

ET3034TUx - 2.2.1 – Band Gap I: Electrons in Atoms

What is the principle of a band gap?

It is not straightforward to quickly explain this principle, but I will give it a try.

I will use a chemical picture to explain the nature of the band gap.

You have to realize that I will make some crucial simplifications in explaining the nature of the band gap, so don't tell it to your physics and chemistry professors.

First we have to consider the question: how do electrons bond in an atom?

As silicon is the most important material for current solar cells, we are going to look how electrons are bound to the nucleus of a silicon atom.

Before we will discuss the silicon atom, I am starting with the most simple atom in our universe, the hydrogen atom.

The hydrogen atom has a nucleus consisting of one proton.

The proton is positively charged.

Around this proton the much lighter electron is moving in orbits.

The electron is negatively charged.

This relatively simple system can be described by complex laws of quantum mechanics, like the well-known Schrödinger Equation.

I won't go into the detailed physics, but the only thing you have to know at the moment is that quantum mechanics and the Schrödinger equation tells us that in the hydrogen atom the electron can only occupy certain discrete energy positions.

The lowest energy position is the ground state indicated by 1s, and the electron is strongly bound to the proton, it is on average in an orbit close to the nucleus.

This energy level is in the so-called first electron shell.

If we give the electron more energy, it can be excited to a higher energy level, to the second shell.

The electron is less strongly bound to the atom and its average orbit is further away from the nucleus.

In the second shell we find two types of electronic energy levels, 2s and 2p.

If we give the electron even more energy, it can be excited to the third shell.

The strength of the bond between nucleus and electron is further reduced, and its average orbit around the nucleus is even further away from the nucleus than for the orbits in the second shell.

In the third shell three types of electronic states are present, however, in this course for simplicity, we only consider two types of electronic energy levels, 3s and 3p.

Here the electronic orbital of the electron in the ground state is shown.

The orbital reflects the volume in which the electron might be present during its journey around the positron.

On the left you can see the 3-dimensional representation of the orbital and on the right you can see the 2-dimensional representation of the orbital.

The orbital of the 1s ground state is symmetric in all directions and has the shape of a sphere.

The orbital of the excited 2s state is a symmetric sphere as well, however, the sphere is larger, indicating that the electrons are in an average orbit at a larger distance from the nucleus.

The orbital referred to as 2p has an asymmetrical shape and in a rough approximation consists out of two lobes.

Due to the asymmetry it can be described in three different directions, the X, Y and Z direction.

Consequently three different 2p states exist.

We can also go up to the third electron shell, in which the orbital corresponding to the 3s is again symmetric and much larger.

The electron is less bounded to the nucleus and its average orbit is further away from the nucleus.

The 3p orbital is again asymmetric and starts to consist in rough approximation out of four lobes and has three different states.

These discrete energy levels can help you understand how the periodic table of elements is built up.

Before we do that, we have to discuss one important additional property of the electron and one important law of the quantum mechanics.

The important property of the electron is that electrons can have spins.

The important law in quantum mechanics is the Pauli exclusion principle.

First, electrons have spins.

What is a spin?

Let's consider a charged body in classical electrodynamics, like these spheres.

We start to rotate these bodies.

The rotation of the charge will induce a magnetic dipole.

Depending on the rotation clockwise or counterclockwise, the magnetic dipole will point up or will point down.

This concept appears to be still valid for a little tiny electron, with having the smallest charge possible, the elementary charge.

This means that an individual electron can be in two quantum states: spin up (magnetic dipole pointing up) and spin down (magnetic dipole pointing down).

Secondly, I introduce the Pauli exclusion principle, which tells us that two identical electrons cannot occupy the same quantum state simultaneously.

Don't worry about why this is the case, just for the moment accept that in nature all electrons obey this law.

Now let's consider two electrons, which both are in a state with their spins up.

Can these electrons both fill the same energy state X?

The answer is no, as both electrons have the same spin and they have the same energy.

This means we have two identical electrons that occupy the same quantum state and this violates Pauli's exclusion principle.

Now let's consider two electrons, which have opposite spins, one spin up and the other one spin down.

Can these electrons fill the same energy state X?

In this case the answer is yes, although the electrons have the same energy state, the electrons are not identical as they have different spins.

Pauli's exclusion principle is not violated and these two electrons fill the same energy level.

Basically, Pauli's exclusion principle allows every electron energy level to be filled by at maximum two electrons.

Using this knowledge, let's consider the next element in the periodic system, the helium atom.

In its nucleus it has two positrons and two neutrons.

Since neutrons do not have a charge, the charge of the nucleus is determined by the two positively charged positrons.

Around the helium nucleus two electrons are in orbit.

This system has similar electronic states in the first, second and third shell as the hydrogen atom.

One of the electrons has a spin up as indicated with the red arrow up.

One electron has a spin down, indicated with the red arrow down.

Following the Pauli exclusion principle, both electrons can be in the ground state.

This means that a He atom in its ground states has its 1s level fully filled.

If we now move to the next element in the periodic system, the lithium atom, the nucleus has besides three neutrons, three positrons and three electrons in orbit around its nucleus.

Following the Pauli exclusion principle, the third electron cannot join the two other electrons in the 1s ground state, 'cause whether it has a spin up or down, it will always will be identical to one of the other electrons in the ground state.

As a result the third electron will fill the next lowest state which is the 2s state.

The next element in the periodic system is beryllium, which has 4 electrons in orbit around the nucleus.

These four electrons fully fill up the 1s and 2s electronic states.

The next element is boron, it has 5 electrons in orbit and can fill up to 1 electron in the 2p states, and has a total of 3 electrons in the second shell.

The next element is carbon, it has 6 electrons in orbit and can fill up to 2 electrons in the 2p states and has in total four electrons in the second shell.

So, basically carbon has its 2nd shell not fully filled.

As we discuss in the next block, the electrons in the not fully filled outer shell are responsible for making the bond with other atoms in molecules or solids.

As carbon has 4 electrons available in the not fully filled shell, carbon can make 4 covalent bonds, like in methane gas or in diamond.

The next element is nitrogen, it has 7 electrons in orbit around the nucleus and can fill up to 3 electrons in the 2p states.

The next element is oxygen, it has 8 electrons in orbit around the nucleus and can fill up to 4 electrons in the 2p states.

Fluorine has 9 electrons in orbit around its nucleus and can fill up to 5 electrons in the 2p states.

Neon has 10 electrons in orbit around its nucleus and fills up the 2p fully with 6 electrons. Neon fills up fully the first and second shell.

We also know that neon has very low chemical reactivity, similar like helium, which fully fills up the first shell.

Both elements belong to the noble gases.

This indicates that atoms with only fully filled shells cannot easily make bonds to other atoms, to make molecules or even solids, while atoms with not fully filled outer shells, are able to make bonds.

The next element sodium fills the 3s state with one electron.

The magnesium fully fills up the 3s state with two electrons.

Aluminum fills up the 3p state with one electron.

Finally, we arrive at the most important element for photovoltaic applications: Silicon.

90% of the commercially available solar panels is based on silicon.

Si has 14 electrons in orbit around its nucleus and fills up to 4 electrons in the 3s and 3p states.

These four outer electrons are the weakest bounded to the nucleus.

Similar, like in the case of carbon, the four outer electrons of the silicon atom will play an important role in making bonds with other atoms in a molecule or in a solid.

How do these molecular bonds determine the band gap of silicon?

I will give the answer to that question in the next block.