UNIT 11: BAND STRUCTURE

After this unit, you should be able to

- Determine whether a material is transparent from the energy levels and filling.
- Determine whether a material is metallic or insulating from the energy levels and filling.
- Use a semi-classical model to explain

Introduction

In this unit, we will discuss the behavior of electrons inside materials, in a qualitative way. The quantum mechanical energy levels become partially continuous in a large system, but there are gaps. These gaps act very similarly to the gaps you've already seen in atoms, in that they can prevent materials from absorbing light of frequencies that don't correspond to energy level differences. This effect explains why for example windows are transparent while metal is not. It is also the reason for variety of colors that we see in the world around us.

We will also consider the momentum of the energy eigenstates, and we will find that the gaps in energy also create a barrier for electrons to change their momentum. To analyze the motion of electrons, we will use a semi-classical model, which is commonly used to predict the behavior of electronics. This model assumes that the dynamics of electrons are as they would be in classical mechanics, but that they can only have states that correspond to quantum states. So while a purely classical model would have continuous momentum and energy, the semiclassical description has gaps. This effect explains the existence of insulators–materials that have many electrons, but do not conduct electricity because the electrons are stuck and cannot change their momentum.

Many particles in an infinite square well

Let's start with a very simple model of electrons in a material, let's imagine something like a copper wire. We will assume that the electrons are freely able to move, which just means that the potential energy is flat. We know how to solve this problem, the energy eigenstates are:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \tag{1}$$

with energies

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \tag{2}$$

For an electron with wave function Ψ_n, the momentum has an equal probability of being

$$p_n = \pm\hbar\frac{n\pi}{L} = \pm\sqrt{2mE_n}, \tag{3}$$

because $\sin(kx) = \frac{e^{ikx} - e^{-ikx}}{2i}$ and the momentum of e^{ikx} is $\hbar k$.

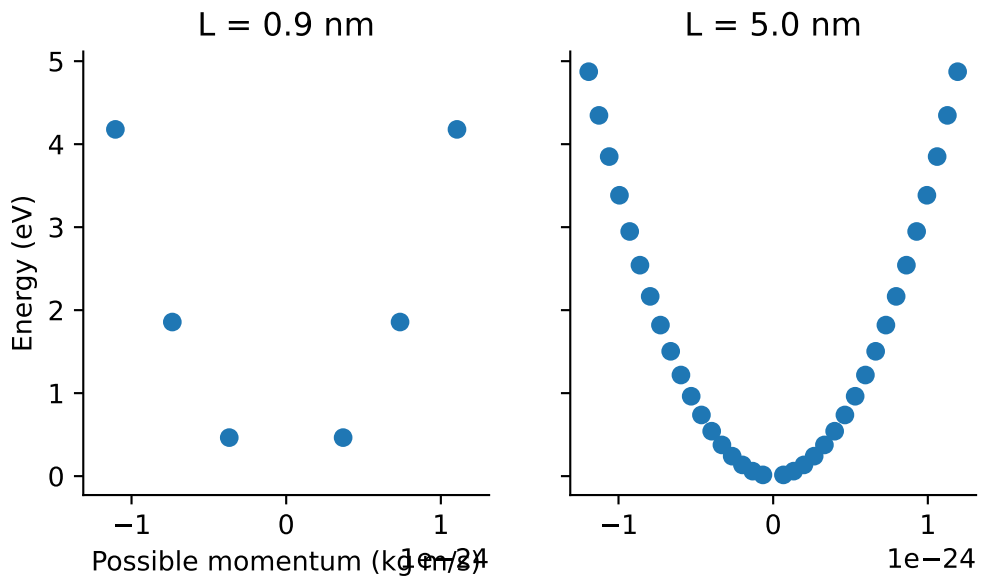

Figure 1: Energy versus momentum of the energy eigenstates for two lengths of infinite square well. As the well becomes larger, the graph fills in.

Now let's consider putting N_e electrons in a wire of length L. To obtain the ground state, all states are filled up to $n_{max} = N_e/2$. So the energy of the highest energy electron is

$$E_{max} = \frac{\hbar^2\pi^2}{8m}\left(\frac{N_e}{L}\right)^2, \tag{4}$$

which is called the **Fermi level**. This only depends on the fraction $\frac{N_e}{L}$, i.e., the number of electrons per length, which is the density of electrons. We will call the electron density $n_e \equiv \frac{N_e}{L}$.

Since the properties only depend on the electron density, we can take the limit as $L \to \infty$ while keeping the electron density constant to approximate a material. This works because a piece of metal or other material is often about 1 mm in size, which is 10^6 times bigger than the 1 nm sizes where the individual energy levels are apparent. This is diagrammed in Fig 2, where the Fermi level is diagrammed on a continuous line (which is really made up of many states) as a function of the electron density.

Adding a little more realism: a corrugated potential.

To add a little more realism, let's add a potential to our infinite square well. This represents (very approximately) the effect of the atoms on the electrons in the material. We will add the potential[1]

$$V(x) = 2U\cos(gx) \tag{5}$$

[1]This model is from Andreas Wacker's band structure introduction. You can find more details here www.teorfys.lu.se/staff/Andreas.Wacker/Scripts/

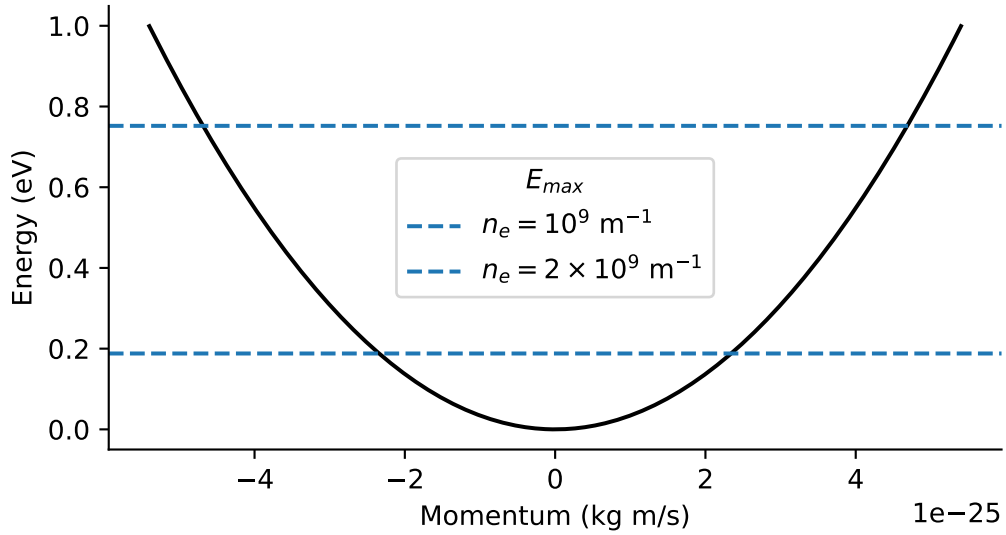

Figure 2: The energy level of the highest energy electron in the ground state depends on the number of electrons per unit volume. This energy level is called the Fermi level.

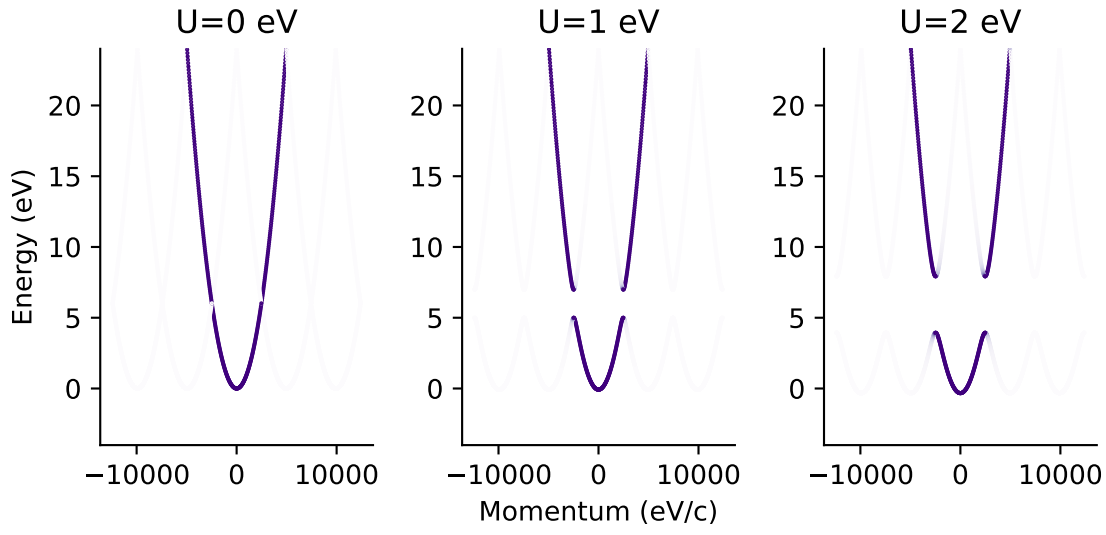

Figure 3: How the electronic states vary as we change U, which represents the strength of the interaction of atoms with the electrons. For U larger than zero, gaps in the allowed energies form. The intensity of the plot is the probability density (in momentum) that a given energy eigenstate has.

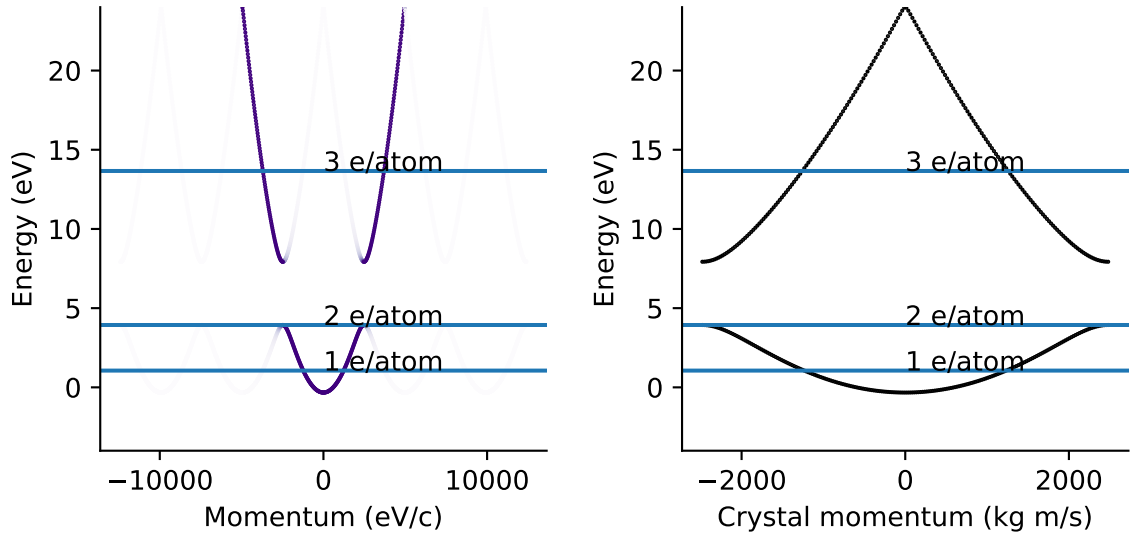

Figure 4: (left) How the filled energy levels (everything below the line is filled in the ground state) depend on the number of valence electrons per atom. The Fermi level increases as the density of electrons increases. (right) The same graph as you'll often see it for materials. Only one period of each energy band is shown, and the x-axis is now the so-called "crystal momentum."

U is the strength of the potential, representing how much the atomic nuclei[2] affect the electrons in the material. We will not go through the solution in detail.

In Fig 3, we show the solutions of this potential. This kind of plot is called a "band structure" diagram; presumably named so because there are bands of allowed energies, rather than isolated allowed energies as in atoms. Each line is called a band. The energy gap between the bands is called the "band gap," for hopefully obvious reasons. Note that the bands fold back on themselves so that high energy does not imply high momentum; this is an effect of the potential, and happens in more realistic models of materials.

Given the energy levels, the behavior of the material depends strongly on how the energy levels are filled, similar to the case of atoms. In Fig 4, we diagram this effect. For example, if this material were made up of sodium (Na), which has one valence electron per atom, then the first band would be half-filled. This means that there are excited states with very little extra energy above the ground state. On the other hand, if we were to make this material out of something with two valence electrons per atom, such as magnesium (Mg), then we would expect the band to be completely filled, and the first excited state is several eV higher than the ground state. Moving to three electrons per atom, now the filled levels are in the middle of a band again.

Light absorption of metals and insulators.

For light absorption, we apply the same rules as we did for atoms. In the case of metals, ($n_e = 1, 3$ in Fig 4) then even very low energy photons can be absorbed, since the lowest excited state is just above the ground state. In fact, the metal can absorb photons of any energy up to the difference

[2]technically there are 'free electrons' and 'bound electrons', and we're really talking about ions.

in energy between the Fermi level and the gap. Metals are reflective because they very efficiently absorb and re-emit visible light.

On the other hand, the first excited state for $n_e = 2$ in Fig 4 requires a promotion of an electron across the gap. If the gap is large enough then the material can be transparent! For example, the reason that diamond is transparent is that it has a gap of over 6 eV, while photons in the visible range of frequencies have energies less than 4 eV. So those photons just don't have enough energy to overcome the gap, no matter how many are sent through the material. This is very similar to the photoelectric effect!

Electrical conductivity: metals and insulators

Finally, let's think about what happens when we apply an electric field to a material. We would like to determine how the electrons respond. While in principle one can do this using quantum mechanics, typically a semi-classical approximation is used. That means that we use quantum mechanics to determine the energy and momentum of electrons, and given that, we approximate their dynamics using classical mechanics. This sort of model is used to accurately model how semiconductors behave and is used to design modern computer hardware.

Consider a single free electron with momentum $p(0) = p_0$ and energy $E(0) = E_0$. We apply a constant electric field, which applies a force on the electron $F = q\mathcal{E}$. Let's assume that the force is in the positive direction. Newton's 3rd law tells us that $F = \frac{dp}{dt}$, so this force causes the momentum to increase, and therefore the energy to increase, since $E(p) = \frac{p^2}{2m}$. The solution is that $p(t) = Ft$, so the electron accelerates. This flow of electrons is electric current. For a free electron, the acceleration is allowed because there are states, and we have derived something we already know–that a free electron accelerates under an electric field.

Now let's consider the 1 electron per atom situation in Fig 4. The electron in the right-most state can increase its momentum and energy slightly due to the force on it. This leaves an empty state, which the second-to-right electron can move into, and so on, so that all electrons shift up in momentum. The entire system then has a non-zero net momentum, which results in a flow of current. This is why metals conduct electricity.

On the other hand, let's consider the 2 electron per atom situation in Fig 4. The electric field wants to increase the momentum of the right-most electron, but there are no allowed energy levels with slightly higher energy and higher momentum. So the right-most electron is stuck. This is true as well for the left-most electron; it cannot increase its momentum because there is another electron there. This is the reason that materials with electrons filled up to the gap block electrical flow, which we call insulators.