product of a plane wave and a function which shares the periodicity of the lattice.

Crystal momentum of an electron

The Bloch wavefunctions are labeled by an index k (as the free electron wavefunctions were earlier), and this quantity, is called crystal momentum. A few comments about crystal momentum

- $e^{ik\cdot T}$ is the phase factor which multiplies a Bloch function when we make a translation by a lattice vector **T**
- If the lattice potential vanishes in the central equation, we are left with $\psi_k(r) = e^{ik\cdot r}$ just like in the free electron case
- Crystal momentum ($\hbar k$) is like regular momentum in that it enters into conservation laws that govern collisions (e.g. electrons with momentum $\hbar k$ colliding with a phonon with momentum $\hbar q$)
- Crystal momentum is different from regular momentum in that it is defined only modulo a reciprocal lattice vector **G**. Thus, if an electron collides with a phonon and is kicked into momentum k', this is expressed in the following way, $k + q = k' + G$

Metals, insulators, and semiconductors

- Metals have E_F (Fermi energy) inside a band, such that there are unoccupied states which the highest energy electrons can make low-energy excitations into
- Semiconductors and insulators have E_F inside band gap, such that the band below E_F is completely full and highest energy electrons must traverse entire band gap to make excitation
- Semiconductors differ from insulators simply by size of and gap. Insulators typically have band gap larger than optical frequencies, such that they are often transparent. Semiconductors have band gap smaller than optical frequencies
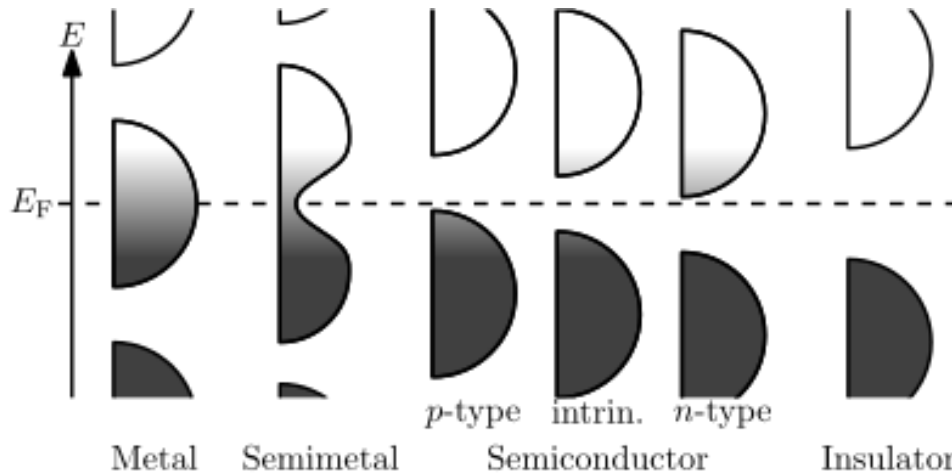
Metals and Fermi surfaces

In this section, we introduce the periodic lattice potential onto a free electron gas in 2D and 3D. The starting point is Brillouin zones (BZ). The first BZ is fairly straightforward—it is a Wigner-Seitz cell (see lecture 1).
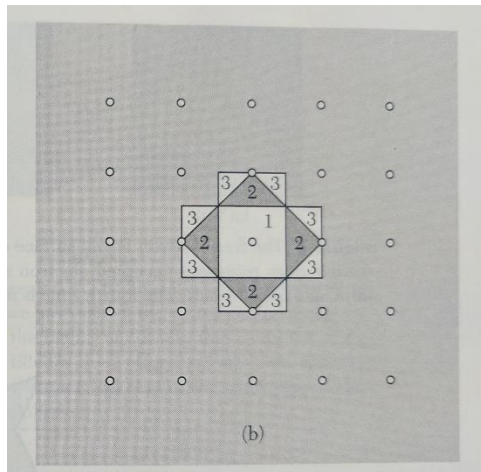
For higher BZs, I am skipping the procedure for deriving them, since this is something one normally looks up. However, these attributes of higher BZs are a good double check if you construct them yourself:

- All BZs must have the same total area (check that disjointed regions of BZ 2 & 3 have the same area as one)
- Disjointed regions of higher BZs must translate into the first BZ via reciprocal lattice vectors without overlap (e.g. translation only, no rotation)
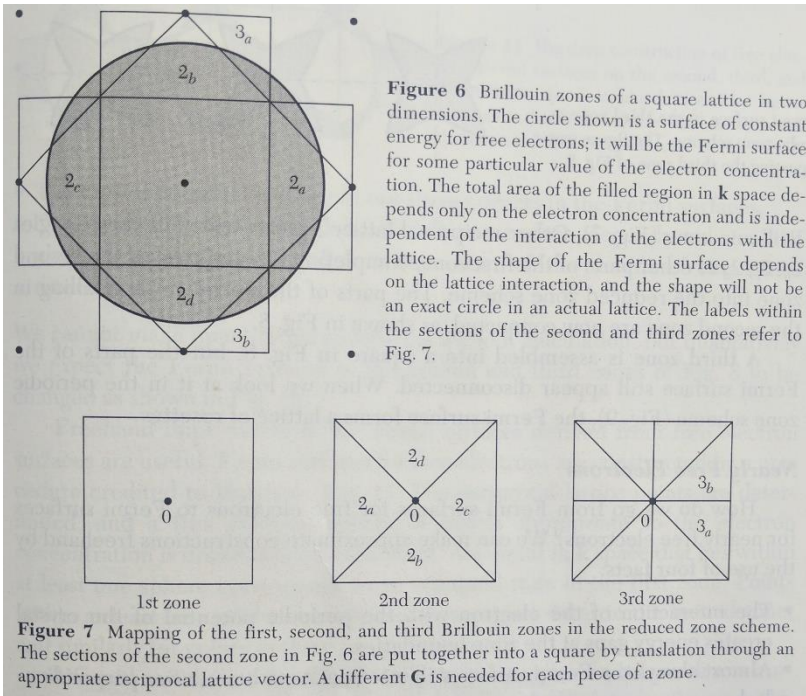
Now add electrons to make a Fermi surface!

Starting off with a free-electron model, the Fermi surface in 2D is a circle centered around $(k_x, k_y) = (0,0)$.

If this circle is small enough to fit entirely within the first Brillouin zone we are done.

If the circle overfills the first Brillouin zone, we do the following:

- Superimpose the circle on all the Brillouin zones (extended zone scheme)

Figure 6 Brillouin zones of a square lattice in two dimensions. The circle shown is a surface of constant energy for free electrons; it will be the Fermi surface for some particular value of the electron concentration. The total area of the filled region in **k** space depends only on the electron concentration and is independent of the interaction of the electrons with the lattice. The shape of the Fermi surface depends on the lattice interaction, and the shape will not be an exact circle in an actual lattice. The labels within the sections of the second and third zones refer to Fig. 7.

Figure 7 Mapping of the first, second, and third Brillouin zones in the reduced zone scheme. The sections of the second zone in Fig. 6 are put together into a square by translation through an appropriate reciprocal lattice vector. A different **G** is needed for each piece of a zone.

- Consider the portion of the Fermi surface that is inside each Brillouin zone, and translate this back into the first Brillouin zone.

For the example shown here, the free electron Fermi surface entirely fills the first Brillouin zone, partially fills the 2nd, and has a small incursion into the 3rd and 4th. Only the first 3 Brillouin zones are shown.

Although the filled areas of the 3rd Brillouin zone look disconnected, they can be shown to form connected propeller shapes in the repeating zone scheme.
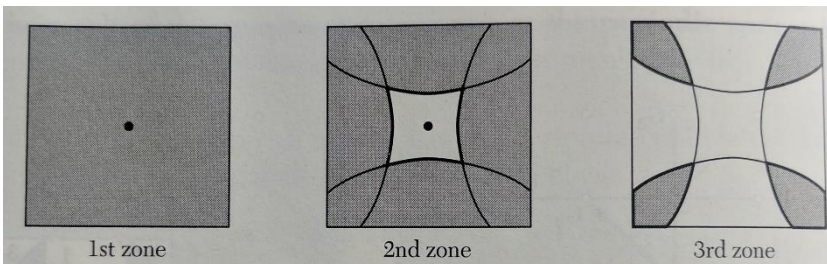
When this procedure is extended to the *nearly free electron model*, where the lattice potential is not ignored, the following considerations are used

- Interactions of electrons with periodic ionic potential opens gaps at Brillouin zone boundaries
- Fermi surface will almost always intersect Brillouin zone boundary perpendicular
- Crystal potential will round sharp corners of fermi surface
- The total volume enclosed by fermi surface depends only on electron concentrations, and will be the same for the free electron case and when the ionic potential is turned on (nearly free electron)

Qualitatively, the Fermi surfaces in the 2nd and 3rd Brillouin zone, for the same example as above, will change slightly to the following shapes:
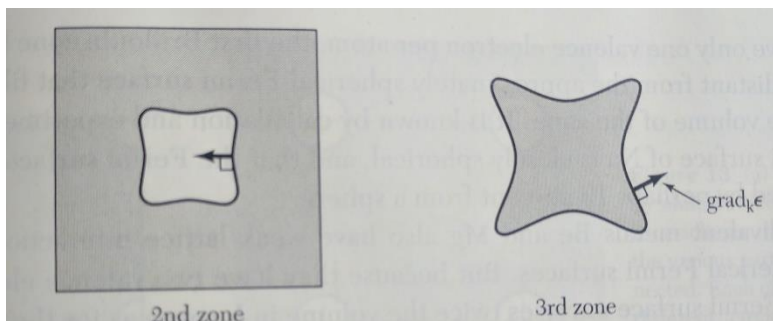
Notice that electrons almost fill the second zone, except for a small empty region in the center. This is considered to be a 'hole-like' fermi surface, because the enclosed surface constitutes the absence of electrons. In the third zone, electrons

fill a minority of the area. This is considered to be an electron-like fermi-surface

The nearly free electron model (start with free electron gas and turn on lattice potential) can explain why some real metals have dominant hole-like charge carriers, and also why the measured charge density in many metals is inconsistent with simply counting the number of valence electrons per atom.

Tight Binding model

The tight binding model is based on combining wavefunctions of individual atomic orbitals.

Suppose an isolated atom has potential $U(\boldsymbol{r})$ and is in an s-state (spherically symmetric), represented by wavefunction $\phi(\boldsymbol{r})$. Now suppose that there is a crystal of N of these atoms, and the presence of other atoms doesn't much affect the single-atom wavefunction. The wavefunction of an electron in this whole crystal can be expressed as:

$$\psi_k(\boldsymbol{r}) = N^{-1/2} \sum_j e^{i\boldsymbol{k}\cdot\boldsymbol{r}_j} \phi(\boldsymbol{r} - \boldsymbol{r}_j)$$

The first order energy is found by calculating the diagonal matrix elements of the Hamiltonian (where the Hamiltonian describes the kinetic and potential energy of electrons in the crystal...but it turns out we won't need to write what it is exactly)

$$\epsilon_k = <\boldsymbol{k}|H|\boldsymbol{k}> = N^{-1} \sum_j \sum_m e^{i\boldsymbol{k}\cdot(\boldsymbol{r}_j - \boldsymbol{r}_m)} < \phi_m|H|\phi_j >$$

Where $\phi_m \equiv \phi(\boldsymbol{r} - \boldsymbol{r}_m)$

Define a new variable $\boldsymbol{\rho}_m = \boldsymbol{r}_m - \boldsymbol{r}_j$

$$<\boldsymbol{k}|H|\boldsymbol{k}> = \sum_m e^{i\boldsymbol{k}\cdot\boldsymbol{\rho}_m} \int dV \phi^*(\boldsymbol{r} - \boldsymbol{\rho}_m)H\phi(\boldsymbol{r})$$

Now, we neglect all of the integrals above **except** for those on the same atom and those between nearest neighbors (separated by $\boldsymbol{\rho}$). This is the tight binding part of the tight binding model: only considering orbital overlap with adjacent atoms assumes that electrons do not make excursion far from their original atom and are hence, tightly bound. Note that it is perfectly acceptable, and sometimes necessary, to consider second nearest neighbors (2nd most closest atom) or even third and fourth, in the tight binding model. However, the solved examples in the book only involve the nearest neighbors.

$$\int dV \phi^*(\boldsymbol{r})H\phi(\boldsymbol{r}) = -\alpha$$

$$\int dV \phi^*(\boldsymbol{r} - \boldsymbol{\rho})H\phi(\boldsymbol{r}) = -\gamma$$

γ can be determined by assuming some specific form of ϕ. For example, for two hydrogen atoms in 1s states, $\gamma = 2\left(1 + \frac{\rho}{a_0}\right)e^{-\rho/a_0}$ where a_0 is the Bohr radius. However, in practice, one often one determines it empirically from experiments or first-principles theory (e.g. we measure or calculate a certain ϵ_k, which is best parametrized by certain values of α and γ.
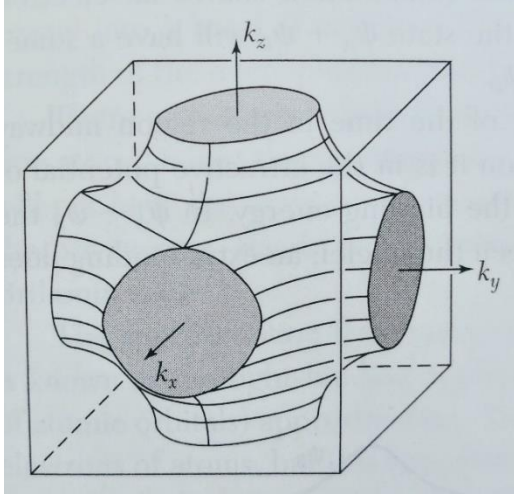
Thus:

$$< k|H|k >= -\alpha - \gamma \sum_m e^{-ik\cdot\rho_m} = \epsilon_k$$

To proceed further, we need information about the crystal structure. For a simple cubic structure, $\rho_m = (\pm a, 0,0); (0, \pm a, 0); (0,0, \pm a)$

Thus, $\epsilon_k = -\alpha - 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a)$

A constant energy surface is shown on the left.

For a BCC crystal structure with 8 nearest neighbors, the dispersion is given by:

$$\epsilon_k = -\alpha - 8\gamma \cos\frac{1}{2}k_x a \cos\frac{1}{2}k_y a \cos\frac{1}{2}k_z a$$

For a FCC structure with 12 nearest neighbors, the dispersion is given by:

$$\epsilon_k = -\alpha - 4\gamma(\cos\frac{1}{2}k_y a \cos\frac{1}{2}k_z a + \cos\frac{1}{2}k_z a \cos\frac{1}{2}k_x a + \cos\frac{1}{2}k_x a \cos\frac{1}{2}k_y a$$