Module 2 : Molecular Structure

Lecture 7 : Homonuclear Diatomic Molecules

Objectives

In this lecture you will learn the following

- Definition of a molecular orbital and the construction of molecular orbitals from linear combinations of atomic orbitals.
- Contour diagrams of σ and π orbitals of H_2^+
- Electronic configurations of homonuclear diatiomics.
- Energy level diagrams for homonuclear diatomics.
- The binding energy of a homonuclear diatomic as a function of the internuclear distance.
- Schrödinger equation for diatomics.

7.1 Introduction

The study of atomic structure dealt with the Schrödinger equation for atoms, atomic energy levels, charge densities and “filling up” the atomic orbitals with electrons using the aufbau principle as well as the Pauli exclusion principle. In the case of molecular structure too, the approach is similar. The Schrödinger equation has to take into account the presence of more than one nucleus and the interaction of each electron with all the nuclei and all the other electrons. In a commonly used method, the atomic orbitals are replaced by molecular orbitals (MOs). Like atomic orbitals, molecular orbitals are also functions of the coordinates of an (a single) electron.

The value of this function (MO) depends on the positions of all the nuclei, which are generally considered fixed for the purpose of calculating MOs. This is reasonable, since the nuclei are far heavier than the electrons. Before beginning our study on homonuclear diatomics, let us see how the Schrödinger equation for a molecule looks like. In the following figure, A, B, C and D are the nuclei and 1,2,3 ….n are electrons.

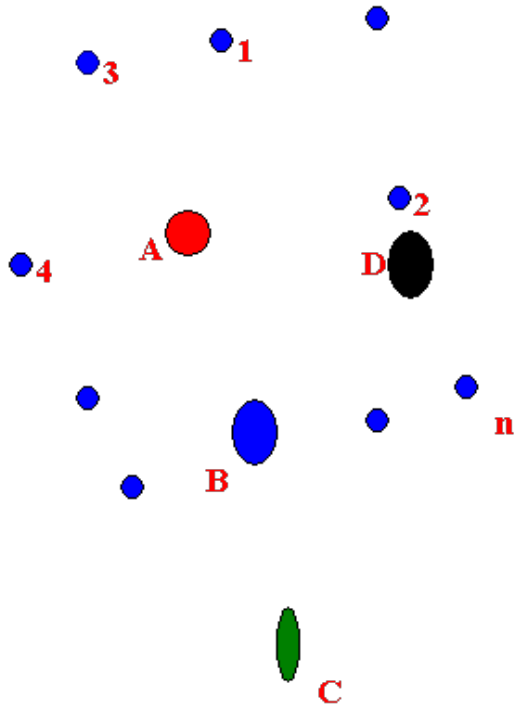


Fig 7.1 Coordinates of nuclei (A, B, C, D, filled circles, considered to be fixed) and electrons (1,2,3,4,….n, shown as dots) of a molecule.

The Schrödinger equation is written as $H\psi = E\psi$, where ψ (1,2,….n) is the molecular wave function and H is the Hamiltonian operator. H (for the molecular system in fig. 7.1) is given by

$$H = -\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2 - \frac{\hbar^2}{2m_C}\nabla_C^2 - \frac{\hbar^2}{2m_D}\nabla_D^2 - \frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\sum_{X=A,B,C,D}\frac{Z_X e^2}{r_{iX}} + \sum_{i<j}^{n}\frac{e^2}{r_{ij}} + \sum_{I<J}\frac{Z_I Z_J}{r_{IJ}}$$

Here ∇_X^2 is the kinetic energy operator for nucleus X, ∇_i^2 is the kinetic energy operator for electron i, r_{iX} is the distance between electron i and nucleus X and r_{ij} is the distance between electron i and electron j. Since the nuclei are held fixed, the nuclear kinetic energy operator terms will be set to zero.

Molecular orbitals of H_2^+

The simplest example of a molecule is H_2, which has two nuclei and two electrons. The Hamiltonian for this species is given in the following equation (7.2) and the coordinates of all the particles are shown in the following figure (fig 7.2)

$$H = -\frac{\hbar^2}{8\pi^2 m}\nabla_1^2 - \frac{k^2}{8\pi^2 m}\nabla_2^2 - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{AB}} \qquad (7.2a)$$

$$\text{where, } \nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \text{ and } \nabla_2^2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \qquad (7.2b)$$

The hydrogen molecular ion H_2^+ has two nuclei and one electron. The Hamiltonian for this species is given in the following equation (7.3). Since there is only one electron, the subscript 1 in r_{1A} can be dropped for convence.

$$H = -\frac{\hbar^2}{8\pi^2 m}\nabla_1^2 - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} + \frac{e^2}{r_{AB}} \qquad (7.3)$$

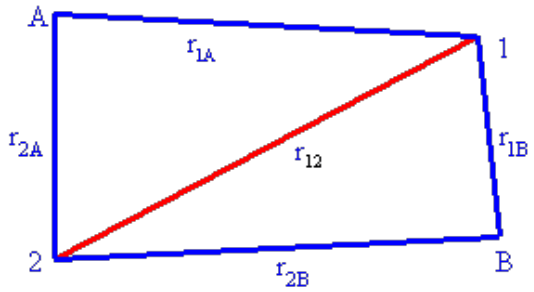


Figure 7.2 The electron coordinates in H_2. In the molecular ion H_2^+ there is only one electron.

In equation (7.1) it is simplest to treat the nuclei as fixed and so, the kinetic energy terms of the nuclei are not considered. In eq (7.2) the kinetic energy terms for the nuclei $(\nabla_A^2 \text{ and } \nabla_B^2)$ are not shown. This is known as the Born_Oppenheimer approximation and helps greatly in simplifying the problem. Equations (7.1) and (7.2) do not have any exact solution. We need to develop strategies to solve these as accurately as possible. In the present chapter we will develop qualitative ideas of the nature of the solutions. A few public domain (free) softwares are available for quantitative solutions. The Schrodinger equation for H_2^+ (a one electron system) has an exact solution, but that is in the bipolar coordinate system. We will instead consider numerical solutions here.

The reason why exact solutions can not be found is that the equation (7.1) and (7.2) can not be split into n independent equations for n electrons. This is because the terms $\sum e^2/r_{ij}$ can not be separated into n terms containing the variables r_i alone. What can be done is to get n effective one particle equations for the n orbitals, just as we did in the case of atomic orbitals in lecture 6.

An important change that you will notice in eq (7.1) and (7.2) is that CGS units are used here and the factor of $4\pi\varepsilon_0$ used in earlier chapters is not there. In these units, the charge on an electron is $4.8 * 10^{-10}$ esu (electrostatic unit of charge). The repulsive force between two charges of 1 esu each separated by 1 cm is 1 erg. For two electrons separated by 1 $\mathring{A}$, the interaction energy ($e^2/r = e^2 / 1\mathring{A}$) is 23.04×10^{-12} erg.

In lecture 6, we have seen that an atomic orbital is a function of the coordinates of one electron. A molecular orbital is also a function of the coordinates of one (a single) electron. The only difference is that since several atoms (more than one) are present in a molecule, the electron will have different distances from the nuclei at each point in space and the value of the molecular orbital (MO) will depend on all these distances, eg : r_{1A} , r_{1B} , r_{1C} ... for electron 1, r_{2A} , r_{2B} , r_{2C} , ... for electron 2 and so on. Here r_{2C}, for example, is the distance of electron 2 from nucleus C.
In H_2^+ , there is only electron and we will omit the subscript 1 and write the MO for H_2^+ as a linear combination of atomic orbitals on A and B.

$$\psi_1 = \varphi_A(r_A) + \varphi_B(r_B) \qquad (7.4)$$

This is a linear combination because the functions occur in the first power. A general linear combination will be

$$\psi = \sum_i c_i \varphi_i \qquad (7.5)$$

where ψ is an MO, φ_i are atomic orbitals and c_i are coefficients. We only wish to comment that the method is extensively used and is iterative in nature (ie, guess an initial solution to equations (7.1) or (7.2) and iteratively improve the solution till a converged final solution is obtained). This is analogous to finding roots (iteratively) of algebraic equations of higher than orders.

7.2 Plots of MOs .

An MO is a function of the coordinates of an electron. To plot a function of x, y, z, we need a four dimensional plot and this is clearly not possible. The other simpler options for plotting the MO are:

a) Plot contour diagrams (a contour connects the points on which the values of the MO are constant) in two or three dimensions and indicate the value of the MO on the contour

b) Plot the values of the MO and the AOs with the inter-nuclear axis taken as the x axis and the values of the function plotted on the y-axis. and

c) Show the pixel plots (charge density plots of the squares of the wave function. In such a plot, dense points indicate the regions where the value of $|\psi|^2$ is large and sparse points correspond to regions wherein the values of $|\psi|^2$ are low.

In fig 7.3 (a) the contour diagram of the atomic orbitals centered on the atoms A and B is shown in the xy plane. There are two atoms A and B and for each orbital on atoms A and B, there are two coordinates in the plane, ie, x_{1A} and y_{1A} for the orbital on atom A and x_{1B} and y_{1B} for the orbital on atom B. We consider the s orbitals, ie e^{-r_{1A}/a_0} and e^{-r_{1B}/a_0} . The distance from the centers A and B are r_{1A} and r_{1B} . The z coordinate is not considered since we are plotting the values of the function in the xy plane.

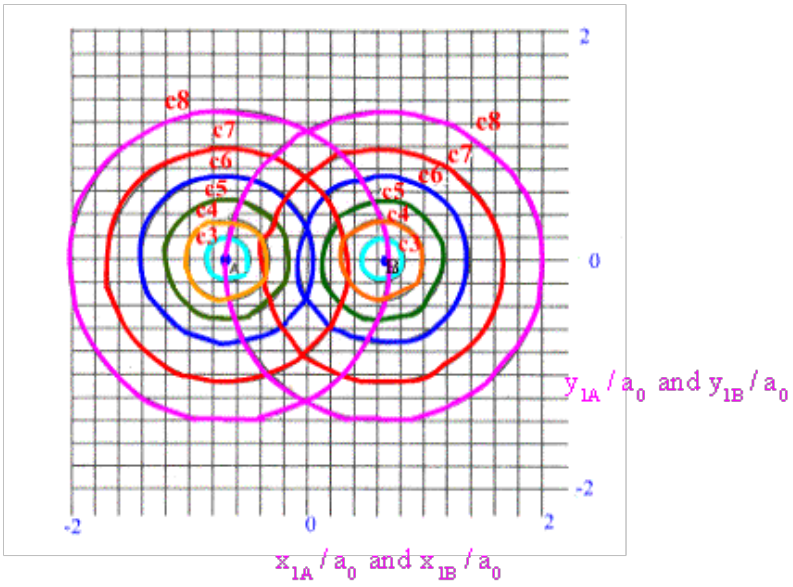


Figure 7.3 (a) Contour diagram of a bonding molecular orbital in H_2^+ at r_{AB} = 0.74 Å

Fig 7.3(b) Contours of the two atomic orbitals on the two hydrogen atoms A and B are shown for comparision with the molecular orbital.

When r (r_{1A} or r_{2A}) is constant, the s orbital is a circle. On different circles, the values of the orbitals are different and they are marked as C_1 , C_2 ….. C_8 . For both the AOs, the normalization constant is $(\pi a_0^3)^{-1/2}$, where a_0 is the Bohr radius, 0.529 $\overset{0}{\text{A}}$. By estimating the value of r from the plot, you can easily estimate the values C_1….C_8 .

In fig 7.3 (b) the contours of the MO are shown. Eight contours, C_1….C_8 are shown. We shall illustrate the calculation of the value of MO on the contour C_6 at two points, P_2 and P_1 . On the x axis we have x_{1A} / a_0 and x_{1B} /a_0 and on the y axis, we have y_{1A} /a_0 and y_{1B} /a_0 . The coordinates of the nuclei are (-0.7a_0, 0) and (0.7a_0, 0) or in terms of $\overset{0}{\text{A}}$, they are (-0.37 $\overset{0}{\text{A}}$, 0) for nucleus A and (0.37 $\overset{0}{\text{A}}$, 0) for nucleus B. The coordinates of point P_2 are (-1.4a_0 , .6a_0).

We need the distance of this point from the nuclei A and B, ie we need r_{1A} and r_{1B} . The values of x_{1A} and y_{1A} are –0.7a_0 and 0.6a_0 and the values of x_{1B} and y_{1B} are –2.1a_0 and 0.6a_0 respectively. For the point P_2 , the values of r_{1A} and r_{1B} are

$$r_{1A} = (0.7^2 + 0.6^2)^{1/2} a_0 = 0.922a_0$$

$$r_{1B} = ((-2.1)^2 + 0.6^2)^{1/2} a_0 = 2.184a_0 \qquad (7.5)$$

And the value of Ψ is

$$\Psi = (\pi a_0^3)^{-1/2}(e^{-r1A/a0} + e^{-r1B/a0})$$

$$= (3.14 \times 0.529^3)^{-1/2} \overset{0}{\text{A}}^{-3/2} (e^{-0.9} + e^{-2.3})$$

$$= 0.75 \overset{0}{\text{A}}^{-3/2} \qquad (7.6)$$

So,Let us verify that the value of Ψ on the same contour at the point P1 is also 0.75 $\overset{0}{\text{A}}^{-3/2}$

In the contours it is seen that the MO looks like the corresponding AOs near the nuclei and far away from the nuclei, it looks the atomic orbitals of the “whole molecule”.

Another way to plot the MO is to sketch the values of ϕ_A^2, ϕ_B^2 and $\psi_1^2 = (\phi_A + \phi_B)^2$ as functions of r_{1A} and r_{1B}. This sketch is shown in fig 7.4

r_{1A} and r_{1B} in units of a_0

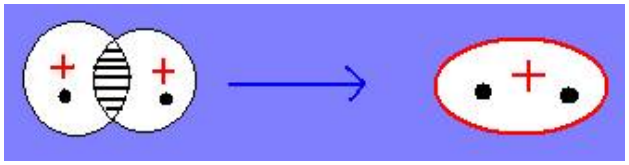
Fig 7.4 (a) A comparison of ψ_1^2 (red thick line) with ϕ_A^2 and ϕ_B^2. (green lines). The values of ψ_2^2 (stars) are also shown.

It is clearly seen that in the region between the nuclei the value of $|\psi_1|^2$ is greater than the sum of ϕ_A^2 and ϕ_B^2. This feature is the central theme of chemical bonding, ie, the charge density between the nuclei is different (generally larger) than the sum of the individual charge densities of the respective atomic orbitals. We will elaborate the meaning of ψ_2 a little latter in this lecture.

In fig 7.5, the plot of the MO ψ_1 as a function of the x and y coordinates of the plane is shown. The highest value of the function is 1.83 $\overset{0}{A}^{-3/2}$ at two points near each of the two nuclei. Can you rationalize why the maximum value occurs at two places?

Fig 7.5 A 3 -dimensional plot of the MO. The value of ψ_1 at the peaks is 1.83 $\overset{0}{A}^{-3/2}$

If we view the molecule along the internuclear axis (and not perpendicular the internuclear axis that we have been doing so far), then the contours are all circular. The MO is often shown as a perspective plot (fig 7.6 (a)) or as an overlap diagram (fig 7.6 (b)) as shown below.



(7.6a) (7.6b)

Figure 7.6 (a) Perspective plot of the MO ψ_1. Fig 7.6 (b) The MO - overlap diagram of ψ_1

We have been considering all along, the behaviour of the MO, [eq (7.4)] which is called a bonding orbital. It is refered to as bonding because it increases the charge density between the nuclei (relative to separately incremented charge densities of φ_A and φ_B). Another MO, which does the opposite of this MO is called the antibonding MO as it decreases the electron density between the nuclei (in comparison to the non interacting or independently contributing AOs) and it is defined as

$$\psi_2 = \varphi_A(r_A) + \varphi_B(r_B) \qquad (7.4)$$

Just as in the case of the bonding MO ψ_1, we can sketch the antibonding MO, ψ_2 in different ways. We shall show these sketches in fig 7.7. The contours of ψ_2 in the xy plane are shown in fig 7.7(a). It is seen that there are two sets of contours separated by a nodal plane. The value of the wavefunction ψ_2 in the plane bisecting the two nucleii (represented by the y_Z plane containing x = 0) is identically zero. The contours on the right C_1 , C_2 , C_3 and C_4) have positive values and the contours on the left (C_1 ', C_2 ', C_3 ' and C'_4) have negative values. This is an antibonding orbital because the charge density between the nuclei is smaller than the charge density resulting from the sum of the two non-interacting charge densities, φ_1^2 and φ_2^2.

A three dimensional plot showing ψ_2 as a function of points in the xy plane is shown in fig 7.7(b). It is seen that near one of the nuclei (the one on the right) ψ_2 has a maximum value (because of the maximum in φ_A which has a positive sign). Near the nucleus B, ψ_2 has a minimum value because φ_B appears with a negative sign in ψ_2 and φ_B has a large value near nucleus B. The density profile of ψ_2 is shown in fig 7.7(c)

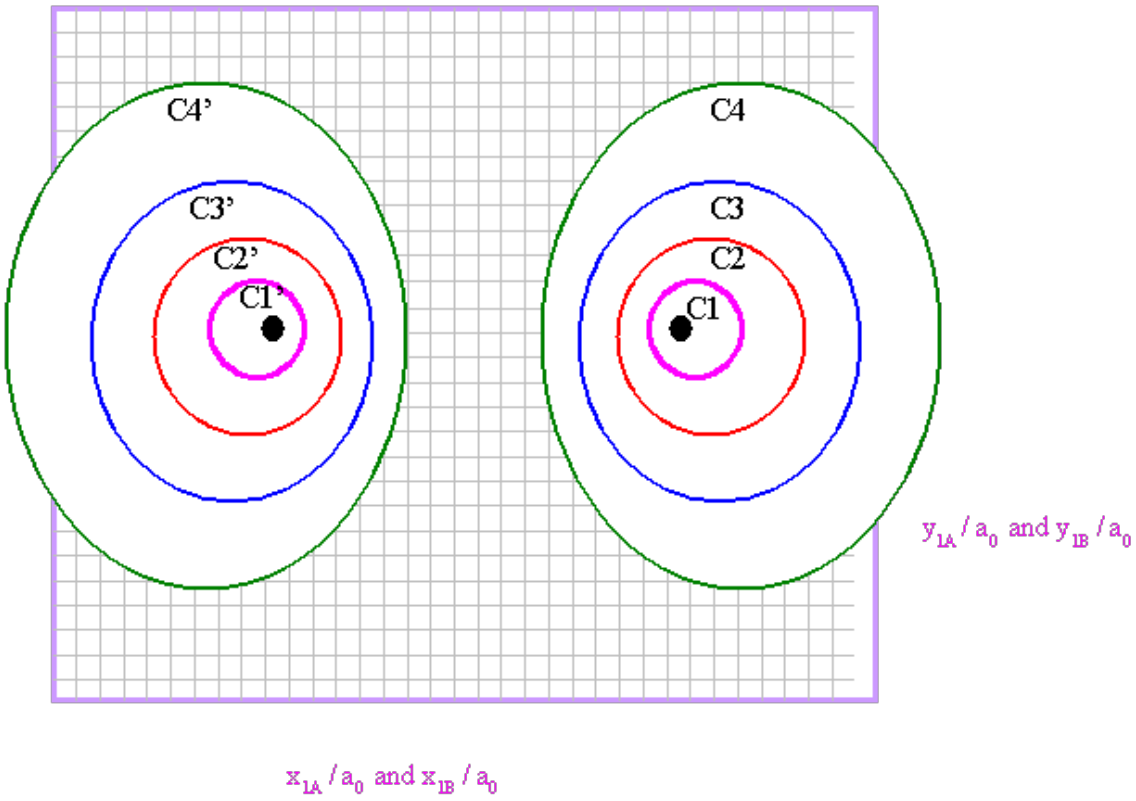


Fig 7.7(a)The contours of the MO ψ_2 in a plane containing the internuclear axis A and B represent the nuclei. The values of ψ_2 on the contours C1, and C3 are 0.85 and 0.37 $\overset{0}{A}^{-3/2}$. The values on contours C1' and C3' are negative of the values on C1 and C3.

Fig 7.7 (b) A three dimensional plot of the MO ψ_2 . The value of ψ_2 on the upper peak is 1.1 $\overset{0}{A}^{-3/2}$ and on the lower peak, it is -1.1 $\overset{0}{A}^{-3/2}$.

Fig 7.7 (c) The dot profiles of the MO ψ_2

The calculation of the contours for ψ_2 is similar to that of ψ_1 except that there are different signs of contours in different regions. The plots of ψ_1 and ψ_2 involved s orbitals on atoms A and B. We can now use the linear combinations using p orbitals. The four combinations that can be made are

$$\psi_3 = \phi_A(2p_z) + \phi_B(2p_z) \quad (7.5)$$

$$\psi_4 = \phi_A(2p_z) - \phi_B(2p_z) \quad (7.6)$$

$$\psi_5 = \phi_A(2p_x) + \phi_A(2p_x) \quad (7.7)$$

$$\psi_6 = \phi_A(2p_x) - \phi_A(2p_x) \quad (7.8)$$

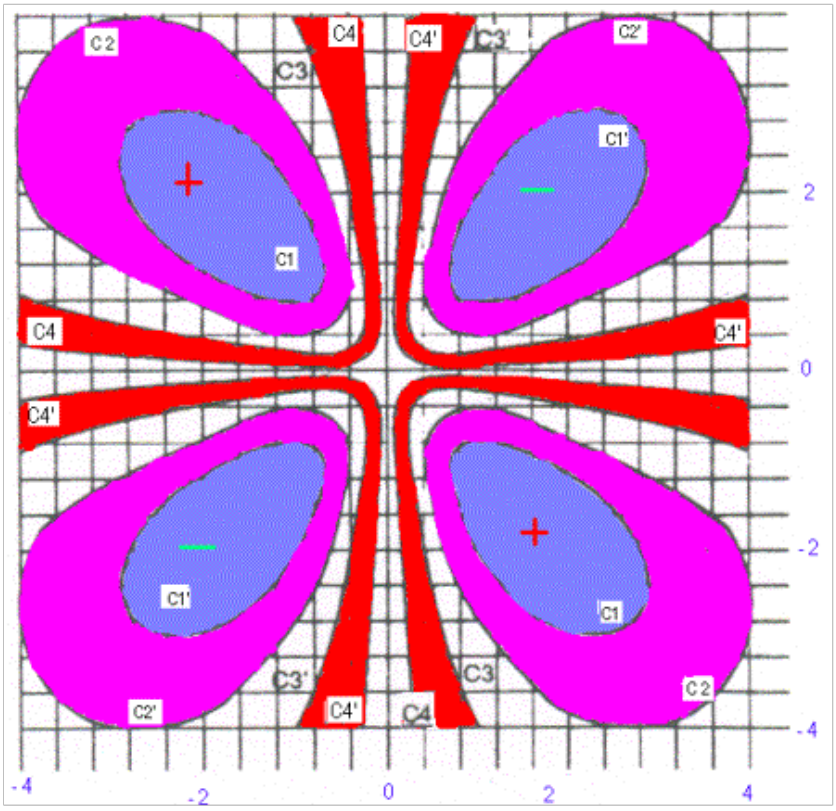
In the orbitals ψ_1 to ψ_4 (fig 7.3 (b) and fig 7.3 (a) the MOs have cylindrical symmetry. What this means is that if the orbital is rotated with respect to the internuclear axis, it does not change in shape (or value) at any point. This is analogous to a sphere which does not change in value (i.e., the value of the function defining the sphere) at any point when it is rotated with respect to any axis passing through the center of the sphere. The orbitals ψ_1 to ψ_4 are called σ (cylindrical symmetry) orbitals. The bonding orbitals are σ and the antibonding ones σ^*. In the orbital ψ_5 and ψ_6, there is a sideways overlap of orbitals and there is planar symmetry (with respect to the xz plane). These are referred to as $\pi(\psi_5)$ and $\pi^*(\psi_6)$ orbitals. Instead of p_x orbitals we could have used p_y orbitals to get the sideways overlap.

The plane of symmetry in this case would have been the yz plane. The molecular axis is usually taken to be the z axis.

The sketches of ψ_3 to ψ_6 are shown in fig 7.8 (a) to (c).

Fig 7.8 (a) The σ^* 2p MO : $(p_z)_A^{(1)} + (p_z)_B^{(1)}$ for $r_{AB} = 7\ a_0$ (> $4\ a_0$) for the hydrogen p-orbitals. The value of the MO on the contours C1', C2' , C3' , C5 and C6 are -0.08, -0.03, 0.17, 0.07 and 0.02 $\text{Å}^{-3/2}$ respectively.

Fig 7.8 (b) π 2p MO : $(p_x)_A^{(1)} + (p_x)_B^{(1)}$. The values of the MO on the contours C1, C2, C3 and C4 are 0.29, 0.20, 0.12 and .04 $\text{Å}^{-3/2}$ respectively. The values on the contours Cn' are negative of the values on the contours Cn.



y_{1A}/a_0 and y_{1B}/a_0

x_{1A} / a_0 and x_{1B} / a_0

Fig 7.8 (c) Sigma and pi molecular orbitals. π^* 2p MO : $(p_x)_A^{(1)}$ - $(p_x)_B^{(1)}$. The values of the MO on the contours C1, C2, C3 and C4 are 0.05, 0.03, 0.02 and .0.01 $\overset{0}{A}^{-3/2}$ respectively. The values on the contours Cn' are negative of the values of Cn. (Sigma and pi molecular orbitals).

7.3 Electronic configurations

For atoms, we obtained electronic configurations by writing them as $1s^2\ 2s^1$, $1s^2\ 2s^2\ 2p^5$ and so on. The principles used in filing the orbitals were the aufbau principle and the Pauli exclusion princilple. For MOs too, similar procedure is used with the labels for MOs being 1σ, 2σ or σ_{1s}, σ_{2p}, σ^*_{3s} and so on where the subscript indicates the atomic orbitals used in the MO and the integer on the left is the label or the index of the MO. The electronic configurations of the first and second row diatomics are given in Table 7.1. Also included in the Table are the number of bonding and antibonding electrons in each molecule, the bond order, the binding energy and the bond length.

Diatomic	Electronic Configuration	No of bonding electrons	No of antibonding electrons	Bond Order	Binding Energy (eV)	Bond Length $\overset{0}{A}$
H_2^+	$1\sigma_g^1$ or $1\sigma'$	1	0	½	2.78V	1.06
H_2	$1\sigma^2$ or $1\sigma_g^2$	2	0	1	4.74	0.74
He_2^+	$1\sigma^2(1\sigma^*)^1$ or $1\sigma_g^2(1\sigma_u^*)^1$	2	1	1/2	3.1	1.08

He_2	$1\sigma^2(1\sigma^*)^2$ or $1\sigma^2 2\sigma^2$	2	2	0	-	-
Li_2	$[He]_2\ 2\sigma^2$	2	0	1	1.1	2.67
Be_2	$[He]_2\ 2\sigma^2\ (2\sigma^*)^2$	2	2	0	-	-
B_2	$[Be]_2\ 1\pi^1 2\pi^1$	4	2	1	3.0	1.59
C_2	$[Be]_2\ 1\pi^2 2\pi^2$	8	4	2	6.2	1.24
N_2^+	$[Be]_2\ 1\pi^2 2\pi^2\ 3\sigma^1$	9	4	2.5	8.73	1.12
N_2	$[Be]_2\ 1\pi^2 2\pi^2\ 3\sigma^2$	10	4	3.0	9.76	1.09
O_2^+	$[Be]_2\ 3\sigma^2\ 1\pi^2 2\pi^2\ (1\pi^*)^1$	10	-	2.5	6.48	1.12
O_2	$[Be]_2\ 3\sigma^2\ 1\pi^2 2\pi^2\ (1\pi^*)^1\ (2\pi^*)^1$	10	6	2	5.08	1.21
F_2	$[Be]_2\ 3\sigma^2 1\ \pi^2 2\pi^2\ (1\pi^*)^2\ (2\pi^*)^2$	10	8	1	1.6	1.44
Ne_2	$[Be]_2\ 3\sigma^2\ 1\pi^2 2\pi^2\ (1\pi^*)^2\ (2\pi^*)^2\ (3\sigma^*)^2$	10	10	0	-	-

Table 7.1 The electronic configurations, bond lengths and bond energies of the first and the second row diatomics.

The subscripts g and u are shown only in the first 3 rows. These indicate inversion symmetry of the MO with respect to the center of the molecule. Symmetric with respect to this inversion is represented by subscript g and antisymmetric (wavefunction changes sign when $\vec{r}$ is replaced by $-\vec{r}$) is represented by u. In heteronuclear diatomics, there is no center of symmetry and hence these subcripts will not appear. Among the π and π^* orbitals in the lower rows, which ones are g and which ones u?

The bond length of a diatomic is the distance between the nuclei when the configuration is most stable. This stability comes about when the binding energy is most favorable. The binding energy (B.E) is defined as

B.E = energy of diatomic in the most stable configuration – 2 x energy of an isolated atom (7.9)

It is seen from the table that the magnitudes of binding energies for single bonds are in the ranges of 1 to 5eV, double bonds around 5 to 7 eV, triple bonds over 7eV. The bond order is a qualitative measures of the number of bonds between the atoms and is defined as (No of bonding electrons – No of antibonding electrons) / 2.

7.4 Energy level diagrams.

The energy of the MOs of diatomics are shown in the energy level diagrams wherein the energies of AOs are shown at the two ends

and the energies of the MOs are shown in the middle. Fig 7.9 shows the energy level diagram for the first and second row diatomics.

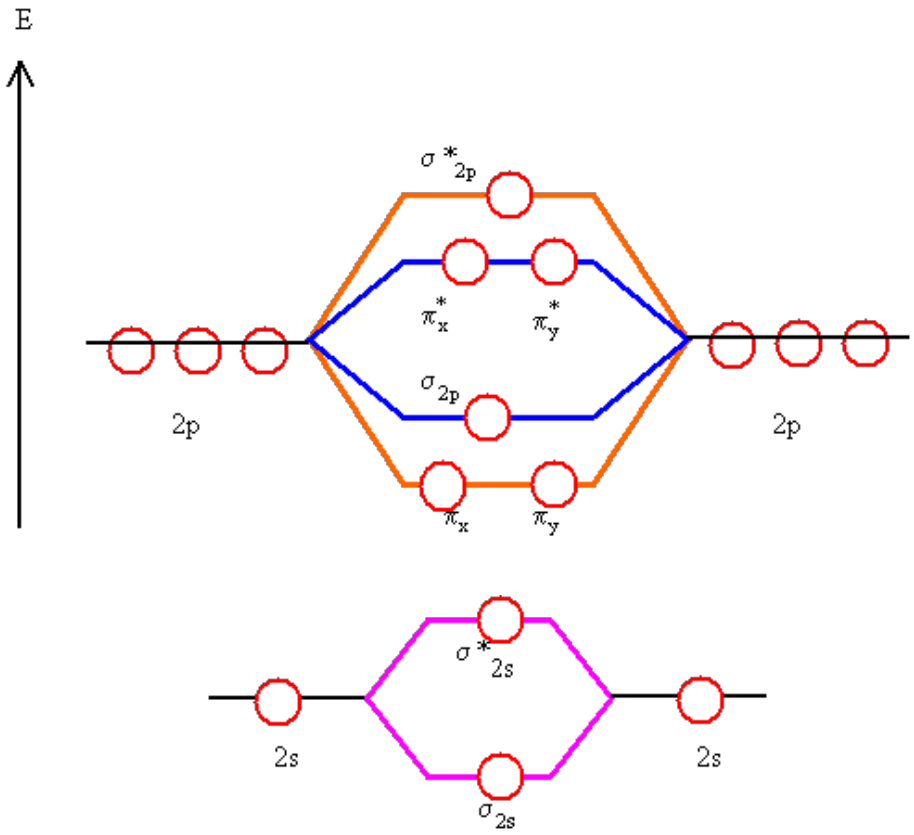


Fig 7.9 (a) The energy level diagrams of the second row diatomics Li_2...N_2

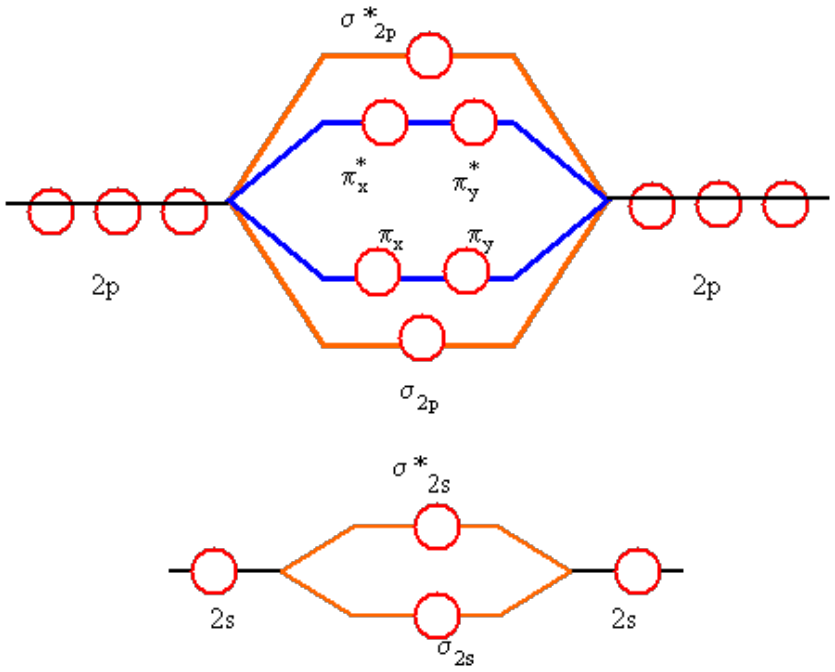


Fig 7. 9 (b) The energy level diagrams of the second row diatomics O_2 and F_2.

As expected the energy of the bonding MO lies below the energy of the antibonding MO. Lower or more negative value of energy implies greater binding or greater stability. It is seen from figure 7.9 that the "aufbau principle" for these diatomics may be stated as $\sigma_{1S} < \sigma^*_{1S} < \sigma_{2S} < \sigma^*_{2S} < \pi_{2p} < \sigma_{2p} < \pi^*_{2p} < \sigma^*_{2p}$. The ordering in the energies of π_{2p} and σ_{2p} undergoes a change in O_2 and F_2 (compared to Li_2 , Be_2 , ...up to N_2) and here we take it as a fact. The reason for the change over is that in O_2 and F_2 the difference of the energies between σ^*_{2s} and σ_{2p} is very large so as not to affect them. If these energy levels are very near, these

orbitals(which are of the same symmetry) would repel each other, pushing σ_{2p} to go higher than π_{2p} as in the case of Li_2 , Be_2 , …..up to N_2 .

It is to be noted that these diagrams are for the minimum energy states or the bound states of the diatomics. If the distance between the atoms change, then the spacings between the MO energy levels also change. Such a diagram, indicating the energy of the MOs as a function of internuclear distance is given in the following figure

Fig 7.10 (a)The energies of bonding and antibonding MOs as a function of internuclear separation.

Fig 7.10 (b) Potential energies of H_2^+, H_2, He_2^+, He_2 as a function of internuclear separation.

There are two main observations in this figure 7.10(b). One is that the energies of the MOs are distance dependent and the other is that as the distance (r) between the nuclei is increased, the difference in the energies of the bonding and antibonding MOs diminish and vanishes as $r \rightarrow \infty$. At very large r, there is no binding and the energies are simply the energy levels of two separated non-interacting atoms. In fig 7.10(a) you will notice that the energy of the antibonding MO, σ^* is greater than zero (the energy of the AO is taken as the reference value of zero) throughout. The reference value of zero is actually the energy of the atomic orbital (AO). The energy of the bonding orbital is lower than the energy of the AO for all but the very short distances. At very short distances, the energies of the MOs rise very steeply; far more steeply than 1/r, which is the formula for Coulomb repulsion between the electrons. The origin of this steep repulsion is not Coulombic, but the Pauli exclusion principle. When electrons are forced to be very close to one another, there arises a possibility that all the four quantum numbers of two electrons may be the same. Since this is forbidden by the exclusion principle, and furthermore since the electrons are indistinguishable as

well (ie labeling the electrons as 1234 is no different from labeling them as 1432 since one can not associate any labels with these "tiny" indistinguishable particles), the energy rises sharply at short distances.

In Fig 7.10 (b), the potential energies of H_2, H_{2+}, He_{2^+} and He_2 are shown. He_2 does not form a stable molecule at room temperature, because its bond order is zero. Only at very low temperatures, such clusters like He_2, Ar_2, or Ar_n, n > 2) are found. These are called van der Waals clusters because their binding energy is very small, less than 1 kcal/mol. The species He_{2^+}, H_{2^+} do have bound states with respectable amounts of stabilities. The bond lengths are all near 1 Å. Similar to the sketch in Fig 7.10(b), the potential energies of other homonuclear diatomics can be drawn.

While concluding this lecture, we need to make an important point. Molecular orbitals are approximate constructs. They describe each electron as moving "independently" of other electrons in an effective field. In reality the motion of all electrons is correlated, ie the concept of an effective field is unreal as the electrons are moving all the time and the fields can not be averaged and the instantaneous influence of electrons on one another contributes (about 15%) to the binding energies and bond lengths. A common way to take into account this feature in the MO framework is through the inclusion of "higher" orbitals for calculating binding energies. This means that orbitals 2s, 2p, 3s, 3p, 3d and so on also make significant contributions to the binding energy in H_2 . These aspects are of prime concern in the computations of binding energies of molecules and solids.

7.5 Problems

7.1) Write the Hamiltonian for a Li atom and a Li_2 molecule.

7.2) Estimate the value of the MO on the contour C_2 of fig 7.3

7.3) What is the difference between binding energy and bond dissociation energy?

7.4) Draw a few contours of the bonding MO of H_2^+ in planes perpendicular to the internuclear axis. Consider three planes

a) A plane bisecting the nuclei,

b) A plane containing one of the two nuclei and

c) Any plane other than (a) and (b) above. Compute the values of contours by calculating the distances of any point on the contour from each of the nuclei.

7.5) What are the electronic configurations of Li_2^+ , Li_2^- , N_2^{3+} and O_2^{2-} ?

7.6) Why does He_2^+ have a bound state while He_2 does not?

Why is the binding energy of H_2 less than that of H_2^+ ? Why is the bond length of H_2 less than that of H_2^+ ? Please note the convention: lower value of potential energy implies a stronger bond.

Recap

In this Lecture you have learnt the following

Summary

In this lecture, we have defined bonding and antibonding molecular orbitals (MOs) and plotted their contour diagrams, overlap diagrams, perspective plots as well as their values as a function of distance from the internuclear axis. A MO is a function of the coordinates of an electron and is a polycentric function. We also learnt how to write the Hamiltonian operator for a molecular system. Electronic configurations of homonuclear diatomics were described and the symmetries of the MOs were captured in the symbols σ and π.

The potential energy of these diatomics was plotted as a function of distance between the nuclei, and the energies of the MOs (relative to the energy of the AOs taken as zero) were also plotted as a function of the distance between the nuclei. The sign of potential energy should be noted with care. The qualitative concept of bond order was invoked to assess the relative strengths of single and multiple bonds.