

# Lecture 1: Electronic materials

## Contents

1	Introduction	1
2	Molecular orbital formation	3
3	Molecular orbitals in extended systems	7
4	Energy bands in metals	9

## 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 ( $\Omega$ ) and is related to the applied voltage and current by Ohm's law

$$V = IR \tag{1}$$

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

Table 1: Resistivity values of some typical metals

<b>Metal</b>	$\rho$ ( $\times 10^{-9} \Omega m$ )
Copper	15.7
Gold	22.8
Platinum	98
Silver	14.6

Table 2: Resistivity values of some typical semiconductors

<b>Semiconductor</b>	$\rho$ ( $\Omega m$ )
Germanium	$10^{-3} - 10$
Silicon	$0.1 - 10^3$
Zinc oxide	$10^{-2} - 10^{-4}$
Gallium Arsenide	$10^{-6} - 10^{-2}$

called **resistivity** ( $\rho$ ) 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  $\Omega m$ . **Conductivity** is defined as the inverse of resistivity. The symbol for conductivity is  $\sigma$  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.

Metals are characterized by low resistivity. The values quoted in table 1 are in the range of nano  $\Omega m$ . 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.

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.

Table 3: Resistivity values of typical insulators

<b>Insulator</b>	$\rho$ ( $\Omega m$ )
Wood (damp)	$10^3 - 10^4$
Deionized water	$10^5$
Glass	$10^{10} - 10^{14}$
Fused quartz	$10^{17}$

## 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  $\psi_{1s}$ . In quantum mechanics  $\psi$  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

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

Here,  $a_0$  refers to the Bohr radius and has a value of  $0.53 \text{ \AA}$ . 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  $\psi_{1s}^A$  and  $\psi_{1s}^B$ . 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,  $\sigma$  or they can be subtracted, giving the anti-bonding orbital,  $\sigma^*$ . This can be represented by

$$\begin{aligned} \sigma &= \psi_{1s}^A + \psi_{1s}^B \\ \sigma^* &= \psi_{1s}^A - \psi_{1s}^B \end{aligned} \quad (4)$$

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

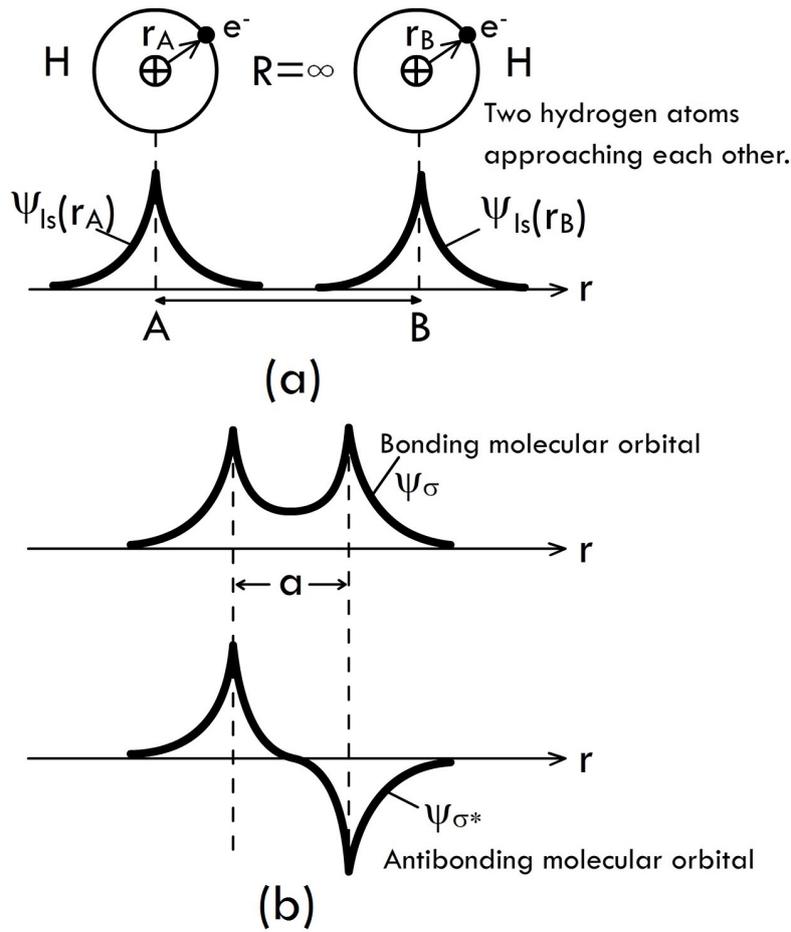


Figure 1: Formation of (a) bonding and (b) anti-bonding orbitals when 2 H atoms come together. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

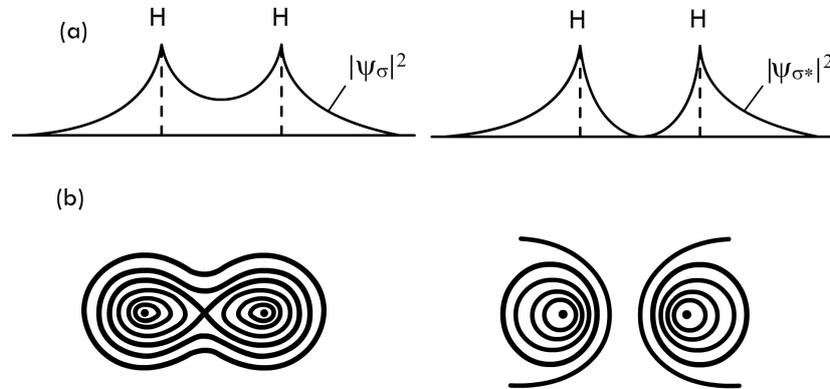


Figure 2: Electron probability distribution in (a) bonding ( $\sigma$ ) and (b) anti-bonding ( $\sigma^*$ ) orbitals. Lines of constant probability are shown. For the anti-bonding orbital there is zero probability of finding the electron between the two atoms i.e. node. Adapted from *Principles of Electronic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

anti-bonding orbital has 1 node. The electron probability distribution is shown in figure 2.

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  $\sigma$  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  $\sigma$  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  $\sigma$  and  $\sigma^*$ . 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. From this diagram it is clear why  $\text{He}_2$  will not form. Each He atom has 2 electrons so that there are a total of 4 electrons. Out of these 2 electrons will go to  $\sigma$  and two to  $\sigma^*$  since each MO can only take a maximum of 2 electrons (opposite spin). The overall energy of the  $\text{He}_2$  molecule will then be higher than the energy of 2 individual He atoms and hence  $\text{He}_2$  will

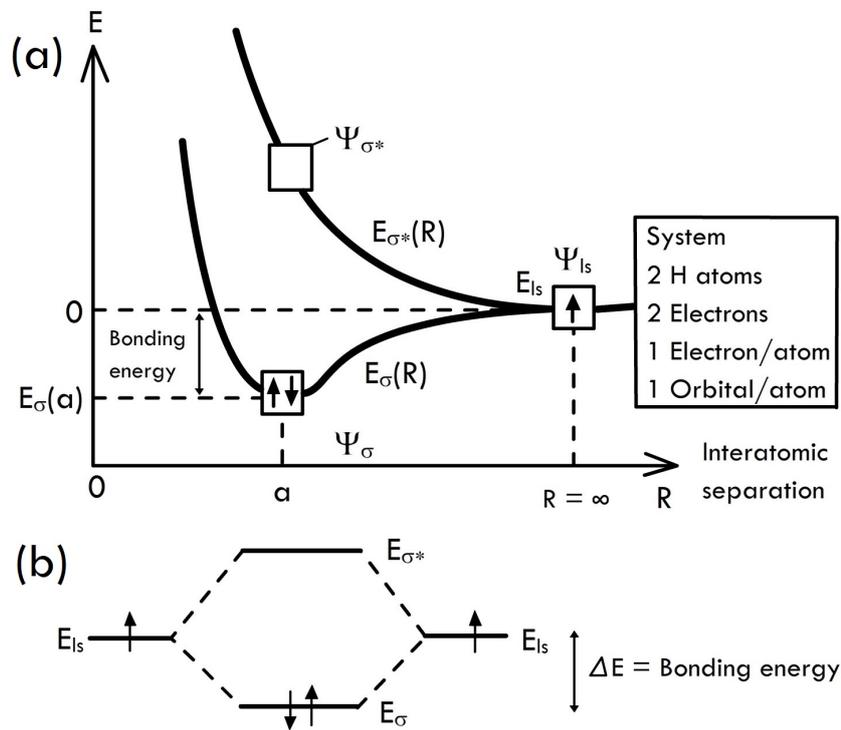


Figure 3: (a) Energy vs. bond length plot for 2 H atoms. (b) The schematic representation of the formation of the  $H_2$  molecule. Both electrons go to the bonding orbital while the anti-bonding orbital is empty. Adapted from *Principles of Electronic Materials - S.O. Kasap*.

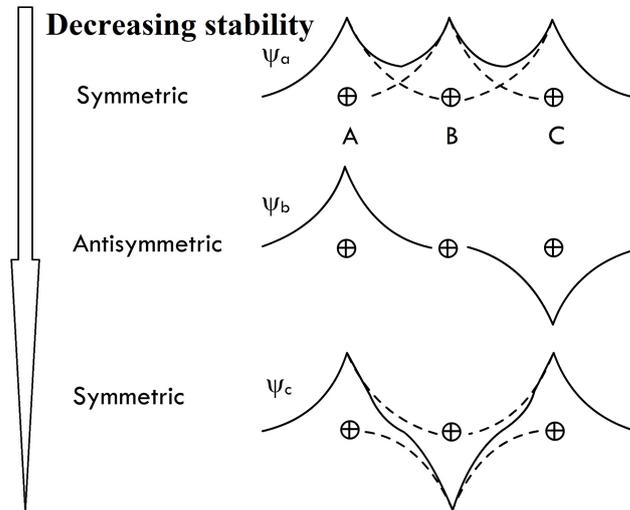


Figure 4: MOs formed when 3 H atoms come together. The number of nodes increases while the stability decreases. The configuration with the lowest number of nodes is most stable. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

not form.

### 3 Molecular orbitals in extended systems

Consider the case when we have 3 H atoms. Each atom has a  $\psi_{1s}$  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  $\psi_{1s}^A$ ,  $\psi_{1s}^B$ , and  $\psi_{1s}^C$ . The 3 AOs can be put together to form 3 MOs while maintaining symmetry of the resultant wave function in the following way.

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

$\sigma_a$ ,  $\sigma_b$ , and  $\sigma_c$  are the 3 MOs that are formed. This formation is shown in figure 4.  $\sigma_a$  is the symmetric solution with no nodes.  $\sigma_b$  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).  $\sigma_c$  is again a symmetric solution but with 2 nodes, between the 2 sets of atoms. In terms of energy  $\sigma_a$  is the lowest followed by  $\sigma_b$  and then  $\sigma_c$ . The energy vs. bond length diagram for

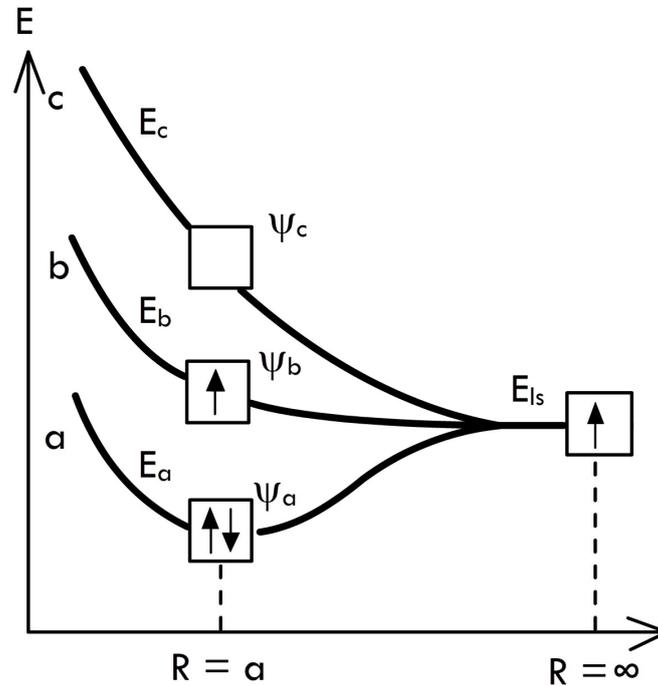


Figure 5: Energy vs. bond length diagram for 3H atoms forming 3 MOs. The 3 electrons occupy the configuration with 0 nodes (2 electrons) and 1 node (1 electron). Adapted from *Principles of Electronic Materials* - S.O. Kasap.

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.  $\sigma_a$  with 0 nodes and the remaining one goes to  $\sigma_b$  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 hence  $2N$  energy states. As long as the energy of the configuration is lower than the individual atoms the solid will be stable.

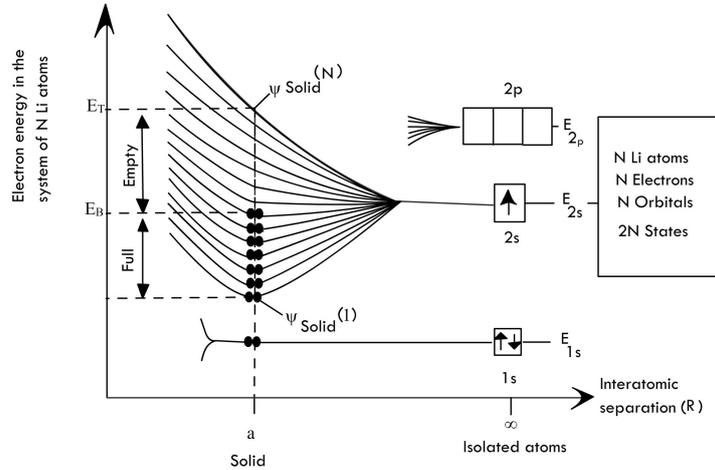


Figure 6: Energy vs. bond length diagram for  $N$  Li atoms. There are a total of  $2N$  energy states (including spin) out of which  $N$  are occupied, half full. This makes Li a metal. Adapted from *Principles of Electronic Materials - S.O. Kasap*.

## 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  $6.023 \times 10^{23}$  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.

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

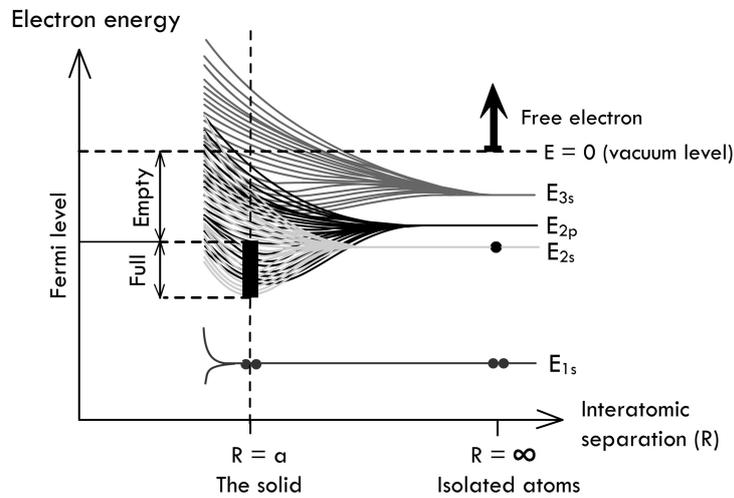


Figure 7: Energy vs. bond length diagram for large values of  $N$  showing a continuous band formation. The overlap between the  $2s$ ,  $2p$ , and  $3s$  levels are also shown. Adapted from *Principles of Electronic Materials* - *S.O. Kasap*.

the electron is free of the influence of the metal) is called the **work function**. 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.

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.

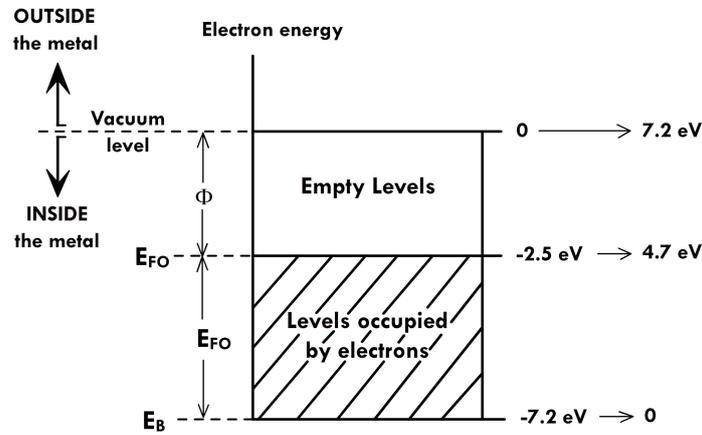


Figure 8: Fermi energy and work function in Li. By convention the vacuum level is taken as zero and energy levels within the metal are shown as negative. If the lowest energy level in the valence band is used as reference all these energy levels become positive. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

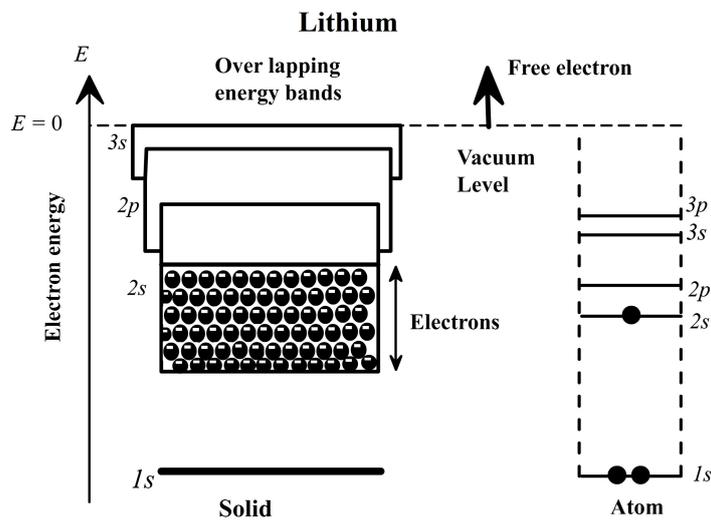


Figure 9: Energy band in a metal formed through overlap of individual bands. This diagram is similar to figure 7, at the equilibrium distance. Adapted from *Principles of Electronic Materials* - S.O. Kasap.