

Physical Theory: The Potential Well Theory

Imagine a metal atom in vacuum. It has energy levels for accepting various electrons. The pit of the well is the lowest potential energy level. That roughly corresponds to the electron closest to the nucleus. Hence, we begin filling electrons in various orbitals from the bottom to the top, following Pauli's exclusion principle and Aufbau's principle.

For Aufbau's Principle:

<https://www.khanacademy.org/science/ap-chemistry-beta/x2eef969c74e0d802:atomic-structure-and-properties/x2eef969c74e0d802:atomic-structure-and-electron-configuration/v/the-aufbau-principle>

For Pauli's Exclusion Principle:

<https://www.youtube.com/watch?v=TIzs5C33ONg>

So when all the electrons for that particular metal atom are filled, the highest energy level after filling the electrons is called Fermi Level. (Think of it like this - after adding the required electrons, if at all you had to add one more extra electron to the atom, you will have to work equal to the energy of the Fermi Level, which is the Fermi energy.)

The work done to remove the electron from the Fermi level to zero potential, is called the work function (ϕ).

Particle in a Box

The Particle in a box is a representation of the uncertainty principle. It basically means that we cannot know all the information about the particle inside the box. According to Heisenberg, we can't simultaneously know the position and momentum of a particle. But the only thing we know is that the particle has to be confined to the box. This is enough to conclude something very important: The dimensions of the box and the wavelength of the particle are related.

The dimensions of the box correspond to the lattice spacing. If an electron can move within this lattice spacing after a collision with an atom, then its paths in between two atomic collisions has to be an integral multiple of half the wavelength, or it has to be in some eigenstate (to be honest, I also don't know what this is, but its notion is very similar to that of an orbital).

The box here is sometimes also called the infinite potential box, which means the walls have infinite potential and the only place an electron can go to (It will never go to the walls as it always moves towards lower potential) will be inside the box. This is analogous to the well theory, as the surrounding air or vacuum also has no scope for electron filling, as there is no positive nuclear force like the metal to attract the electron, and the only place the electron can go to is the metal nucleus.

Band Theory of Solids

The band theory basically applies for N atoms of a particular element combining to form a crystal lattice. When so many trillions of atoms come together to form a lattice, then it makes absolutely no sense talking about the energy levels of each of the atoms. While it is convenient to imagine two electrons per orbital in a single energy level, having so many electrons in trillion equivalent orbitals violates Pauli's exclusion principle - no two electrons can have the same set of four quantum numbers.

Hence, two things become clear:

1. Molecular orbitals are helpful in understanding this here. When two same orbitals of different atoms overlap, they form a stable bonding molecular orbital and a slightly unstable antibonding molecular orbital. This resolves the violation of Pauli's exclusion principle, as we have only two electrons in each of these two orbitals.
2. Trillions of molecular orbitals overlapping with each other because of lattice formation will basically look like one giant band with infinitesimally small variations of energy levels. These bands are energy bands, and they satisfactorily replace the idea of energy levels, as in individual atoms.

For an intuitive explanation of Band Theory:

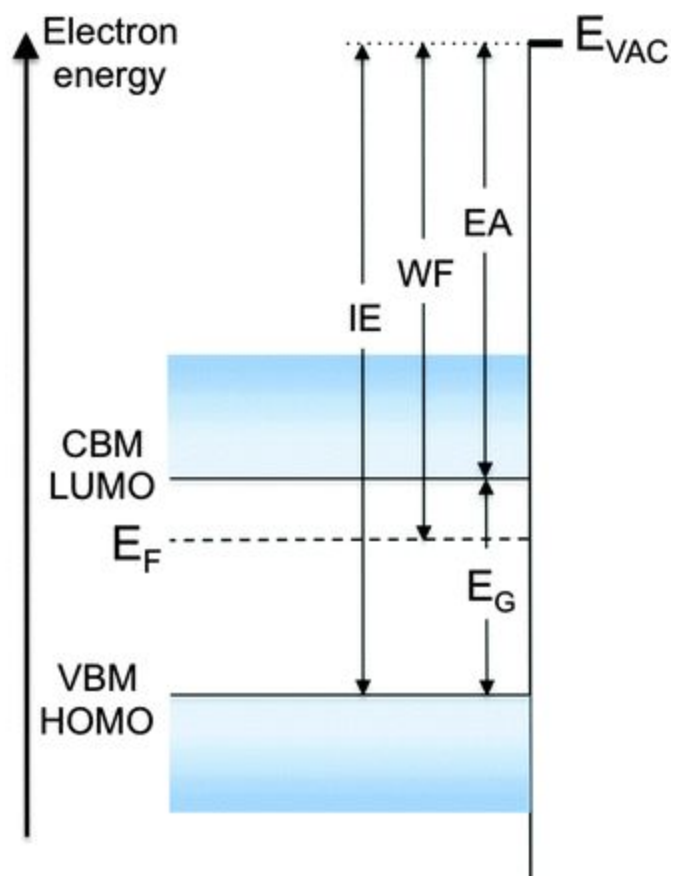
<https://www.khanacademy.org/science/in-in-class-12th-physics-india/in-in-semiconductors/in-in-band-theory-of-solids/v/band-theory-of-solids-class-12-india-physics-khan-academy>

For the best ever explanation of that energy vs interatomic distance graph:

<https://www.youtube.com/watch?v=FVc1S2CO4qg>

For the explanation of Bragg's Law and Why it affects the Energy gaps:

https://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/backbone/r2_1_3.html



Energy diagram of a semiconductor with flat bands to the surface. Band edges (CBM/LUMO and VBM/HOMO), vacuum level E_{VAC} , work function WF , energy gap E_G , ionization energy IE and electron affinity EA are defined.

MOT and Band Theory:

<http://faculty.chem.queensu.ca/people/faculty/mombourquette/FirstYrChem/Molecular/bands/#:~:text=Bands%20are%20distributions%20of%20many,move%20along%20delocalized%20energy%20levels.>