5.4 Quantum Model of Conduction in Metals

While the classical model of metals gave reasonable explanations of some aspects of electrical and thermal conduction, it was deficient in some other aspects. We saw in the last chapter that an application of quantum mechanics to atoms gives us satisfactory explanation of many properties of atoms and molecules - spectroscopy, their arrangement in the periodic table, angular momentum, magnetic dipole moment, bonding between atoms, and so on. The questions now are: could an application of quantum mechanics to a block of solid also give us insights into properties of solids, and is it mathematically possible to solve the complicated problem of electrons in solids? Recall that solving Schrödinger equation for any atom beyond the Hydrogen atom is too difficult. If multielectron-atom problems are difficult, there is no hope of solving the problem of 10^22 electrons in a metal sample. Clearly, we need drastic approximation such as the the one made in the Drude model. In this section we will look at the Drude model quantum mechanically.

5.4.1 Fermi Level

Free Electron Approximation

If electrons are considered free of each other, we can solve the problem of one electron first, and then use the Aufbau principle together with the Pauli's exclusion principle to find the quantum state of the solid. Each electron in the metal would be considered to be confined to the body and surface of the metal. This is same as a particle in a box problem. To be concrete and for the sake of simplicity, suppose the metal is a cube of side a with one corner at the origin. Then, the quantum wave function of any one electron will be

$$\psi_E(x, y, z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right), \qquad (5.21)$$

with quantum numbers $n_x = 1, 2, 3, \cdots$, $n_y = 1, 2, 3, \cdots$, $n_z = 1, 2, 3, \cdots$, corresponding to energy

$$E = \frac{\pi^2 \hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right). \qquad (5.22)$$

According to Pauli's exclusion principle, each state designated by the quantum numbers (n_x, n_y, n_z) can have at most two electrons, one with up spin and the other with down spin. For instance, the first electron will go in the lowest energy state $(1, 1, 1)$, the second electron can also go in this state but with opposite spin. The first two electrons each have energy

$$E = \frac{3\pi^2 \hbar^2}{2ma^2}.$$

The third electron will have to go in the next higher energy state, which will be either $(2, 1, 1)$ or $(1, 2, 1)$ or $(1, 1, 2)$. Suppose, we place the third electron in

$(2, 1, 1)$, then the fourth electron can have the same spin as the third electron if it is in $(1, 2, 1)$ or $(1, 1, 2)$ states. In this way, a total of six electrons will go into states $(2, 1, 1)$, $(1, 2, 1)$, and $(1, 1, 2)$, which all have the same energy.

$$E = \frac{3\pi^2 \hbar^2}{ma^2}.$$

The next six electrons go into $(2, 2, 1)$ or $(1, 2, 2)$ or $(2, 1, 2)$ states which all have the same energy

$$E = \frac{9\pi^2 \hbar^2}{2ma^2}.$$

This process of successively filling the allowed states will be continued till we have placed all conduction electrons in the available quantum states. The highest energy level occupied is called the **Fermi level**. We will next calculate the expression of the energy of the Fermi level.

Fermi Energy

In a macroscopic size metal, say 1 cm × 1 cm × 1 cm, there will be a large number of conduction electrons, of the order of the Avogadro number. Suppose there are N_e total conduction electrons. They will fill up $N_e/2$ states. We can calculate the energy of the highest energy state occupied by the following argument.

Note that the quantum numbers (n_x, n_y, n_z) in the energy expression Eq. 5.22 come as sum of their squares. Therefore, if we think of (n_x, n_y, n_z) as the x-, y- and z-coordinates of the n-space, energy will depend on the "radial" distance in that space. Let us denote the "radial" distance in this space by n.

$$E = \frac{\pi^2 \hbar^2}{2ma^2} n^2 \tag{5.23}$$

The states to fill up go as $n = \sqrt{3}$, $\sqrt{6}$, $\sqrt{9}$, $\sqrt{11}$, $\sqrt{12}$, and so on. Eventually, the spacing between the successive n values narrow and we can treat n as a continuous variable. If the final n to fill up by conduction electrons is n_F, then the volume of the sphere of "radius" $n = n_F$ in the positive octant will be occupied with each n being occupied by two electrons, one an up spin and the other the down spin. Therefore, this volume times 2 will equal the total number of conduction electrons, N_e.

$$\left(\frac{1}{8} \times \frac{4}{3} \pi n_F^3 \right) \times 2 = N_e. \tag{5.24}$$

This gives the following for n_F.

$$n_F = \left(\frac{3N_e}{\pi} \right)^{1/3} \tag{5.25}$$

Now, putting $n = n_F$ in Eq. 5.23 gives us the energy of the highest occupied level, which we denote by E_F.

$$E_F = \frac{\pi^2 \hbar^2}{2ma^2} n_F^2, \tag{5.26}$$

which upon simplification yields

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N_e}{a^3}\right)^{2/3},\tag{5.27}$$

Often it is written by replacing a^3 by the volume V of the cube.

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N_e}{V}\right)^{2/3}.\tag{5.28}$$

The energy E_F is called **Fermi energy** and the energy level with $E = E_F$ is called the Fermi level. The Fermi energy of a system is related to the energy required to extract an electron from the metal, which is the work function of the metal.

Density of States

How many states will there be between energy E and $E + \Delta E$? The number of states below any energy level is one-eights (times two) of the volume of the sphere of radius n corresponding to that energy. Thus, the number of states $\Delta\mathcal{N}$ in the energy range E to $E + \Delta E$ will be

$$\Delta\mathcal{N} = 2 \times \frac{1}{8}\left[\frac{4}{3}\pi(n + \Delta n)^3 - \frac{4}{3}\pi n^3\right].$$

Simplifying this we get

$$\Delta\mathcal{N} = \pi n^2 \Delta n,$$

where I have dropped higher power of Δn since we are interested in infinitesimal Δn. We can write this expression in terms of energy E by noting that

$$E = \frac{\pi^2\hbar^2}{2ma^2}n^2 \implies \Delta E = \frac{\pi^2\hbar^2}{ma^2}n\Delta n.$$

Therefore, the number of states between energy E and $E + \Delta E$ is

$$\Delta\mathcal{N} = \pi\sqrt{2}\left(\frac{m}{\pi^2\hbar^2}\right)^{3/2}V\sqrt{E}\Delta E.$$

Therefore, the number of states per unit energy range per unit volume, called the **density of states**, $\rho(E)$ is

$$\rho(E) = \frac{\Delta\mathcal{N}}{V\Delta E} = \pi\sqrt{2}\left(\frac{m}{\pi^2\hbar^2}\right)^{3/2}\sqrt{E}.\tag{5.29}$$

This says that as you go on filling electrons in various states, the number of available states per unit energy of the last filled state increases with energy. This has the effect of most conduction electrons to end up near the highest energy state filled by the electrons.

Fermi-Dirac Distribution

So far in our studies we have ignored the role of temperature. Our discussion above has tacitly assumed that the metal sample is at the absolute zero, $0K$, temperature. At temperature $T = 0K$, there is no thermal energy available to push an electron into higher energy states above the Fermi level. If the sample is in thermal contact with a thermal bath at a non-zero temperature, $T > 0K$, electrons at the Fermi level will be excited leaving some lower energy states unoccupied and some higher energy states occupied. For a metal we can also define a **Fermi temperature** T_F by equating the thermal energy for that temperature to the Fermi energy of the metal.

$$k_B T_F = E_F, \implies T_F = E_F/k_B. \tag{5.30}$$

We will see below that thermal effects are significant even when the temperature of the metal is well below the Fermi temperature for the metal. The probability that a state of energy E is occupied at temperature T (Kelvin) is given by the Fermi-Dirac distribution function give by

$$f_{\text{FD}} = \frac{1}{e^{(E-E_F)/k_B T} + 1}. \tag{5.31}$$

To see the impact of temperature on a sample it is instructive to plot f_{FD} at different temperatures. Figure 5.11 shows the Fermi-Dirac distribution function for gold at $0K$ and at $\frac{1}{10}T_F = 6,420K$. The T_F of gold was calculated from the Fermi energy of 5.53 eV of gold as

$$T_F = \frac{E_F}{k_B} = \frac{5.5 \text{ eV}}{8.62 \times 10^5 \text{ eV/K}} = 64,200 \text{ K}.$$

From the figure it is clear that, although the Fermi energy is 5.53 eV, the probabilities of the occupancy of states from around 2.5 eV and up are less than 1 at $T = 0.1T_F$. While all states below $E = E_F$ are occupied at $T = 0K$, some of the states below $E = E_F$ will be un-occupied at $T > 0K$. For instance, gold has 5.90×10^{22} conduction electrons per cm^3. At $T = 0K$ all of these electrons will be in states with $E \leq E_F$. At $T > 0K$, some of these electrons will be promoted to states with $E > E_F$ and therefore, some of the states below the Fermi level will be empty.

Figure 5.11 shows the density of the available states and the density of occupied states with respect to energy of the state at $T = 0K$ and $T = 0.1T_F$ for a gold sample. The number of states per unit energy per unit volume varies as $\sqrt{E}$ as given in Eq. 5.29 and the probability that any one of these states is occupied is given by the Fermi-Dirac distribution f_{FD}. The density of occupied states will equal the density of states times the probability that the state is occupied given by f_{FD}. That is

$$\rho_{\text{occupied}}(E) = \rho(E) \times f_{\text{FD}}. \tag{5.32}$$
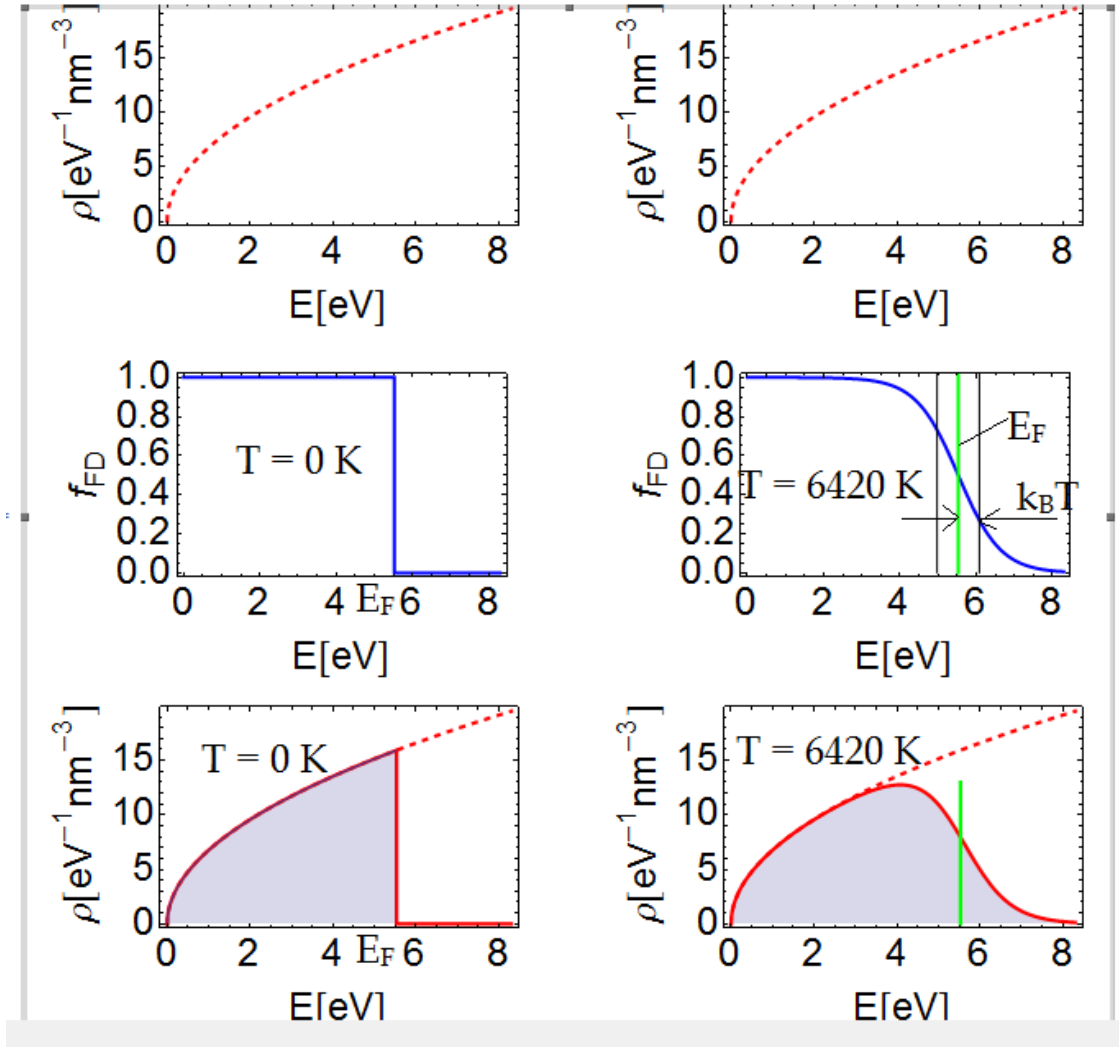
Figure 5.11: The effect of temperature on the distribution of electrons in available quantum states. The top figure is the density of available states in the free-electron approximation. The middle figures are the Fermi-Dirac distribution at $T = 0$ K and $T = 6420$ K, which is one-tenth of the T_F of gold. The bottom figure shows the product of the two and displays actual density of states occupied. The temperature mostly affects the distribution near the Fermi energy.

While the lowest energy electrons are not affected much by the thermal energy that is not too large, the electrons at the Fermi level are affected greatly. This can be seen in the expression of the Fermi-Dirac distribution. The dependence on energy is is exponential in the difference $E - E_F$ and temperature T. The limits of f_{FD} in $E >> E_F$ and $E << E_F$ limits are

$$f_{\text{FD}} = \frac{1}{e^{(E-E_F)/k_B T} + 1} = \begin{cases} 1 & E << E_F \\ 0 & E >> E_F \end{cases} \tag{5.33}$$

Thus, the only electrons that play active role in the electrical properties of a metal are the ones whose energies are close to the Fermi energy.

5.4.2   Mean Free Path of Electrons in Metal

To study conduction it is useful to introduce a speed associated with an electron at the Fermi level, called the **Fermi speed** v_F, by equating the Fermi energy to the kinetic energy of the electron. Since the electron speed even the ones at the Fermi level are in the non-relativistic regime we use the nonrelativistic formula of the kinetic energy.

$$\frac{1}{2}mv_F^2 = E_F, \quad v_F = \sqrt{2E_F/m}. \tag{5.34}$$

For simplicity of discussion we will assume $T = 0K$. In this case, the speed of electrons in the metal will be between 0 and v_F which would correspond to the energy of the occupied states between 0 and E_F. In the absence of an applied electric field, the velocity of conduction electrons will be in all directions, or put another way, same number of electrons will flow in opposite directions. Therefore, even with large speed, there will be no net drift in any particular direction.

Due to the symmetry of directions in space, in the absence of an external applied field, the Fermi-Dirac distribution will be symmetric with respect to positive and negative components of the velocity in any direction. Now, if we apply an electric field pointed towards the negative x direction, there will be an external force on the electron towards the positive x direction, which will accelerate the electrons moving towards the positive x direction and decelerate the electrons which were moving towards the negative x direction. This will cause the shift of the Fermi-Dirac distribution with respect to the velocity towards the positive x direction as shown in Fig. 5.12.
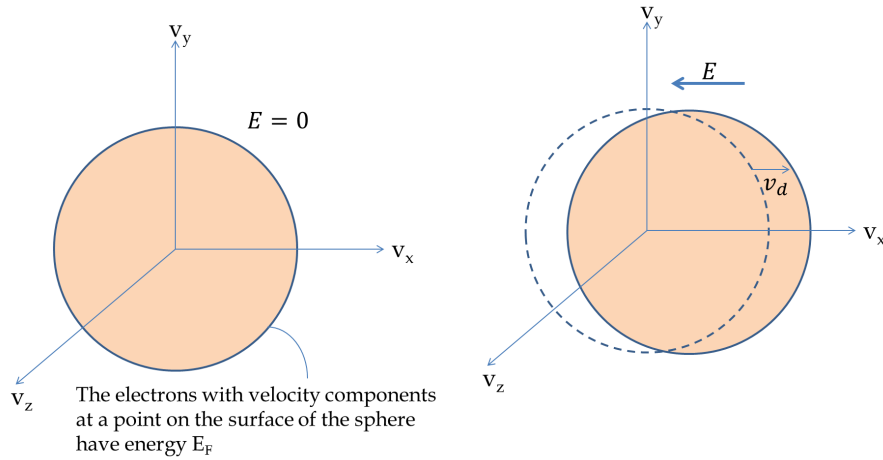

Figure 5.12: The Fermi surface is centered at the origin in the velocity space when there is no external electric field. When an electric field is applied in the direction of negative x-axis, electrons pick up speed in the positive x-direction moving the Fermi surface to the right.

In Fig. 5.12 we note that mostly the electrons at the Fermi level will be active in the conduction. They have the Fermi speed v_F. Therefore, in place of the rms

speed v_{rms} used in the classical model we should use v_F.

For quantum gas, use $v_F = \sqrt{2E_F/m}$. in place of v_{rms}.

With this change we will notice a difference in the predicted conductivity with the conductivity now given by

$$\sigma = \frac{ne^2\lambda}{mv_F}. \tag{5.35}$$

Recall that the problem with the Drude model was the short mean free path in the model. Now, since we are using electrons as waves, we would like to know what is the mean free path of the electron that would give the correct σ. Solving Eq. 5.35 for λ gives

$$\lambda = \frac{mv_F\sigma}{ne^2}. \tag{5.36}$$

Example 5.4. Mean free path of an electron in metal Find the mean free path of an electron in gold using quantum gas formulas.

Solution.

Gold has Fermi energy 5.53 eV. This gives the following for the Fermi speed v_F.

$$v_F = c\sqrt{2E_F/mc^2} = c\sqrt{\frac{2 \times 5.53\ \text{eV}}{0.511\ \text{MeV}}} = 1.40 \times 10^6\ \text{m/s}.$$

Assuming that each gold atom contributes one electron to the conduction, we can readily calculate the density of conduction electrons from the density of gold (19.32 g/cm³) and atomic weight (197 g) with the result

$$n = 5.90 \times 10^{28}\ \text{electrons/m}^3.$$

Putting numerical values in Eq. 5.36 we get the following for the mean free path.

$$\lambda = \frac{9.1 \times 10^{-31}\ \text{kg} \times 1.40 \times 10^6\ \text{m/s} \times 4.10 \times 10^7\ \Omega^{-1}\text{m}^{-1}}{5.90 \times 10^{28}\ \text{electrons/m}^3 \times (1.6 \times 10^{-19}\ \text{C})^2}$$

$$= 3.46 \times 10^{-8}\ \text{m} = 34.6\ \text{nm}.$$

Assuming the inter-atomic distance between gold atoms to be 0.30 nm, the mean free path here is about 115 times longer than expected in the classical Drude model.

5.4.3 Band Structure, Conductors, Semiconductors, Insulators

We have seen in this section and the previous section that we can understand several aspects of electric and heat conduction of metals by modeling metals as free electrons, whether as a classical gas or as a quantum gas. This begs the question: What is the role of the core of the atoms in a metal? Since ignoring the complications from the electron-electron repulsion has led us to some stunning

results already, we would continue to treat the conduction electrons as independent of each other and only attracted to the cores by the Coulomb force. Modeling the metal as a perfect crystal without impurities or defects will also simplify the problem. Then, the answer to the question of the role of the nucleus of a metal atom should be present in the solution of the Schrödinger equation of an electron moving in a periodic potential $U(\vec{r})$.

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right]+U(\vec{r})\psi = E\psi, \tag{5.37}$$

with

$$U(\vec{r}+\vec{R}) = U(\vec{r}), \tag{5.38}$$

where $\vec{R}$ is a vector connecting any two points in the lattice, reflecting the periodicity of the lattice. In 1928 Felix Block proved that the wave function of an electron in a periodic potential will have a particular form, called the **Block wave** form, in which a periodic wave $u(\vec{r})$ is modulated by a plane wave of wavelength $\lambda = 2\pi/|\vec{k}|$.

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u(\vec{r}), \tag{5.39}$$

where $u(\vec{r})$ is a periodic function with the period of the lattice,

$$u(\vec{r}+\vec{R}) = u(\vec{r}), \tag{5.40}$$

and $\vec{k}$ has units of inverse length or wave number. Using vector $\vec{k}$ we define the **crystal momentum**, $\vec{p}$, by

$$\vec{p} = \hbar\vec{k}. \tag{5.41}$$

Note the vector $\vec{p}$ is not the momentum of crystal, but instead it is a momentum associated with the electron wave. When you insert the Block form in Eq. 5.37 you obtain a complicated equation for $u(\vec{r})$ which can be solved for simple examples of the periodic potential $U(\vec{r})$. There are infinitely many solutions for each value of $\vec{k}$. We label these solutions by an integer n, called the **band index**. Thus, the wave function of an electron in a periodic lattice is characterized by a wave number vector $\vec{k}$ and an integer n, and the same goes for the energy $E_{\vec{k},n}$.

Solutions: $\psi_{\vec{k},n}(\vec{r})$ corresponding to energy $E_{\vec{k},n}$.

A plot of the energy $E_{\vec{k},n}$ for different n versus $\vec{k}$ for copper are shown in Fig. 5.13. In these diagrams the values of k are plotted towards various directions of $\vec{k}$ in the $\vec{k}$-space. The diagram shows continuous bands of allowed energy values. Although some bands have gaps at some values of k, but there is no gap here if every direction of $\vec{k}$ is taken into account: there is at least one state at all energies. Therefore, as you fill electrons in these energy levels, the electrons have continuous energy up to the bands labeled Δ_1, Q_-, and Σ_1, which are not fully filled by conduction electrons. The unfilled band at the Fermi energy is a hallmark of metals - actually, we take this to be the electronic definition of a conductor. If the band is partially
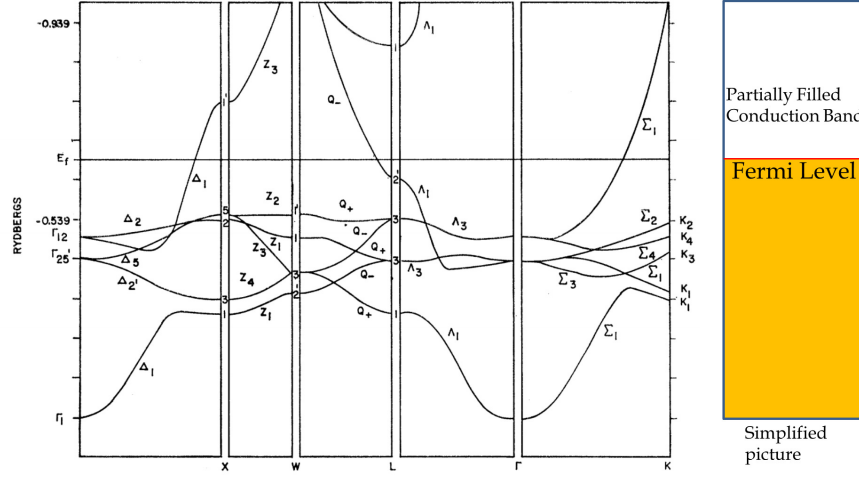
Figure 5.13: Energy bands of copper calculated by Glenn Burdick published in Physical Reviews, vol 129, p 138-150 (1963). The simplified diagram captures essential aspects of the complete band diagram. Here, 1 Rydberg = 13.605 eV.

filled, as is the case here, there are states available to the conduction electrons within an infinitesimally small energy range of the highest filled state, which makes conduction possible with the slightest push.

The band structure of copper should be compared with that of a semiconductor such as silicon whose band structure is given in Fig. 5.14. The band at the Fermi level of silicon is completely filled with a gap in energy before the next energy states are possible. If there is enough thermal energy $k_B T$ or photon energy hf from an incident photon is supplied to the electrons of the filled band, some of the electrons will move to the next level, which will cause two partially filled levels, one upper level and the other the lower level. The excitation is necessary to cause Si to conduct electricity. The lower band is called the **valence band** and the upper level the **conduction band**. The energy gap between the two bands is called the **band gap**.

Continuing in the spirit of band structure of materials, if we analyze the band structure of diamond, which is a good insulator, we find that the bands of carbon in the diamond structure are similar to the bands of silicon, which is not a surprise since both are Group IV elements in the periodic table and both have the same lattice structure. However, the band gap in diamond is 5.5 eV, which is much larger than the band gap of 1.1 eV in silicon. The energy gap in diamond is almost 200 times the thermal energy 0.026 eV at room temperature, $T = 300$ K. The probability that an electron from the valence band will be excited to the conduction band thermally can be calculated from the Fermi level and the energy of the final state.

$$f_{\text{FD}} = \frac{1}{e^{(E-E_F)/k_B T} + 1}.$$

To perform this calculation, we need to know E_F in the case where the valence band is completely filled. Note that, in this case, the energy required to remove an
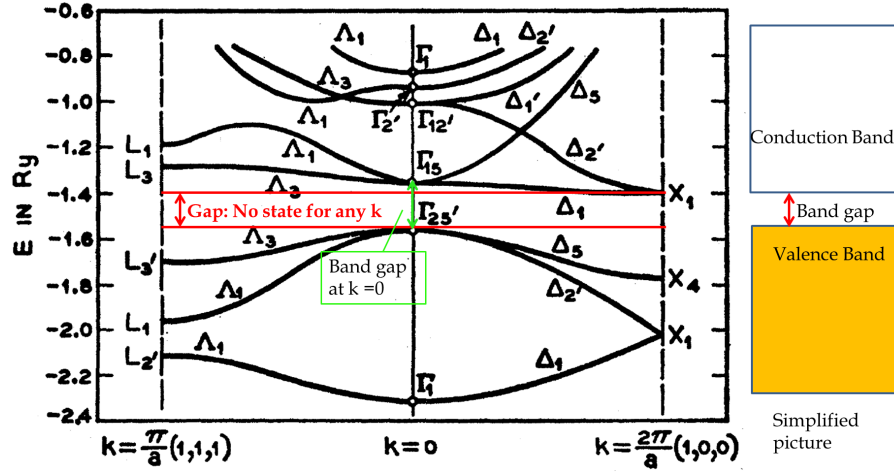
Figure 5.14: Energy bands of silicon calculated by J.C. Phillps published in Physical Reviews, vol 125, p 1931-36 (1962). At T=0 K, the lower three bands are completely filled. There is a gap in energy for the next available state. The simplified diagram captures essential aspects of the complete band diagram. The band gap in Silicon is 1.1 eV which is much larger than the thermal energy 0.026 eV at room temperature, $T = 300$ K. For insulators, the band gap, $E_g >> k_B T$.

electron will be equal to the the binding energy of the top of the valence band; on the other hand, when you want to add an electron you cannot add it to the valence band, instead you will need to place the electron in the conduction band - to add an electron, we need to extract only the energy corresponding to the bottom of the conduction band. Therefore, we place the Fermi level in the middle of the gap. Therefore, E_F will be taken to be

$$E_F = E_V + E_g/2,$$

where E_V is the energy of the top of the valence band and E_g the gap. With $E = E_C$, the energy of the bottom of the conduction band, after simplification, we get the following probability

$$f_{\text{FD}} = \frac{1}{e^{(E_g)/2k_B T} + 1}.$$

Now, putting in the numbers we get the probability to be

$$f_{\text{FD}} = \frac{1}{e^{5.5\,\text{eV}/(2\times 0.026\,\text{eV})} + 1} = 1.2 \times 10^{-46}$$

This makes it extremely unlikely that any electron in diamond will be in the conduction band. That is why diamond is a good conductor. Figure 5.15 illustrates the essential difference between a conductor, a semiconductor, and an insulator.
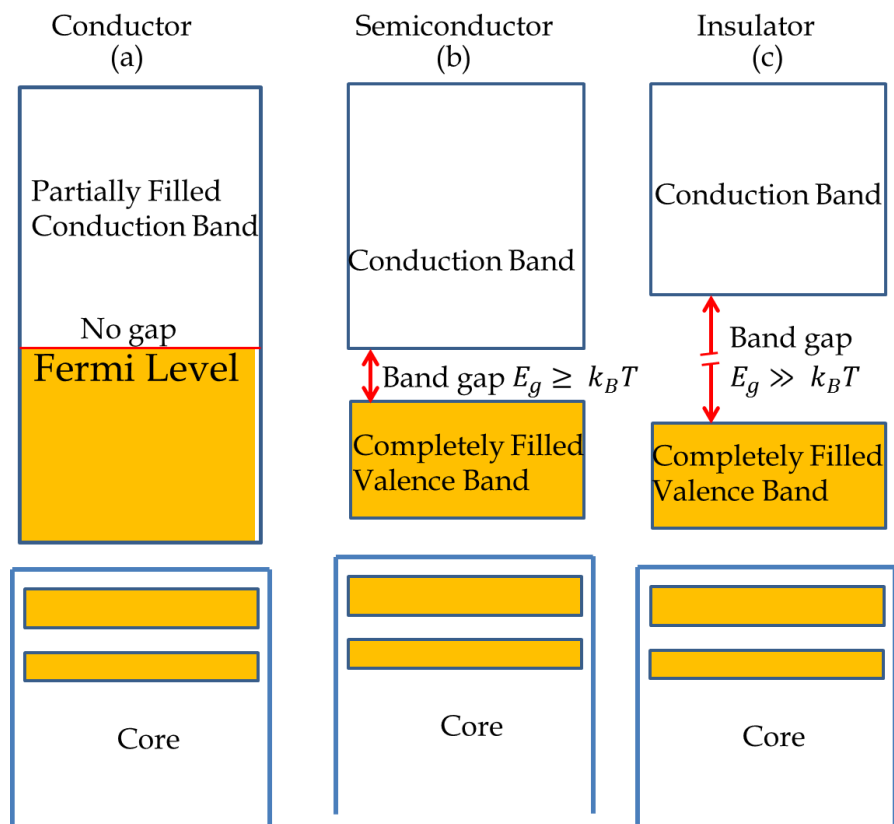
Figure 5.15: A simplified picture of the band strucures of (a) a conductor, (b) a semiconductor, and (c) an insulator.