

Lecture 1: Electronic materials

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1 Introduction

When we think of electronic materials the physical property that is important is *resistance*. Based on resistance materials can be classified into 3 major types

- Conductors
- Semiconductors
- Insulators

The unit of resistance is Ohm (Ω) and is related to the applied voltage and current by Ohm's law

$$V = IR \quad (1)$$

where V is the applied voltage (units Volts), I is the current (units Amperes) and R is the resistance. Resistance depends on the sample dimensions. Reducing the thickness of a film or decreasing the diameter of a wire would lead to an increase in resistance. We can define a material independent property

called **resistivity** (ρ) which removes this dependence on sample dimensions. Resistance is related to resistivity by

$$R = \frac{\rho l}{A} \quad (2)$$

where l is the length of the sample and A is the cross sectional area. The unit of resistivity is Ωm . **Conductivity** is defined as the inverse of resistivity. The symbol for **conductivity** is σ and unit is $\Omega^{-1}m^{-1}$. We can compare typical values for resistivity for conductors, semiconductors, and insulators. When we deal with conductors they will mostly be metals. Some typical values of metal conductivity are shown in table 1.

Table 1: Resistivity values of some typical metals

Metal	ρ ($\times 10^{-9} \Omega m$)
Copper	15.7
Gold	22.8
Platinum	98
Silver	14.6

Metals are characterized by low resistivity. The values quoted in table 1 are in the range of nano Ωm . Compared to metals, semiconductors have higher resistivity values, as seen in table 2. Semiconductor resistivities usually have a range since they depend on the impurity level and also on the crystalline state (single or poly crystalline). Overall, semiconductor resistivities are 5-6 orders of magnitude higher than metals. Insulators have the highest resistivities, these are tabulated in 3.

Table 2: Resistivity values of some typical semiconductors

Semiconductor	ρ (Ωm)
Germanium	$10^{-3} - 10$
Silicon	$0.1 - 10^3$
Zinc oxide	$10^{-2} - 10^{-4}$
Gallium Arsenide	$10^{-6} - 10^{-2}$

Table 3: Resistivity values of typical insulators

Insulator	ρ (Ωm)
Wood (damp)	$10^3 - 10^4$
Deionized water	10^5
Glass	$10^{10} - 10^{14}$
Fused quartz	10^{17}

Thus, we have a range of values for resistivity for different materials and this is related to their electronic properties. To understand this range we need to understand how band gap evolves in materials. We will look at a basic picture of how band gap forms, with a focus mainly on metals and then semiconductors. We will also introduce some concepts on density of states, Fermi energy, and Fermi-Dirac statistics to understand the difference in conductivity.

2 Molecular orbital formation

Energy levels in an atom are sharp and well defined. To understand what happens when these atoms come together to form solids, we can start with the simplest atom, hydrogen (H). Hydrogen has 1 electron located in the K shell with electronic configuration $1s^1$. When 2 H atoms come together there are 2 $1s$ atomic orbitals (AOs) and these form 2 molecular orbitals (MOs). For simplicity, let us denote the atomic orbital of H atom by ψ_{1s} . In quantum mechanics ψ refers to the wave function of the electron in the $1s$ orbital. The wave function can be solved using Schrödinger's equation in spherical coordinates and the wavefunction solution for the $1s$ orbital is

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \exp\left(-\frac{r}{a_0}\right) \quad (3)$$

Here, a_0 refers to the Bohr radius and has a value of 0.53 \AA . This is an exponential function with the maximum when $r = 0$, corresponding to the nucleus and exponentially decreasing away from the nucleus.

Consider two H atoms A and B, with AOs ψ_{1s}^A and ψ_{1s}^B . There are two ways in which the 2 AOs can come together to form two MOs. The two AOs can be added, this the bonding orbital, σ or they can be subtracted, giving the anti-bonding orbital, σ^* . This can be represented by

$$\begin{aligned}\sigma &= \psi_{1s}^A + \psi_{1s}^B \longrightarrow \text{bonding orbital} \\ \sigma^* &= \psi_{1s}^A - \psi_{1s}^B \longrightarrow \text{anti-bonding orbital}\end{aligned}\tag{4}$$

The bonding orbital represents the symmetric MO while the anti-bonding orbital represents the anti-symmetric MO. They are shown pictorially in figure 1.

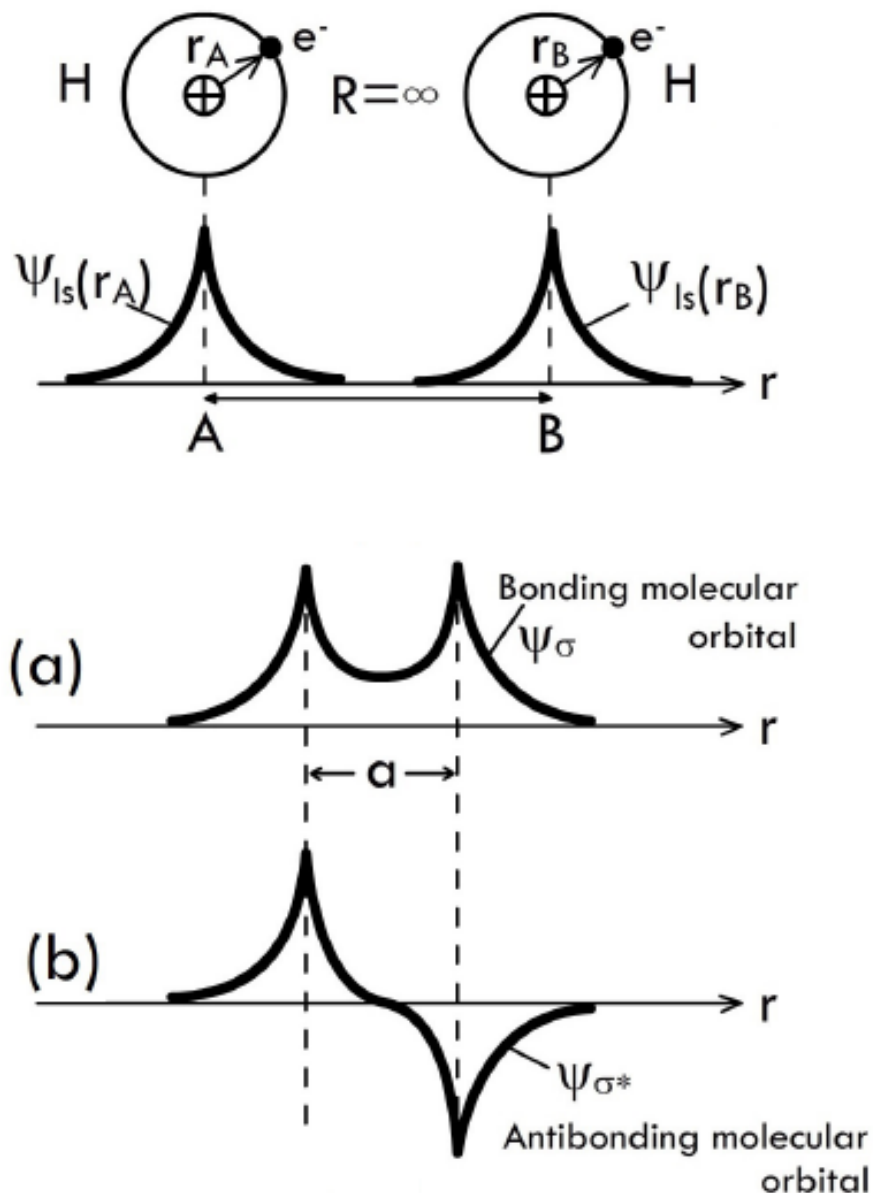
Figure 1: Formation of (a) bonding and (b) anti-bonding orbitals when 2 H atoms come together.

The bonding orbital (a) shows a local minimum in the wavefunction in the region between the 2 H atoms but the function does not go to zero.

Thus there is a finite probability of finding the electron between the 2 atoms (they partially share electrons).

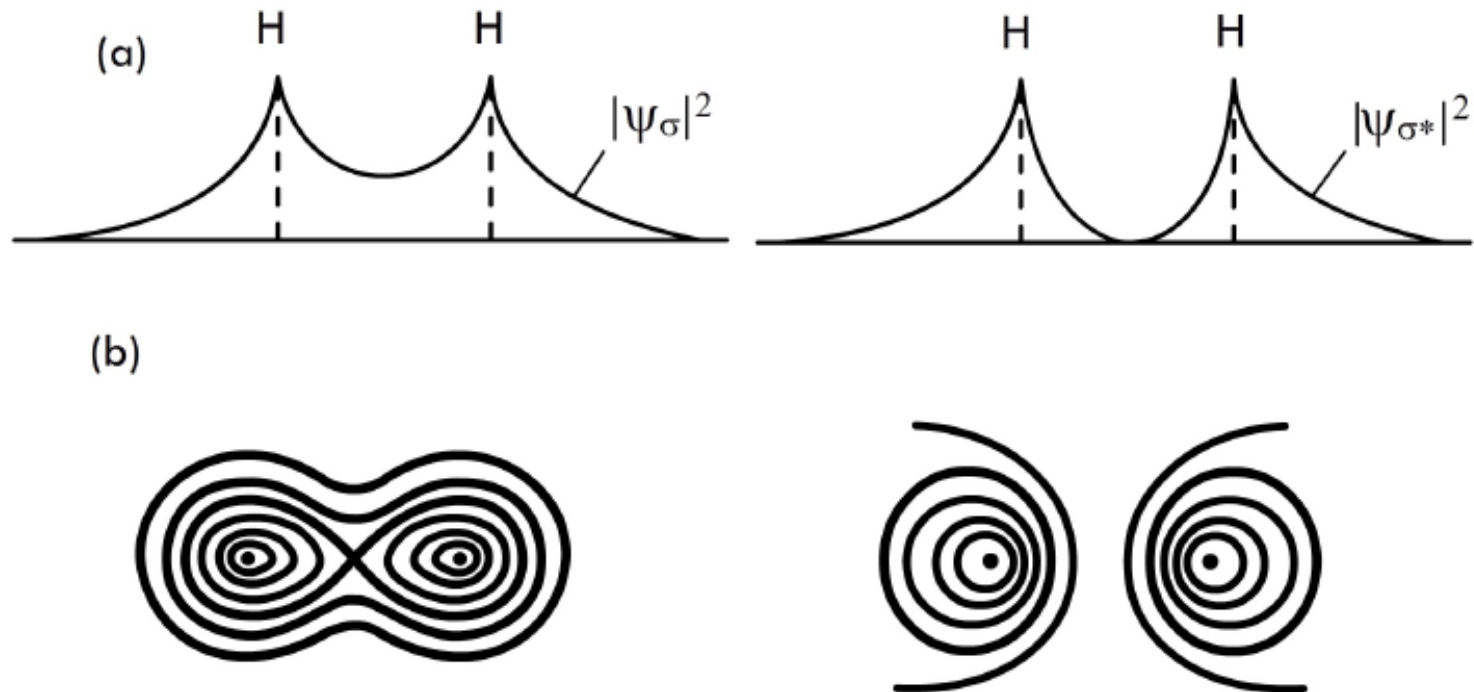
The anti-bonding orbital (b) wavefunction goes to zero between the 2 atoms and hence the probability of finding the electron between the 2 atoms is zero. This is called a **node**.

Thus, the bonding orbital has zero nodes and the anti-bonding orbital has 1 node



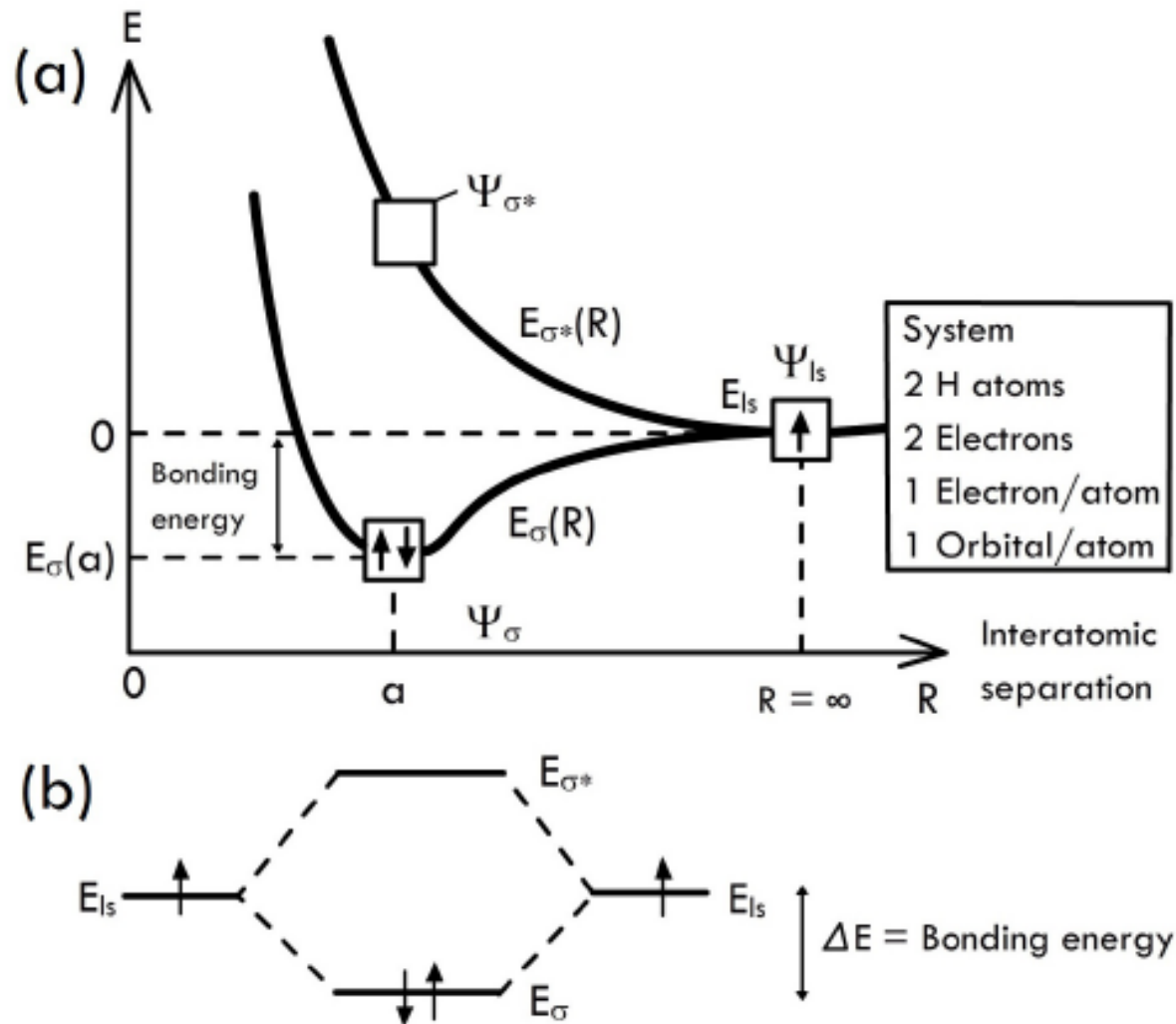
The electron probability distribution is shown in figure 2.

Figure 2: Electron probability distribution in (a) bonding (σ) and (b) anti-bonding (σ^*) orbitals. Lines of constant probability are shown. For the anti-bonding orbital there is zero probability of finding the electron between the two atoms i.e. node. Adapted from *Principles of Electronic Materials - S.O. Kasap*.



In terms of energy the bonding orbital has a lower energy than the individual orbitals which have a lower energy than anti-bonding orbital. This is because in σ the electron can be influenced by both the nuclei which leads to a lower energy. If two H atoms come together then both electron will go to the bonding σ orbital (with opposite spin) since this will lower the overall energy of the system. This can be represented by a energy vs. bond length plot. This is shown in figure 3. At large interatomic distances the H atoms have individual atomic energy levels. When they start to come together (R starts to reduce) the 2 atoms start to 'see' the influence of each other. The atomic orbitals start to mix and form the MOs σ and σ^* . There is an equilibrium distance of separation when the energy of the system is at a minimum. Both electron occupy this minimum in the bonding orbital. Figure 3 also shown the schematic representation of the formation of the MOs and the energy minimization using horizontal lines to represent the orbitals.

Figure 3: (a) Energy vs. bond length plot for 2 H atoms. (b) The schematic representation of the formation of the H₂ molecule. Both electrons go to the bonding orbital while the anti-bonding orbital is empty.



3 Molecular orbitals in extended systems

Consider the case when we have 3 H atoms. Each atom has a ψ_{1s} atomic orbital and these 3 AOs will come together to form 3 MOs. Let the 3 H atoms be A, B, and C with atomic orbitals ψ_{1s}^A , ψ_{1s}^B , and ψ_{1s}^C . The 3 AOs can be put together to form 3 MOs while maintaining symmetry of the resultant wave function in the following way.

$$\begin{aligned}\sigma_a &= \psi_{1s}^A + \psi_{1s}^B + \psi_{1s}^C \\ \sigma_b &= \psi_{1s}^A - \psi_{1s}^C \\ \sigma_c &= \psi_{1s}^A - \psi_{1s}^B + \psi_{1s}^C\end{aligned}\tag{5}$$

σ_a , σ_b , and σ_c are the 3 MOs that are formed. This formation is shown in figure 4. σ_a is the symmetric solution with no nodes. σ_b is the antisymmetric solution with a node in the location of the middle atom (this is the reason for no contribution from B in equation 5). σ_c is again a symmetric solution but with 2 nodes, between the 2 sets of atoms. In terms of energy σ_a is the lowest followed by σ_b and then σ_c . The energy vs. bond length diagram for

Decreasing stability

Increasing energy

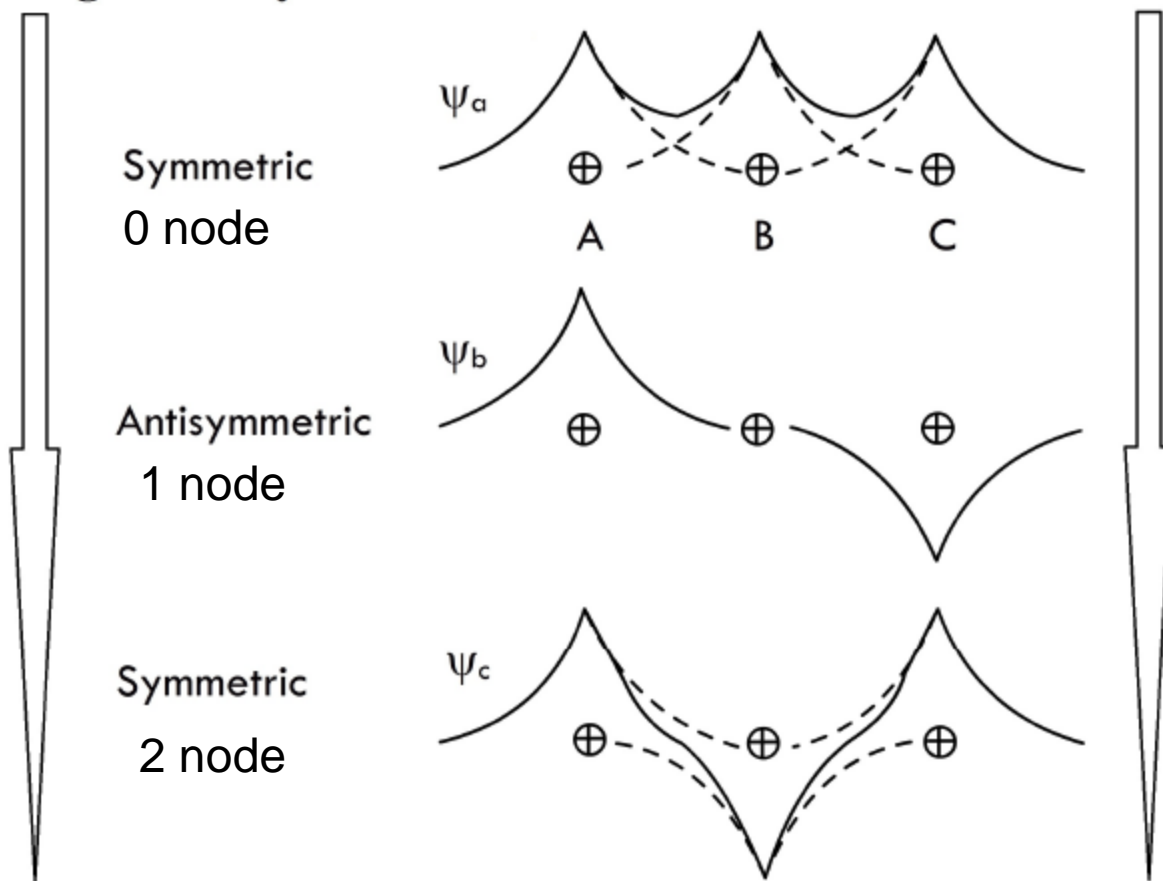
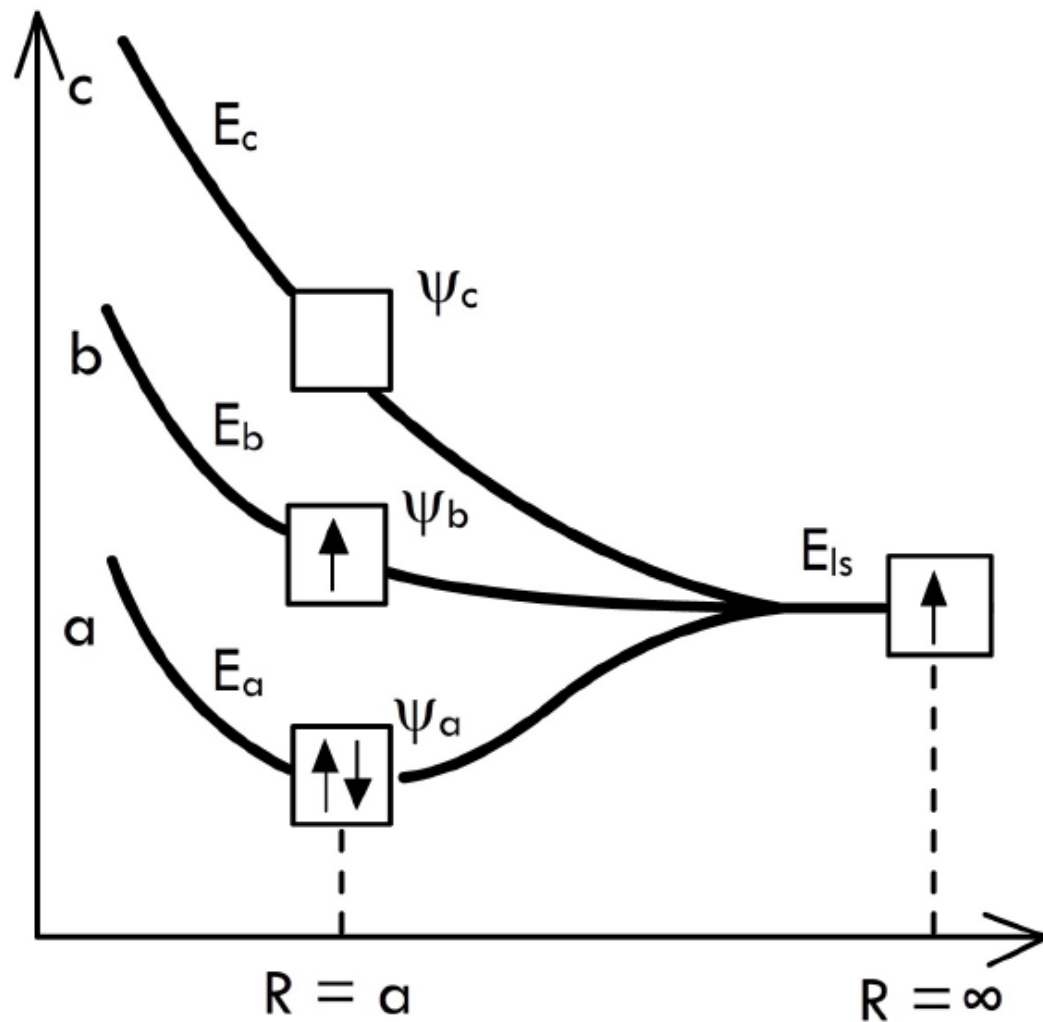


Figure 4: MOs formed when 3 H atoms come together. When the number of nodes increases, the energy increases while the stability decreases. The configuration with the lowest number of nodes is most stable.

Figure 5: Energy vs. bond length diagram for 3H atoms forming 3 MOs. The 3 electrons occupy the configuration with 0 nodes (2 electrons) and 1 node (1 electron)



3 H atoms is shown in figure 5. Out of the 3 electrons that are available 2 go to the lowest energy MO i.e. σ_a with 0 nodes and the remaining one goes to σ_b with 1 node. More the number of nodes greater is the energy of the MO.

Instead of 3 H atoms, if we have 4 atoms then there are 4 AOs which form 4 MOs with 0, 1, 2, and 3 nodes (arranged in order of increasing energy). Each of these MOs can take 2 electrons (opposite spin) so that there are a total of 8 **energy states** (including spin). The argument can be generalized saying that if there are **N** atoms, there are **N** atomic orbitals, and hence **N** molecular orbitals, and **2N** energy states. As long as the energy of the configuration is lower than the individual atoms the solid will be stable.

4 Energy bands in metals

We can try to extend this model beyond H. Consider the case of Li, which has 3 electrons. The electronic configuration is $1s^2 2s^1$. The 1s electrons form the inner shell and are usually not involved in bonding. Hence, for bonding we have the 2s shell with 1 electron and this can be considered similar to the H atom. So, if we have N Li atoms, there will be N MOs, and $2N$ energy states (including spin). This is shown schematically in figure 6.

The spacing between the individual MOs depends on the equilibrium interatomic spacing and the value of N . Larger the value of N , closer the individual levels. For really large N (e.g. if we have 7 g of Li then N will be 6.023×10^{23} or Avogadro's number) the individual MOs are so close that we can consider them to be continuous. Thus an **energy band** will be obtained. This band is called the **valence band** since it is obtained from the outermost shell. The band formation for Li is shown in figure 7. In the case of Li the band formed from the outer 2s levels is half full since there are a total of $2N$ energy states and only N electrons.

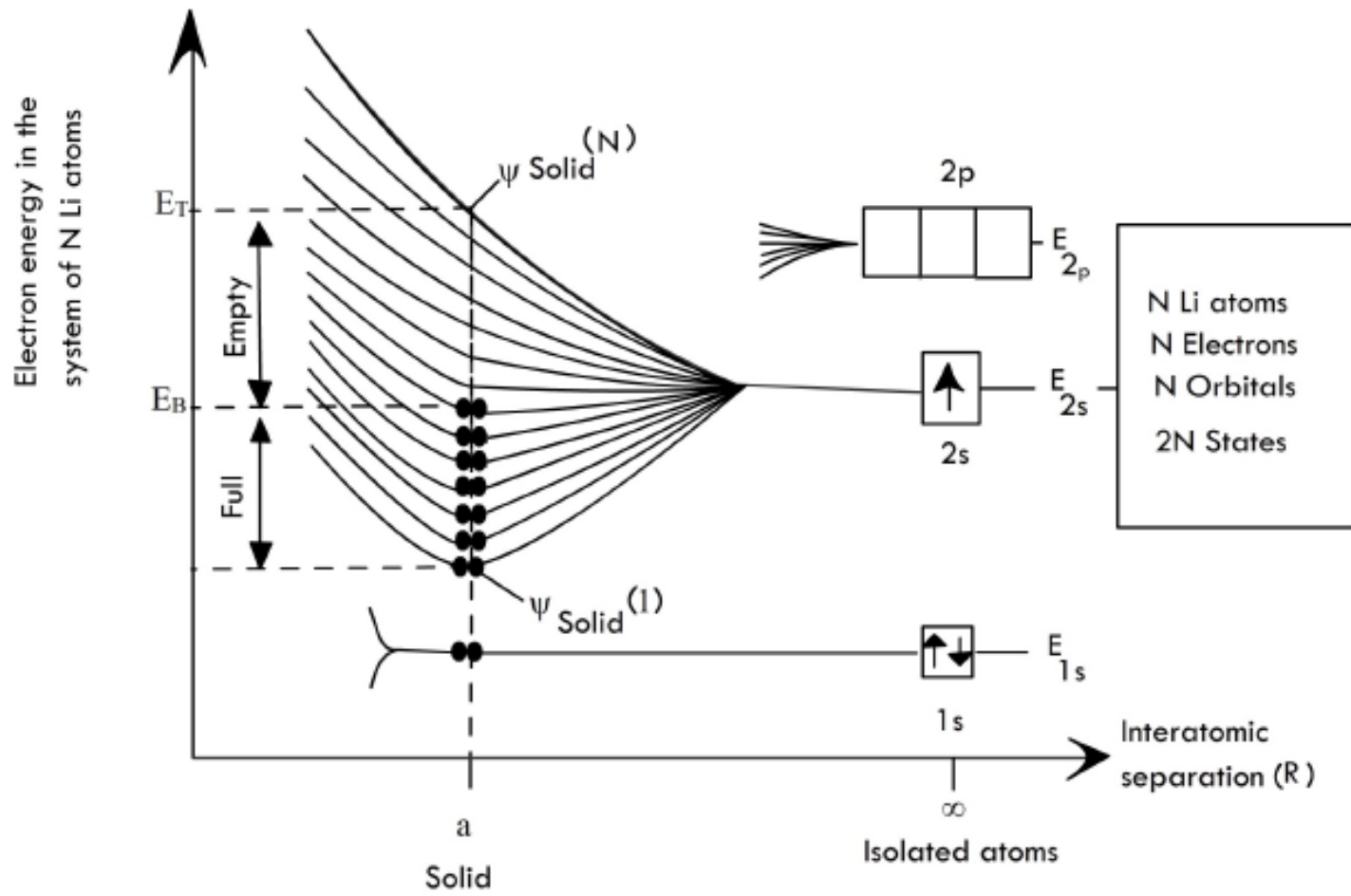
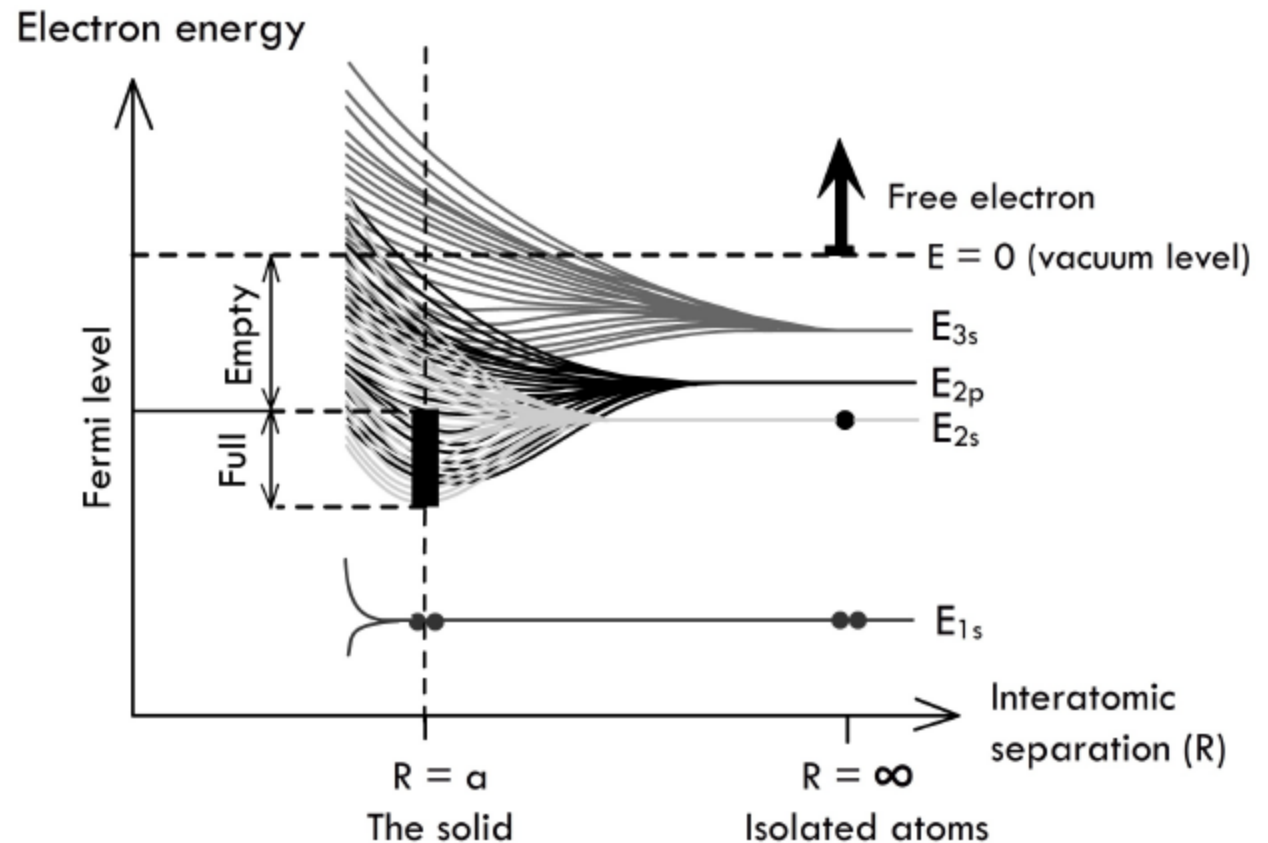


Figure 6: Energy vs. bond length diagram for N Li atoms. There are a total of $2N$ energy states (including spin) out of which N are occupied, half full. This makes Li a metal

The *separation between the filled states and the empty states* is called the **Fermi energy** and is denoted by E_F . Another way of defining the Fermi energy is that *this is the highest filled state in a metal at 0 K*. The energy required to remove an electron from the Fermi level to vacuum level (where the electron is free of the influence of the metal) is called the **work function**.

Figure 7: Energy vs. bond length diagram for large values of N showing a continuous band formation. The overlap between the 2s, 2p, and 3s levels are also shown



The Fermi level and work function for Li are shown in figure 8. Energy levels can be referenced either with respect to the vacuum level (takes as zero) or with respect to the bottom of the valence band. Thus, metals like Li have a partially filled valence band.

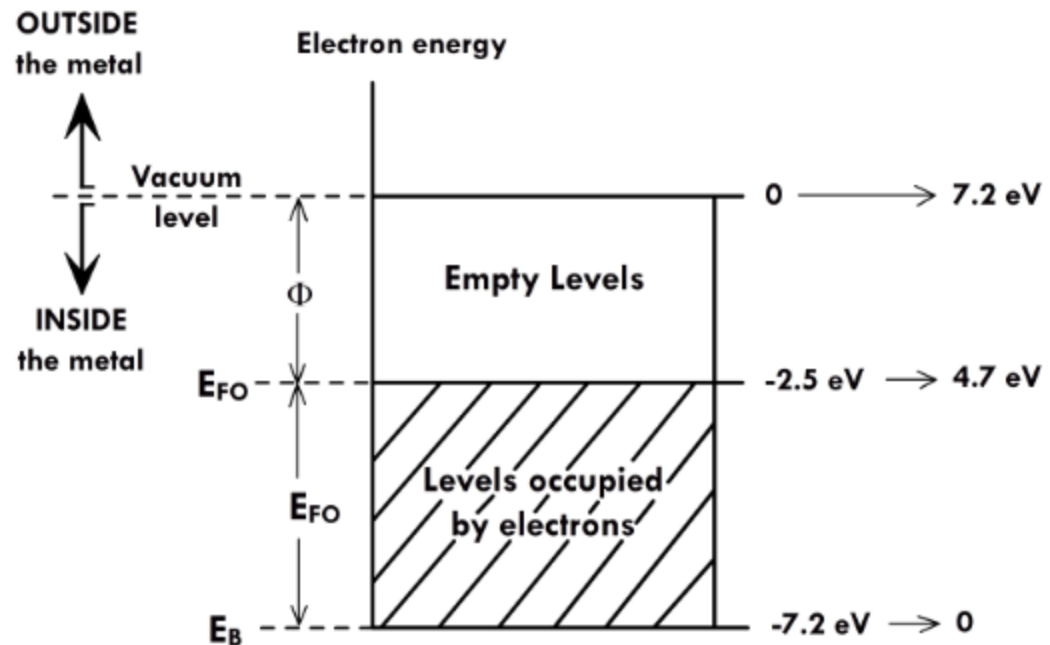


Figure 8: Fermi energy and work function in Li. By convention the vacuum level is taken as zero and energy levels within the metal are shown as negative. If the lowest energy level in the valence band is used as reference all these energy levels become positive.

We can extend this model to Be, which has 2 electrons in the outer $2s$ shell. According to the model we developed for Li where we have a band with $2N$ energy states and N electrons we have now have $2N$ states and $2N$ electrons so that the band should be completely full. So how is Be a metal? The reason is because Be has empty $2p$ shells which are close in energy to the $2s$ shell and they overlap. Because of this overlap there are empty states available for conduction. There are overlap states in Li as well, but we do not need these to explain conduction since the starting band is half full anyway. We can call the band formed by the empty $2p$ shell as the **conduction band**. In metals, the valence and conduction band overlap to give a continuous band of filled and empty states. This is shown schematically in figure 9. In the presence of an electric field electrons can move by occupying these empty energy states and this makes metals good conductors of electricity.

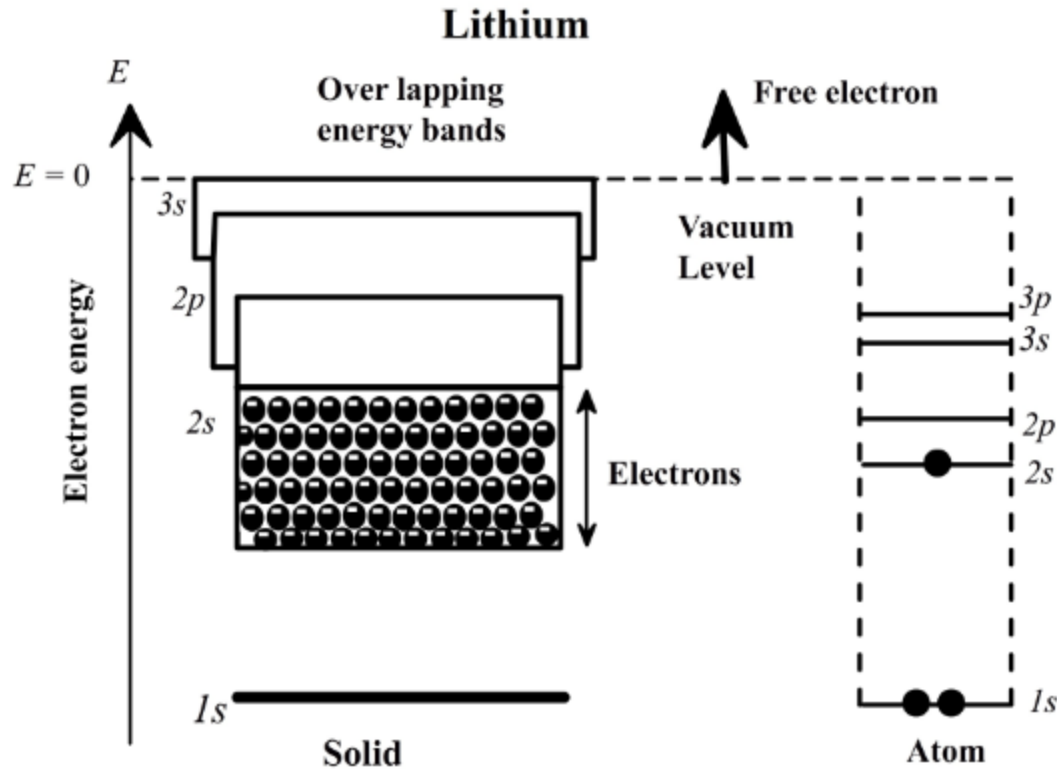


Figure 9: Energy band in a metal formed through overlap of individual bands. This diagram is similar to figure 7, at the equilibrium distance. For N Li atoms, $2s$ forms the valence band and $2p$ forms the conduction band which overlaps with valence band