4. Carrier statistics and Density of States

We have so far discussed the case of a single electron where the charge density was given as \( \rho(\mathbf{r}) = \epsilon \psi_0^*(\mathbf{r}) \psi_0(\mathbf{r}) \) and the total quantity of \( \psi_0 \) electrons \( n(\mathbf{r}) = \frac{\psi_0^*(\mathbf{r}) \psi_0(\mathbf{r})}{\epsilon} \) is obtained by integrating \( n(\mathbf{r}) \) over space to get

\[
\int n(\mathbf{r}) \, d^3r = \frac{1}{\epsilon} \int \psi_0^*(\mathbf{r}) \psi_0(\mathbf{r}) \, d^3r = \langle \psi_0 | \psi_0 \rangle = 1.
\]

Now we turn to the question of having multiple electrons and ask how we can "count" or obtain things like charge density for many electrons. To do so, we must understand 2 things:

one is the "distribution function" \( f(\mathbf{k}) \) which tells us about the probability of finding an electron in a state \( \mathbf{k} \) (or having a wavevector \( \mathbf{k} \)). This function is a probability, so \( 0 \leq f(\mathbf{k}) \leq 1 \).

Then with this function we can count the electrons simply as

\[
\hat{n}(\mathbf{r}) = \sum_{\mathbf{k}} f(\mathbf{k}) \frac{\psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r})}{\epsilon}
\]

and

\[
\int \hat{n}(\mathbf{r}) \, d^3r = \frac{1}{\epsilon} \sum_{\mathbf{k}} f(\mathbf{k})
\]
When the system is in equilibrium, the distribution function is given by the Fermi-Dirac distribution

\[ f(\varepsilon) = \frac{1}{\exp \left( \frac{E(\varepsilon) - E_F}{k_B T} \right) + 1} \]

We can see that \( f(\varepsilon) \) really only depends on \( E(\varepsilon) \), not \( \varepsilon \) directly. Then we can write our expression for the electron density per unit volume as

\[ n_e = \frac{1}{\text{Vol.}} \sum_{\varepsilon} f(E) \]

Since the states \( \varepsilon \) are spaced by \( 2\pi/L \) in each direction (each unit cell of size \( a \) contributed one state), so there are \( N \) states in a length \( L = Na \) the \( \varepsilon \)'s are densely packed (if \( L \gg a \) so it usually is) and we can approximate the sum by an integral

\[ n_e = \frac{1}{\text{Vol.}} \sum_{\varepsilon} f(E) = \frac{1}{\text{Vol.}} \int f(E) d\varepsilon \]

\[ = \frac{1}{(2\pi L)^3} \int f(E) d\varepsilon \]

because there are \( (2\pi L)^3 \) states in \( d\varepsilon \).
because \[ \frac{1}{\text{Vol.}} \mathcal{F} = \frac{N^3}{\text{Vol.}} = \frac{(L/a)^3}{L^3} = \frac{1}{a^3} \]

while \[ \int \frac{d\mathbf{k}}{\sqrt{2}} = \mathcal{D} = \left( \frac{2\pi}{a} \right)^3 \]

so \[ \left( \frac{1}{2\pi} \right)^3 \int \frac{d\mathbf{k}}{\sqrt{2}} = \frac{1}{\text{Vol.}} \mathcal{F} \]

Finally we have

\[ n_c = \left( \frac{1}{2\pi} \right)^3 \int \frac{d\mathbf{k}}{\sqrt{2}} f(E) dE + \mathcal{D} \left[ E(k) \right] \]

We now break this integral up into two steps: one over energy and another over \( k \) having a given energy:

\[ n_c = \left( \frac{1}{2\pi} \right)^3 \int f(E) dE \int S(E(k) - E) \, d\mathbf{k} \]

\[ = \int f(E) g(E) \, dE \]

where the quantity \( g(E) = \frac{1}{(2\pi)^3} \int S(E-E(k)) \, d\mathbf{k} \)

is called the density of states.
Using the property of the $S$ function that
\[
S f(x) dx = \frac{f(x-x_0)}{df/dx}
\]
we have the more general definition
\[
S(E_0) = \frac{1}{(2\pi)^3} \int \frac{S(E_0 - E(k))}{\sqrt{\|\nabla E(k)\|^2}} dk
\]
where $S$ is the surface given by all the points $k$ satisfying $E(k) = E_0$. This surface is the constant energy contour of $E(k)$.

Another way to arrive at this equation is to consider breaking up the integral over all $k$ into two parts: the integral over a thin shell of energies between $E_0$ and $E_0 + dE$ and then over all such energies $E_0$. Since the $k$ vector perpendicular to the surface $E(k) = E_0$, let's call it $k_0$, is colinear with the gradient $\nabla E(k)$ (remember that the gradient always points in the direction of the greatest change so it is perpendicular to the constant energy surface $E(k) = E_0$), we can write...
\[ dE = \frac{\partial}{\partial k} E(k) \mid_{\text{d}k} \] and then

say that \[ dE = \frac{\partial E}{\partial \text{d}S} \text{d}k = \frac{\partial}{\partial \text{d}S} \frac{\text{d}S \text{d}E}{\partial E(k)} \]

with \( S \) being the surface \( E(k) = E_0 \).

We have reduced the sum over \( k \)'s into an integral over energy and an integral over the constant energy surface, but now we still have to compute \( g(E) \). For the case of effective mass \( E(k) = \frac{\hbar^2 k^2}{2m^*} + E_0 \)

which is independent of direction of \( \vec{k} \), only depending on its magnitude.

Hence the constant energy surface is a sphere

\[ |k^*| = \sqrt{\frac{2m^*}{\hbar^2}(E(k^*) - E_0)} \]

of radius

with surface area \[ S = \frac{4\pi}{3} |k^*|^2 \]

\[ S = \frac{4\pi}{3} \frac{2m^*}{\hbar^2} (E - E_0) \]

The gradient \[ \frac{\partial E(k^*)}{\partial k^*} \]

\[ = \frac{\hbar^2}{2m^*} \sqrt{\frac{2m^*}{\hbar^2} (E - E_0)} \]
Putting everything together we get:

\[ g(E) = \frac{1}{(2\pi)^3} \frac{1}{\sqrt{|\mathbf{\nabla} \cdot \mathbf{E}(\mathbf{k})|}} \left( \frac{2\pi}{\hbar^2} \right)^3 \frac{1}{\sqrt{\frac{2m^*}{\hbar^2}} (E-E_0)} \]

\[ = \frac{1}{4\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E-E_0} \]

However this only works if the effective mass tensor is just a simple diagonal matrix:

\[ \begin{pmatrix} m^*_{xx} & 0 & 0 \\ 0 & m^*_{yy} & 0 \\ 0 & 0 & m^*_{zz} \end{pmatrix} \]

In Si, for example, there are 6 equivalent conduction band minima, one in each \( K \) direction at \((0.85, 0, 0)\). Each of these minima has an ellipsoidal constant energy surface:

\[ \begin{aligned} & k_x \\ & \downarrow \text{ellipsoidal constant energy surface} \\ & (0.85, 0, 0) \end{aligned} \]

with a longitudinal and transverse masses \( m^*_{xx} \) and \( m^{*2} \). In that case:

\[ g(E) = \frac{1}{V m^*_L m^{*2}} \left( \frac{e^2}{\hbar^2} \right)^2 \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E-E_c} \]
4. Density of States Revisited.

We used a more formal approach to derive the DOS and motivate its use. The goal now is to give a more intuitive approach to how it is computed. Let us count the number of states in some interval between \( E \) and \( E + dE \) directly and equate that to the density of states. It is easiest to start by counting the states in reciprocal space (\( k \)-space).

Imagine a thin shell at some radius \( k \) with thickness \( dk \). In this shell between \( k \) and \( k + dk \), we have \( N = 4\pi k^2 \, dk \) volume. Each state occupies a volume \( \frac{(2\pi/L)^3}{(2\pi/L)^3} \) so

\[
\text{\# states} = \frac{4\pi k^2 \, dk}{(2\pi/L)^3} = \frac{Vk^2 \, dk}{2\pi^2}
\]

Now we want a density so divide this by \( V \) to get \( \frac{\text{\# states}}{\text{volume}} = \frac{k^2 \, dk}{2\pi^2} \).

Finally, we want states in the interval between \( E \) and \( E + dE \) so convert \( k \rightarrow E \) and \( dk \rightarrow dE \) by using \( E - E_0 = \frac{\hbar^2 k^2}{2m^*} \).
so that \( dE = \frac{\hbar^2}{2m^*} k \, dk \)

and \( k = \sqrt{\frac{2m^*}{\hbar^2}} \sqrt{E-E_c} \)

Now using \( dk \, dl = \frac{m^*}{\hbar^2} \, dE \)

we get

\[
\frac{\# \text{ states}}{\text{Vol} \times dt \, dE} = \frac{k^2}{2 \pi^2} \frac{dE}{dE} = \frac{1}{4\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E-E_c}
\]

This we can call our density of states per unit interval of energy and per unit volume \( g(E) \).