

Lecture 26 Title: Fundamentals of the Quantum Theory of molecule formation

Page-0

In the last module, we have discussed about the atomic structure and atomic physics to understand the spectrum of atoms.

However, many atoms can combine to form particular molecules, e.g. Chlorine (*Cl*) and Sodium (*Na*) atoms form *NaCl* molecules.

Bonding between ions, as in the negative charged chlorine ion and the positively charged sodium ion, could be understood in the light of coulomb interaction (attraction) between oppositely charged bodies.

But atoms of the same type can also form bonds, as for example in the case of H_2 .

It remained, however, inexplicable that two similar atoms, which are electrically neutral, could form a bound state.

In this lecture, we will understand the formation of molecule from atom in the quantum mechanical framework.

It only became possible with the aid of quantum mechanics to attain a fundamental understanding for the formation of molecule.

Even in the case of ionic bonding, basic new insights have been obtained through quantum theory.

First, for example, it must be understood why the ions form in the first place, and why the electron which is transferred from sodium to chlorine thus finds an energetically more favorable state.

In the following, we will develop some important basic ideas for the quantum theory of chemical bonding. However, Physics & Chemistry are still far away from a complete solution to these problems.

To understand chemical bonding, the interactions of several particles must be taken into account: given n atomic nuclei and m electrons, one would have to find the complete wavefunction and the corresponding energies of the total system.

It is useful to keep in mind that the nuclear masses are much greater than those of the electrons. Thus the electronic motions are much faster than nucleus.

Then we may ignore the motion of the nuclei and treat them as fixed.

In atomic physics, we were able to obtain much information from spectroscopic observations and could direct our attention to both the ground states and the excited states.

In the study of chemical bonding, the determination of the wavefunction of the ground state of the particular molecule plays a more important role.

The Hydrogen – Molecule Ion H_2^+

Certainly the simplest case of chemical bonding occurs in the hydrogen molecule ion H_2^+ . This species is observed as a bound state in gas discharges in a hydrogen atmosphere, in such a gas discharge, the hydrogen molecule loses one electron.

The bonding energy, equivalent to the dissociation energy, has been determined to be 2.65 eV.

We are dealing with two nuclei (a and b in figure-26.1) and one electron. If the nuclei are far removed from one another, we can imagine that the electron is localized on one nucleus or other.

The wavefunctions are those of the hydrogen atomic ground state.

So the Hamiltonian for nucleus a ,

$$\underbrace{\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_a} \right)}_{H_a} \phi_a(r_a) = E_a^0 \phi_a(r_a) \quad \dots (26.1)$$

And correspondingly for nucleus b ,

$$H_b \phi_b(r_b) = E_b^0 \phi_b(r_b) \quad \dots (26.2)$$

$$\text{So, } E_a^0 = E_b^0 = E^0$$

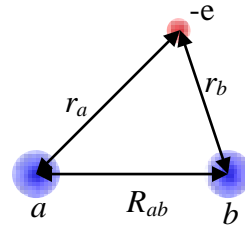


Figure-26.1

If we let the nuclei approach one another, the electron, which was, for example, at first attached to nucleus a , will experience the attractive Coulomb force of nucleus b .

Conversely, an electron which was at first bound to nucleus b will experience the attractive Coulomb force of nucleus a . We must therefore set up a Schrodinger Equation which contains the Coulomb potential for both.

Further in order to calculate the total energy of the system, we must take into account the Coulomb repulsion between nuclei. The additional energy $\left(\frac{e^2}{R_{ab}} \right)$ is not directly related to the energy of the electron, it will only produce a constant shift of all the energy eigen values. We will introduce it at the end.

Referring to the figure 26.1, let us define,

$$R_{ab} = |R_a - R_b| \quad r_a = |r - R_a| \quad r_b = |r - R_b|$$

Thus, Schrödinger equation, then

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b} \right) \psi = E \psi \quad \dots (26.3)$$

Here E and ψ are energy eigen value and the wavefunction for the whole system respectively and are yet to be calculated.

We will use the perturbation method. In principle, the electron could be in the neighborhood of nucleus a or of nucleus b , with the same energy. These two states ϕ_a and ϕ_b are thus degenerate. Now however, the other nucleus, from which the electron is by chance more distant, acts, as a perturbation to the electronic state. We thus expect that the degeneracy will be lifted by this perturbation.

In the presence of the degeneracy, we take the total wavefunction is the linear combination of the hydrogen wavefunctions defined in equation 26.1 and 26.2 and defined as,

$$\psi = c_1 \phi_a + c_2 \phi_b$$

Where c_1 and c_2 are the coefficients. This is generally known as linear combination of the atomic orbital (LCAO) and ψ is known as the molecular orbital.

So, putting this, in equation 26.3, and rearranging we get,

$$\left(H_a - \frac{e^2}{r_b} \right) c_1 \phi_a + \left(H_b - \frac{e^2}{r_a} \right) c_2 \phi_b = E (c_1 \phi_a + c_2 \phi_b) \quad \dots (26.5)$$

Where $H_a = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_a}$ and $H_b = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_b}$

Substituting the values from equations 26.1 and 26.2 in 26.5, we get,

$$\begin{aligned} \left(E^0 - \frac{e^2}{r_b}\right)c_1\phi_a + \left(E^0 - \frac{e^2}{r_a}\right)c_2\phi_b &= E c_1\phi_a + E c_2\phi_b \\ \Rightarrow \left(\underbrace{E^0 - E}_{-\Delta E} - \frac{e^2}{r_b}\right)c_1\phi_a + \left(\underbrace{E^0 - E}_{-\Delta E} - \frac{e^2}{r_a}\right)c_2\phi_b &= 0 \end{aligned} \quad \dots (26.6)$$

While ϕ_a and ϕ_b are functions of position, the coefficients are independent of positions.

We assume that the functions ϕ_a and ϕ_b are real, as in the case of hydrogen atom ground state wavefunctions, and the functions ϕ_a and ϕ_b are not orthogonal since the electron is associated with two different nuclei a and b . So,

$$\int \phi_a \phi_b dV = S \quad \text{and} \quad \int \phi_a \phi_a dV = \int \phi_b \phi_b dV = 1 \quad \dots (26.7)$$

Now, Equation 26.6 is multiplied by ϕ_a

$$\begin{aligned} \int \phi_a \left(-\Delta E - \frac{e^2}{r_b}\right)c_1\phi_a dV + c_2 \int \phi_a \left(-\Delta E - \frac{e^2}{r_a}\right)\phi_b dV &= 0 \\ \Rightarrow -\Delta E c_1 - c_1 \int \phi_a(r_a) \frac{e^2}{r_b} \phi_a(r_a) dV + c_2 (-\Delta E) \int \phi_a \phi_b dV - c_2 \int \phi_a(r_a) \frac{e^2}{r_a} \phi_b(r_b) dV &= 0 \\ \Rightarrow (-\Delta E c_1 - c_1 C) + (-\Delta E c_2 S - D c_2) &= 0 \\ \Rightarrow (-\Delta E - C)c_1 + (-\Delta E \cdot S - D)c_2 &= 0 \end{aligned} \quad \dots\dots\dots(26.8)$$

Where,

$$\begin{aligned} + \int \phi_a(r_a) \frac{e^2}{r_b} \phi_a(r_a) dV &= C \\ + \int \phi_a(r_a) \frac{e^2}{r_a} \phi_b(r_b) dV &= D \end{aligned}$$

Equation 26.6 is multiplied by ϕ_b and following the same procedure we get,

$$(-\Delta E \cdot S - D)c_1 + (-\Delta E - C)c_2 = 0 \quad \dots\dots\dots (26.9)$$

So, to get the solution, following determinant from equations 26.8 and 26.9 should vanish.

The determinant:

$$\begin{pmatrix} \Delta E + C & \Delta E \cdot S + D \\ \Delta E \cdot S + D & \Delta E + C \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

So,

$$\begin{aligned} & (\Delta E + C)^2 - (\Delta E \cdot S + D)^2 = 0 \\ \Rightarrow & \Delta E^2 + C^2 + 2\Delta E C - \Delta E^2 S^2 - D^2 - 2\Delta E DS = 0 \\ \Rightarrow & \Delta E^2 (1 - S^2) + 2(C - DS)\Delta E + (C^2 - D^2) = 0 \\ \Rightarrow & \Delta E = \frac{-2(C - DS) \pm \sqrt{4(C - DS)^2 - 4(1 - S^2)(C^2 - D^2)}}{2(1 - S^2)} \\ & = \frac{-(C - DS) \pm \sqrt{C^2 + D^2 S^2 - 2CDS - C^2 + D^2 + C^2 S^2 - D^2 S^2}}{(1 - S^2)} \\ & = \frac{-(C - DS) \pm \sqrt{(D - CS)^2}}{(1 - S^2)} \\ & = \frac{-(C - DS) \pm (D - CS)}{(1 - S^2)} \end{aligned}$$

Two solutions:

$$\begin{aligned} (i) \quad & \frac{-C + DS - D + CS}{1 - S^2} = -\frac{C + D}{1 + S} \\ (ii) \quad & \frac{-C + DS + D - CS}{1 - S^2} = -\frac{C - D}{1 - S} \quad \dots\dots\dots(26.10) \end{aligned}$$

$$\text{So, } \Delta E = -\frac{C \pm D}{1 \pm S}$$

If we take, solution (i) in equation 26.10 and then,

$$\begin{aligned}
 & \text{Substituting } \left[\Delta E = -\frac{C+D}{1+S} \right] \quad \text{in Eqn. (26.8)} \\
 & (\Delta E + C)c_1 + (\Delta E \cdot S + D)c_2 = 0 \\
 & \Rightarrow \left(-\frac{C+D}{1+S} + C \right) c_1 + \left(-\frac{(C+D)S}{1+S} + D \right) c_2 = 0 \\
 & \Rightarrow \left(\frac{-\cancel{C} - D + \cancel{C} + CS}{1+S} \right) c_1 + \left(\frac{-CS - \cancel{DS} + D + \cancel{DS}}{1+S} \right) c_2 = 0 \\
 & \Rightarrow \left(\frac{CS - D}{1+S} \right) c_1 + \left(\frac{D - CS}{1+S} \right) c_2 = 0 \\
 & \Rightarrow \left(\frac{CS - D}{1+S} \right) c_1 - \left(\frac{CS - D}{1+S} \right) c_2 = 0
 \end{aligned}$$

So, $c_1 = c_2 = c$ and thus, $\psi_+ = c(\phi_a + \phi_b)$

$$\begin{aligned}
 & E^0 - E = -\Delta E \\
 & \Rightarrow E = E^0 - \frac{C+D}{1+S} = E_+ \quad \dots\dots\dots(26.11)
 \end{aligned}$$

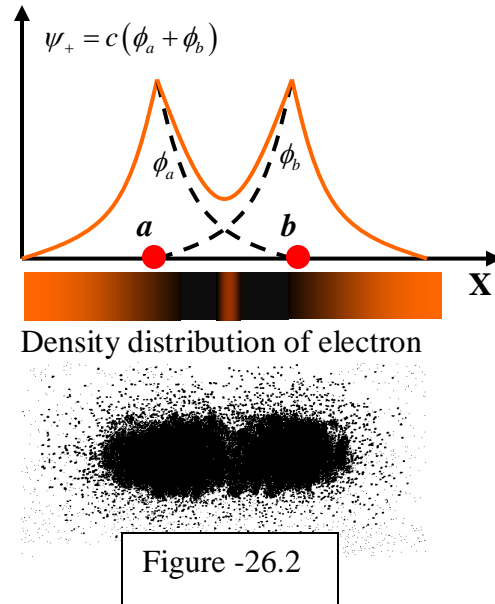
Now if we take, solution (ii) in equation 26.10 and

$$\begin{aligned}
 & \text{Substituting } \left[\Delta E = -\frac{C-D}{1-S} \right] \quad \text{in Equation. (26.9)} \\
 & (\Delta E \cdot S + D)c_1 + (\Delta E + C)c_2 = 0 \\
 & \Rightarrow \left(-\frac{(C-D)S}{1-S} + D \right) c_1 + \left(-\frac{C-D}{1-S} + C \right) c_2 = 0 \\
 & \Rightarrow \left(\frac{-CS + \cancel{DS} + D - \cancel{DS}}{1-S} \right) c_1 + \left(\frac{-\cancel{C} + D + \cancel{C} - CS}{1-S} \right) c_2 = 0 \\
 & \Rightarrow \left(\frac{D - CS}{1-S} \right) c_1 + \left(\frac{D - CS}{1-S} \right) c_2 = 0
 \end{aligned}$$

So, $c_1 = -c_2 = c$ and thus $\psi_- = c(\phi_a - \phi_b)$

$$E = E^0 - \frac{C-D}{1-S} = E_-$$

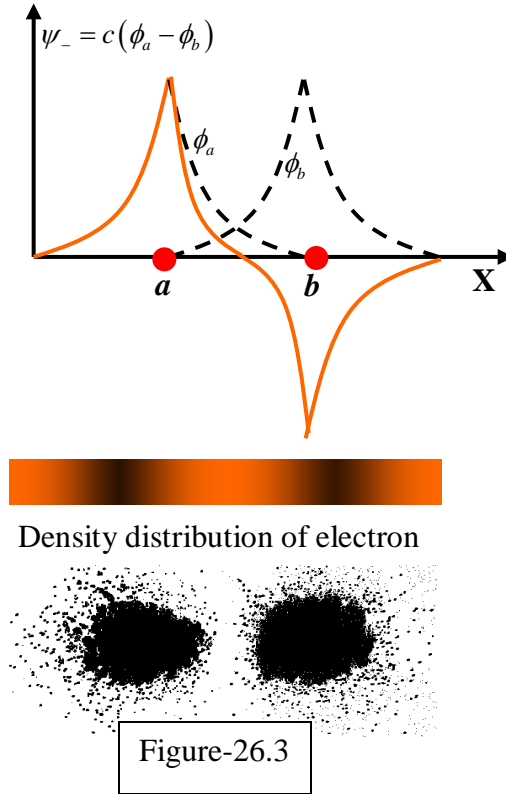
Let us understand the meaning of these wavefunctions ψ_+ and ψ_- . Figure-26.2 shows the plotting of wavefunctions ϕ_a and ϕ_b as well as $(\phi_a + \phi_b)$.



The following observations can be made.

- (a) Symmetric wavefunction ψ_+ is formed by $\phi_a + \phi_b$. Because of the overlap, the occupation probability for ψ_+ between two nuclei is increased.
- (b) Thus the density distribution of electron in the ψ_+ state shown in the lower part of figure 26.2 increases as the distance between a and b decreases.

Antisymmetric wavefunction ψ_- is formed from $\phi_a - \phi_b$. The occupation probability is clearly zero in the plane of symmetry.



As can be seen from figures-26.2 and 26.3 that the distance between a and b is an important factor to have finite overlap between the ϕ_a and ϕ_b .

Now we will concentrate on the energy values E_+ and E_- . To do that we have to understand the meaning of the quantities S , C and D . We will try to evaluate these quantities through the diagrams.

The quantity $\int \phi_a \phi_b dV = S$

From figure 26.4 it is clear that this quantity S is considerable when R_{ab} is sufficiently close and S increases when R_{ab} decreases. The quantity S is known as *overlap integral*.

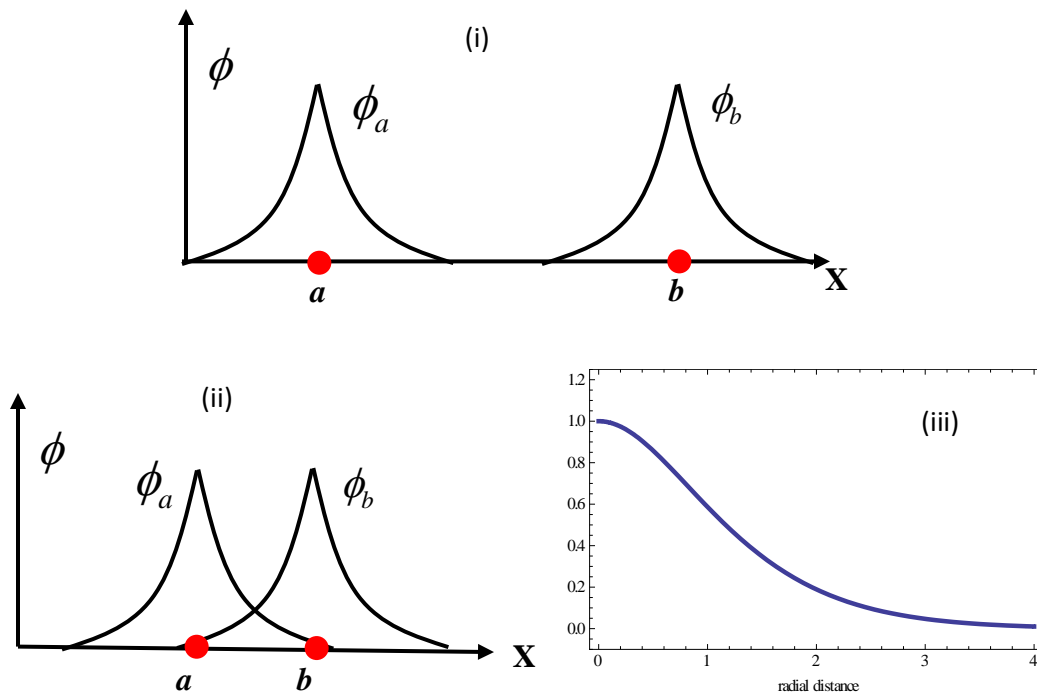


Figure-26.4

Figure-26.4(i) represents the 1s atomic orbital of hydrogen for two nuclei a and b .

Figure-26.4(ii) shows that when the nuclei are close enough the overlap increases.

Figure-26.4(iii) plots the value of overlap integral S with respect to the internuclear distance R_{ab} . When both the nuclei are coming closer the overlap increases and the value of S increases. When they fall on each other, the overlap integral becomes 1. However, this situation does not arise due to the nuclear-nuclear repulsion term. We will visualize this picture later.

$$C = + \int \phi_a(r_a) \frac{e^2}{r_b} \phi_a(r_a) dV$$

$$= + \int \phi_b(r_b) \frac{e^2}{r_a} \phi_b(r_b) dV$$

This term is known as the direct coulomb term. Figure-26.5(i) shows the orbital $|\phi_a^2|$ and the coulomb attraction potential. As the two nuclei approaches to each other, the overlap between them increases. Figure-26.5(ii) plots the term C with respect to the internuclear distance R_{ab} . Here also we see that, this term is appreciable when the both the nuclei are close enough.

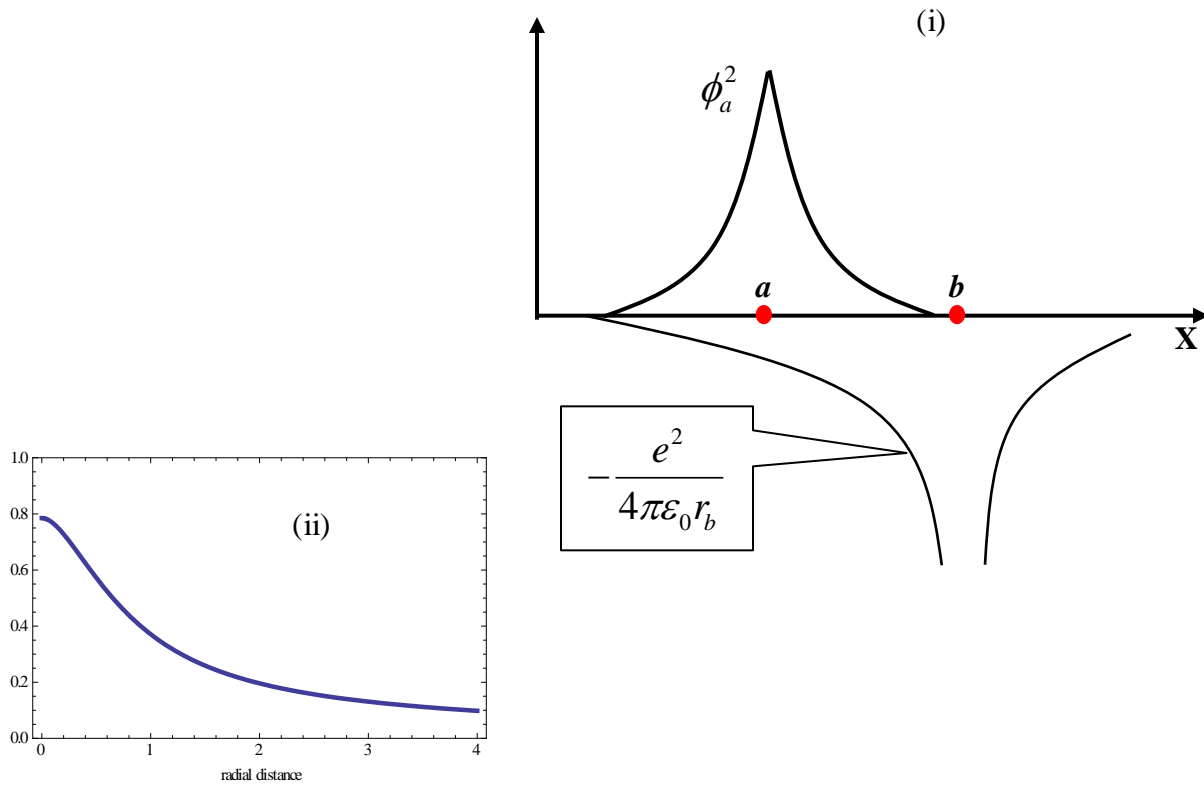
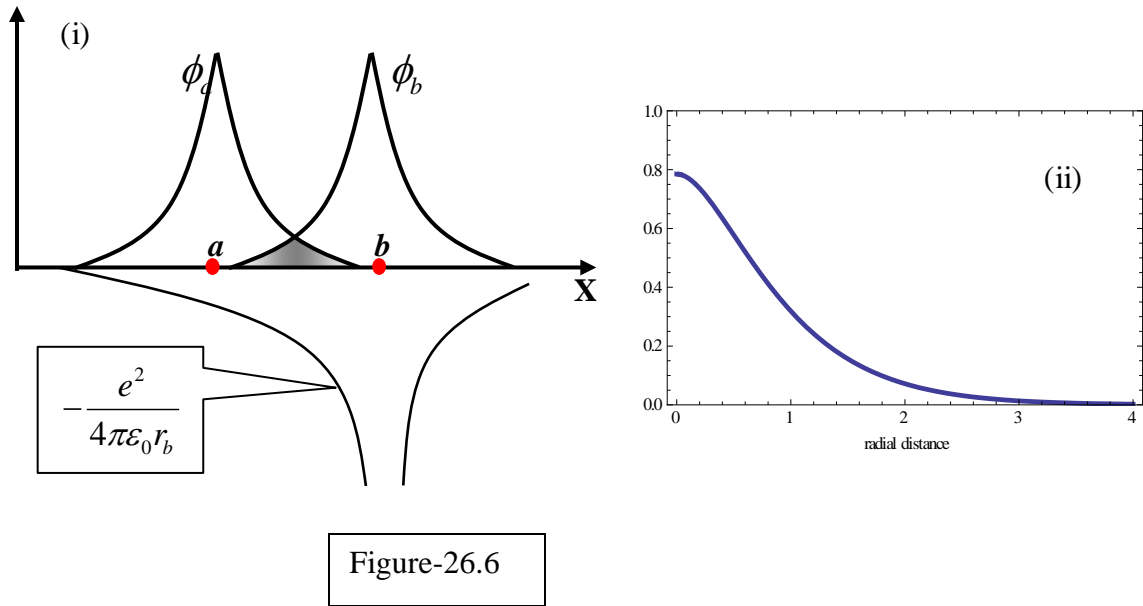


Figure-26.5

$$D = + \int \phi_a(r_a) \frac{e^2}{r_a} \phi_b(r_b) dV$$

$$= + \int \phi_a(r_a) \frac{e^2}{r_b} \phi_b(r_b) dV$$



The term D is known as cross integral term. The meaning of this is that there should be overlap between ϕ_a , ϕ_b and coulomb attraction term $(-\frac{e^2}{4\pi\epsilon_0 r_b})$ as shown in figure 26.6(i). The value of this integral is plotted in figure 26.6(ii). It is clear from this figures that when there is no overlap between ϕ_a and ϕ_b , the value of D goes to zero.

In figure 26.7(i), the quantity S, C, D are plotted together to have a comparison. It can be seen that all these quantities depend on the R_{ab} .

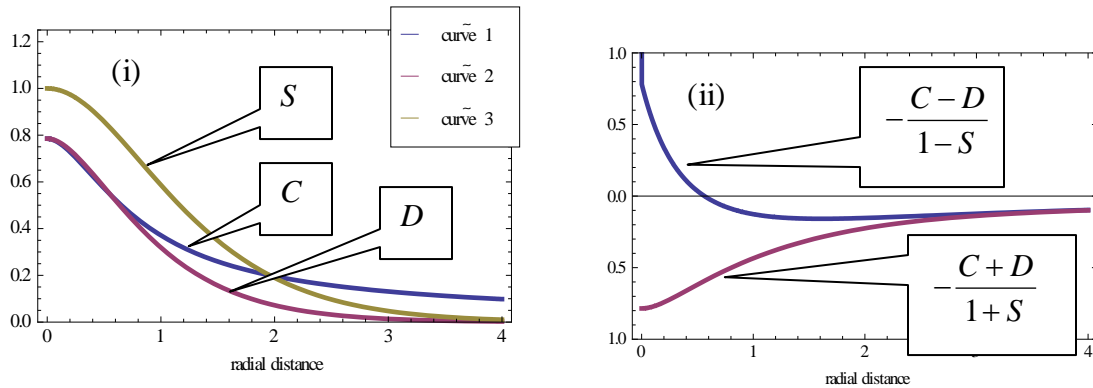


Figure-26.7

In figure 26.7(ii), the quantities $-\frac{C+D}{1+S}$ and $-\frac{C-D}{1-S}$ are plotted with respect to the internuclear distance R_{ab} . As can be seen, from this plot that these quantities are degenerate when the two nuclei are far away from each other. If two nuclei approach one another the quantities split up in a way depending on whether symmetric or antisymmetric / bonding or antibonding. In Symmetric case energy reduces whereas in Antisymmetric case energy increases.

Now, if we add nuclear energy, the energy diagram is shown in figure-26.8 symmetric case there is a minimum, so it forms a bound state. Antibonding is not a stable state.

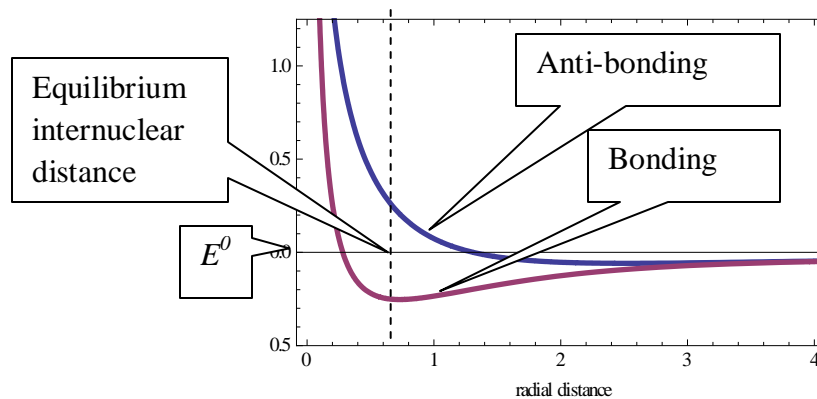


Figure-26.8

Physical meaning: in the bound state the probability density of electron is quite large in the middle, profit Coulomb attraction from both the nuclei, energy goes down. Whereas in the antibonding case, only electron experiences attractive force of one nucleus at a time. The internuclear distance where the energy is having a minimum is known as equilibrium internuclear distance. Thus, this molecule H_2^+ - ion is stable with the bonding energy lower than the individual hydrogen atom.

Page-14

Recap

From this lecture we have developed the basic idea of the quantum theory of chemical bonding.

To understand chemical bonding, the interactions of several particles should be taken into account: given n atomic nuclei and m electrons, one would have to find the complete wavefunction and the corresponding energies of the total system.

It is useful to keep in mind that the nuclear masses are much greater than those of the electrons. Thus the electronic motions are much faster than nucleus. This is known as Born-Oppenheimer approximation.

In the study of chemical bonding, the determination of the wavefunction of the ground state of the particular molecule plays a more important role.

The degenerate atomic energy levels split due to the interaction between the atomic orbitals. The no. of molecular orbital is same the no. of atomic orbital.

The molecule will be stable only if a minimum is achieved during the calculation of ground state energy of the molecule.

The minimum arises because the coulomb attractions bring the nuclei closer on the other hand the nuclear-nuclear repulsion restrict them to come too close. An optimum distance, the two energies form a minimum for the molecule and thus equilibrium is achieved. The inter-nuclear distance at equilibrium is the bond length of the molecule.