CHM205: Chemical Binding

Credits: 3

1. Fundamental background: Postulates and theorems of quantum mechanics, angular momentum, rigid rotor.
2. The Schrödinger equation and its exact solutions: The particle-in-a-box, Hydrogen atom, the variation theorem–Ritz variation principle.
3. Atomic structure: many electron wave functions, Pauli exclusion principle, Helium atom, atomic term symbols.
4. Symmetry point groups: Determination of point group of a molecule, representations, the great orthogonality theorem, character table, construction of character tables for c_{2v} and c_{3v} groups, symmetry adapted atomic basis sets, construction of molecular orbitals.
5. **Molecular structure:** Born-Oppenheimer approximation, molecular orbital treatment for H_2^+, MO treatment of homo- and hetero nuclear diatomic molecules, Hückel MO treatment of simple and conjugated polyenes.

References:

1. Quantum Chemistry, I.N. Levine, Pearson Educ., Inc.
2. Quantum Chemistry, D.A. McQuarrie Viva Books.
3. Introductory Quantum Chemistry, A.K. Chandra, Tata Mcgraw Hill.

Born-Oppenheimer Approximation: (Already done in the class)

$$\psi(q_i q_\alpha) = \psi_{el}(q_i; q_\alpha)\psi_N(q_\alpha)$$

Molecular Orbital Treatment for H_2^+: (Already done in the class)

$$\Psi = c_a 1s_a + c_b 1s_b$$

where the c’s are variational parameter and

$$1s_a = k^{3/2}\pi^{-1}e^{-kr_a} \qquad 1s_b = k^{3/2}\pi^{-1}e^{-kr_b}$$

Finally we get,

$$\psi_1 = \frac{1s_a + 1s_b}{\sqrt{2(1+S_{ab})}} \qquad \psi_2 = \frac{1s_a - 1s_b}{\sqrt{2(1-S_{ab})}}$$

$$E_{1,2} = -\frac{1}{2}k^2 + \frac{k^2 - k - R^{-1} + R^{-1}(1+kR)e^{-2kR} \pm k(k-2)(1+kR)e^{-kR}}{1 \pm e^{-kR}(1 + kR + k^2R^2/3)}$$

Molecular Orbitals of the Homonuclear Diatomic Molecules:

From the LCAO-MO treatment of H_2^+ we have seen that, when two similar atoms bring together, two molecular orbitals are formed

$$\psi_{\pm} = 1s_A + 1s_B$$

In ψ_+ electron density concentrates in the region between the two nuclei, whereas ψ_- excludes electron density from the region between the two nuclei and have a nodal plane in between the two nuclei. Consequently, ψ_+ is a bonding orbital and ψ_- is an antibonding orbital. Because the electron density is symmetric about the internuclear axis, both ψ_+ and ψ_- are called σ orbitals, similar to spherically symmetric atomic orbital is called *s* orbital. As these σ orbitals are made out of 1s orbitals, they are denoted by σ1s.

There are two common notations to distinguish a bonding orbital from an antibonding orbital. One of these notations is to denote the bonding orbital by $\sigma 1s$ and to denote the antibonding orbitals by $\sigma^* 1s$. The other way is to indicate the symmetry of the molecular orbital under an inversion of the wave function through the point midway between the two nuclei. If the wave function does not change its sign under this inversion, then we label the wave function *gerade* (after the German word for even) and we subscript the molecular orbital with a g. As in ψ_+ in H_2^+ does not change its sign under inversion, so we denote ψ_+ by $\sigma_g 1s$. whereas, ψ_- changes sign under inversion and we denote ψ_- by $\sigma_u 1s$, where u stands for *ungerade* (the German word for odd).

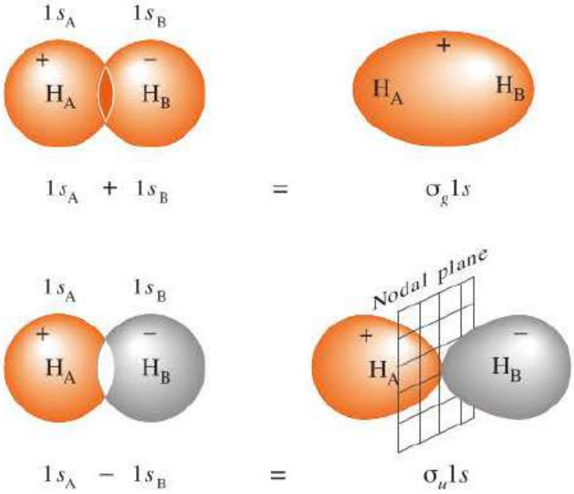


Figure 1: *The linear combinations of two 1s atomic orbitals gives the bonding (σ1s or σ_g1s) and antibonding (σ^*1_s or σ_u1s) molecular orbitals.*

Now we will try to construct molecular orbitals out of other kind atomic orbitals in a similar way. In a first approximation of LCAO-MO theory only orbitals of close energies combine, so we consider combinations such as $2s_A \pm 2s_B$. The two molecular orbitals look like the molecular orbitals in **Figure 1** but are larger in extent and we shall designate the two molecular orbitals $2s_A \pm 2s_B$ by $\sigma 2s$ and $\sigma^* 2s$ or by $\sigma_g 2s$ and $\sigma_u 2s$. Because a $2s$ atomic orbital is associated with a higher energy than a $1s$ orbital, we expect that the energy of the $\sigma 2s$ will be higher than that of the $\sigma 1s$ orbitals. In addition, because bonding orbitals have lower energy than antibonding orbitals, we have the energy order $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s$.

Now let consider linear combinations of p orbitals. Although p orbitals have the same energy as s orbitals in the case of H-atom, that is not so for the other atoms and so we expect that molecular orbitals built up from p orbitals will have a higher energy than $\sigma 2s$ orbitals. If we consider z axis to be the internuclear axis, then we can see from **Figure 2 and 3** that p_z orbitals combine to give a different molecular orbital than p_x or p_y give.

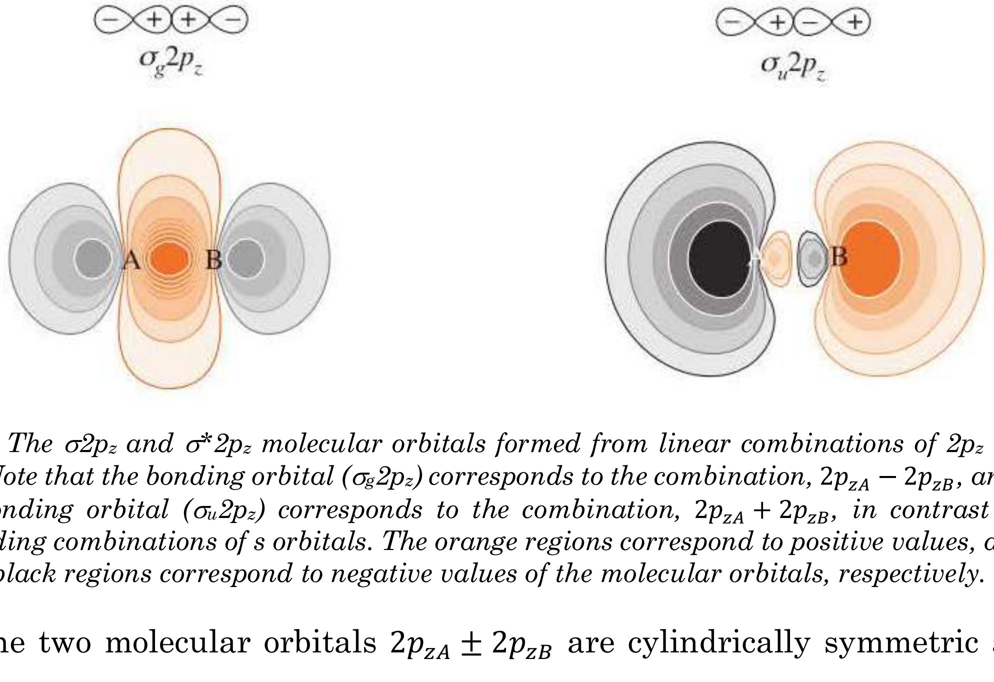
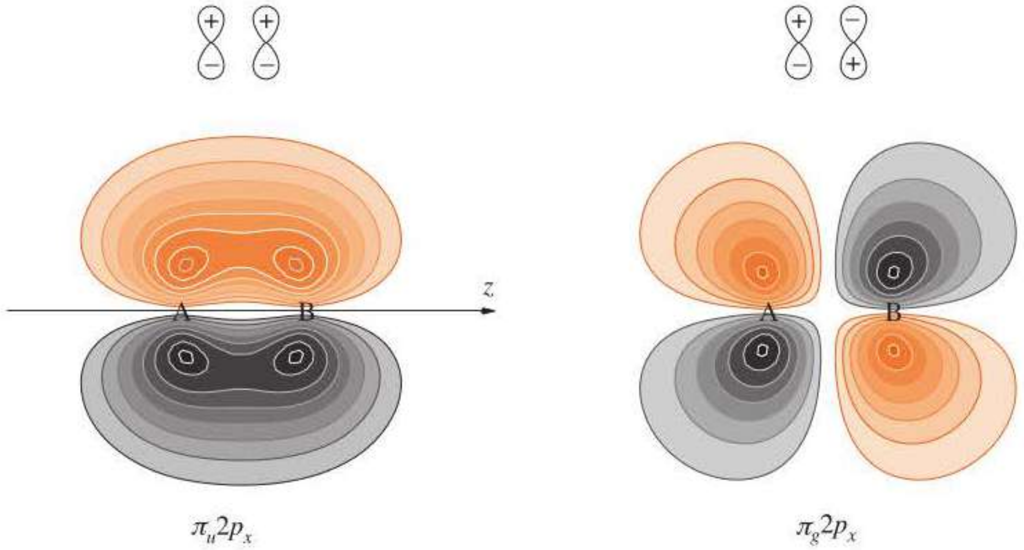


Figure 2: *The $\sigma 2p_z$ and $\sigma^* 2p_z$ molecular orbitals formed from linear combinations of $2p_z$ atomic orbitals. Note that the bonding orbital ($\sigma_g 2p_z$) corresponds to the combination, $2p_{zA} - 2p_{zB}$, and that the antibonding orbital ($\sigma_u 2p_z$) corresponds to the combination, $2p_{zA} + 2p_{zB}$, in contrast to the corresponding combinations of s orbitals. The orange regions correspond to positive values, and the gray and black regions correspond to negative values of the molecular orbitals, respectively.*

The two molecular orbitals $2p_{zA} \pm 2p_{zB}$ are cylindrically symmetric about the internuclear axis and therefore are a σ orbitals. Once again, both a bonding orbital and an antibonding molecular orbital are generated, and the two orbitals are designated by $\sigma 2p_z$ and $\sigma^* 2p_z$ or by $\sigma_g 2p_z$ and $\sigma_u 2p_z$.



$\pi_u 2p_x$ $\pi_g 2p_x$

Figure 3: *The* $\pi 2p_x$ *and* $\pi^* 2p_x$ *molecular orbitals formed from linear combinations of* $2p_x$ *atomic orbitals. Another notation for these molecular orbitals is* $\pi_u 2p_x$ *and* $\pi_g 2p_x$ *for the bonding and antibonding orbitals respectively. The orange regions correspond to positive values, and the gray and black regions correspond to negative values of the molecular orbitals, respectively.*

The $2p_x$ and $2p_y$ orbitals combine to give molecular orbitals that are not cylindrically symmetric about the internuclear axis. **Figure 3** shows that the *y-z* plane is a nodal plane in both the bonding and antibonding combinations of the $2p_x$ orbitals. As we know, molecular orbitals with one nodal plane that contains the internuclear axis are called π orbitals. The bonding and antibonding molecular orbitals that arise from a combination of the $2p_x$ orbitals are denoted $\pi_u 2p_x$ and $\pi_g 2p_x$ respectively. Note that the antibonding orbital $\pi_g 2p_x$ also has a second nodal plane perpendicular to the internuclear axis that is not present in the $\pi_u 2p_x$ bonding orbital. The $2p_y$ orbitals combine in a similar manner, and the resulting molecular orbitals look like those in **Figure 3** but are directed along the y axis instead of the x axis. The x- z plane is the nodal plane for the $\pi_u 2p_y$ and $\pi_g 2p_y$ orbitals. Because the $2p_x$ and $2p_y$ orbitals have identical energy and the resulting molecular orbitals differ only in their spatial orientation, the orbitals $\pi_u 2p_x$ and $\pi_u 2p_y$ are degenerate, as are $\pi_g 2p_x$ and $\pi_g 2p_y$. Note that unlike the bonding σ orbitals, the bonding π orbitals have *ungerade* symmetry and the antibonding π orbitals have *gerade* symmetry.

So, we have developed a set of molecular orbitals by combining atomic orbitals. However, we cannot give a definitive order of these molecular orbitals with respect to energy. Because the energy difference varies with the atomic number of the nuclei in the homonuclear diatomic molecule and with the internuclear separation. As the atomic number increases from three for lithium to nine for fluorine, the energies of the $\sigma_g 2p_z$ and $\pi_u 2p_x$, $\pi_u 2p_y$ orbitals approach each other and actually interchange order in going from N_2 to O_2, as shown in **Figure 4**. The somewhat complicated ordering shown in **Figure 4**, which is consistent with calculations and experimental spectroscopic observations, is reminiscent of the ordering of the energies of atomic orbitals as the atomic number increases.

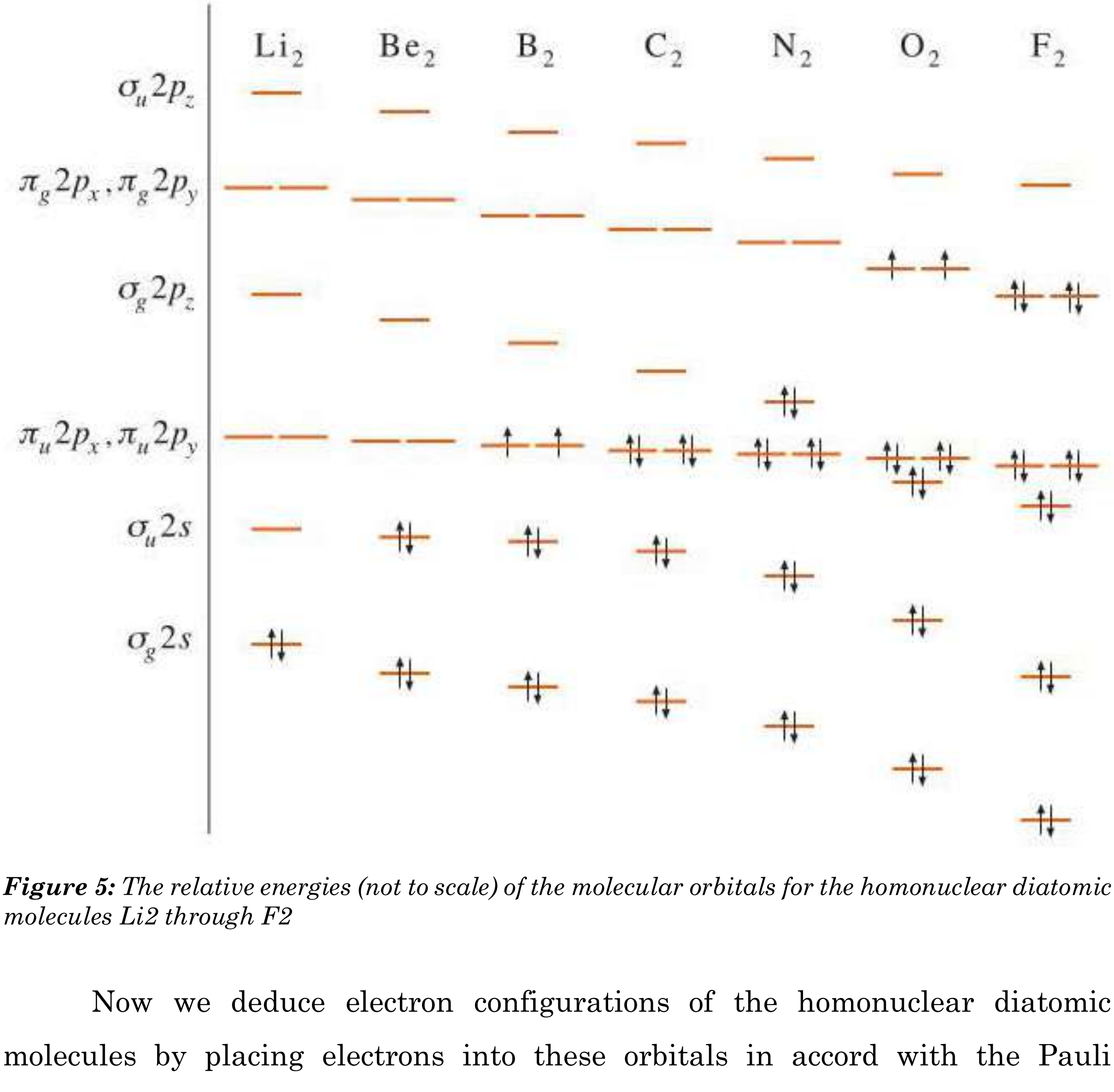


Figure 5: *The relative energies (not to scale) of the molecular orbitals for the homonuclear diatomic molecules Li2 through F2*

Now we deduce electron configurations of the homonuclear diatomic molecules by placing electrons into these orbitals in accord with the Pauli exclusion principle and Hund's rules, just as we did or many-electron atoms. Fortunately, many of the predictions of the two schemes in **Figure 4** are the same and are of real chemist interest.

Molecular Orbital Theory Predicts that Diatomic Helium does not Exist

Let us consider H_2 first. According to the Pauli exclusion principle, two electrons of opposite spin are placed in the $\sigma_g 1s$ orbital and the electron configuration of H_2 is $(\sigma_g 1s)^2$. The two electrons in the bonding orbital constitute a bonding pair of electrons and account for the single bond of H_2. Now consider He_2. This molecule has four electrons, and its ground-state electron configuration is $(\sigma_g 1s)^2(\sigma_u 1s)^2$. This assignment for He_2 gives one pair of bonding electrons and one pair of antibonding electrons. Electrons in bonding orbitals tend to draw nuclei together, whereas those in antibonding orbitals tend to push them apart. The result of these opposing forces is that an electron in an antibonding orbital approximately cancels the effect of an electron in a bonding orbital. Thus, in the case of He_2, there is no net bonding. Thus, simple molecular orbital theory predicts that diatomic helium does not exist.

The above results are formalized by defining a quantity called bond order by

$$Bond\ order = \frac{\begin{pmatrix} number\ of\ electrons \\ in\ bonding\ orbitals \end{pmatrix} - \begin{pmatrix} number\ of\ electrons \\ in\ antibonding\ orbitals \end{pmatrix}}{2}$$

Single bonds have a bond order of one; double bonds have a bond order of two; and so on. The bond order for H_2 is one and the bond order in He_2 is zero. The bond order does not have to be a whole number; it can be a half-integer as shown in the following example.

EXAMPLE 1: Determine the bond order of He_2^+.

SOLUTION: The ground-state electron configuration of He_2^+ is $(\sigma_g 1s)^2(\sigma_u 1s)^1$, and so the bond order is

$$Bond\ order = \frac{2-1}{2} = \frac{1}{2}$$

Table 1: Molecular properties of H_2^+, H_2, He_2^+, and He_2.

Species	*Number of electrons*	*Ground state electron configuration*	*Bond Order*	*Bond length/pm*	*Bond energy/kJ·mol⁻¹*
H_2^+	*1*	$(\sigma_g 1s)^1$	*1/2*	*106*	*255*
H_2	*2*	$(\sigma_g 1s)^2$	*1*	*74*	*431*

He_2^+	*3*	$(\sigma_g 1s)^2(\sigma_u 1s)^1$	*1/2*	*108*	*251*
He_2	*4*	$(\sigma_g 1s)^2(\sigma_u 1s)^2$	*0*	*Not observed*	

Molecular Orbital Theory Correctly Predicts that Oxygen Molecules are Paramagnetic

The prediction of the correct electron configuration of an oxygen molecule is one of the most impressive successes of qualitative molecular orbital theory. Oxygen molecules are paramagnetic; experimental measurements indicate that the net spin of the oxygen molecule corresponds to two unpaired electrons of the same spin.

Let's see what molecular orbital theory has to say about this. The predicted ground-state electron configuration of O_2 is $KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g 2p_x)^1(\pi_g 2p_y)^1$. Because then $\pi_g 2p_x$ and $\pi_g 2p_y$ orbitals are degenerate, according to Hund's rule, we place one electron in each orbital such that the spins of the electrons are parallel. Thus, the molecular orbital configuration correctly accounts for the paramagnetic behaviour of the O_2 molecule.

We can use molecular orbital theory to predict relative bond lengths and bond energies, as shown in **Example 2**.

EXAMPLE 2: Discuss the relative bond lengths and bond energies of O_2^+, O_2, O_2^- and O_2^{2-}.

SOLUTION: O_2 has 12 valence electrons. The ground-state electron configurations and bond orders for these species are as follows:

	Ground-state configuration	Bond order
O_2^+	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g 2p_x)^1$	$2\frac{1}{2}$
O_2	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g 2p_x)^1(\pi_g 2p_y)^1$	2
O_2^-	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g 2p_x)^2(\pi_g 2p_y)^1$	$1\frac{1}{2}$
O_2^{2-}	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g 2p_x)^2(\pi_g 2p_y)^2$	1

We predict that the bond lengths decrease and the bond energies increase with increasing bond order. This prediction is in nice agreement with the experimental values, which are as follows:

	Bond length/pm	*Bond energy/kJ·mol^{-1}*
O_2^+	*112*	*643*
O_2	*121*	*494*
O_2^-	*135*	*395*
O_2^{2-}	*149*	---

Molecular Orbital Theory Also Applies to Heteronuclear Diatomic Molecules

The molecular orbital theory we have developed can be extended to heteronuclear diatomic molecules. It is important to realize that the energies of the atomic orbitals on the two atoms from which the molecular orbitals are constructed will now be different. This difference must be considered in light of the approximation made earlier that only orbitals of equal energy combine to give molecular orbitals. For small changes in atomic number, the energy difference for the same atomic orbital on the two bonded atoms is small (e.g., CO and NO). For many heteronuclear diatomic molecules (e.g., HF and HCl), however, the energies of the respective atomic orbitals can be significantly different, and we will need to rethink which atomic orbitals are involved in constructing the molecular orbitals for such molecules

Let's consider a cyanide ion (CN^-) first. The atomic numbers of carbon (6) and nitrogen (7) differ by only one unit, so the energy ordering shown in **Figure 4** may still be valid. The total number of valence electrons is 10 (carbon has four electrons and nitrogen has five electrons in the $n = 2$ shell), and the overall charge on the ion is -1. Accordingly, the ground-state electron configuration of CN is predicted to be $KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\sigma_g 2p_z)^2$, with a bond order of three.

Photoelectron Spectra Demonstrate the Existence of Molecular Orbitals

The idea of atomic orbitals and molecular orbitals is rather abstract and sometimes appears far removed from reality. It so happens, however, that the electron configurations of molecules can be demonstrated experimentally. The approach used is very similar to the photoelectric effect. If high-energy electromagnetic radiation is directed into a gas, electrons are ejected from the molecules in the gas. The energy required to eject an electron from a molecule, called the binding energy, is a direct measure of how strongly bound the electron is within the molecule. The binding energy of an electron within a molecule depends upon the molecular orbital the electron occupies; the lower the energy of the molecular orbital, the more energy needed to remove an electron from that molecular orbital.

The measurement of the energies of the electrons ejected by radiation incident on gaseous molecules is called *photoelectron spectroscopy*. A photoelectron spectrum of N_2 is shown in **Figure 5**.

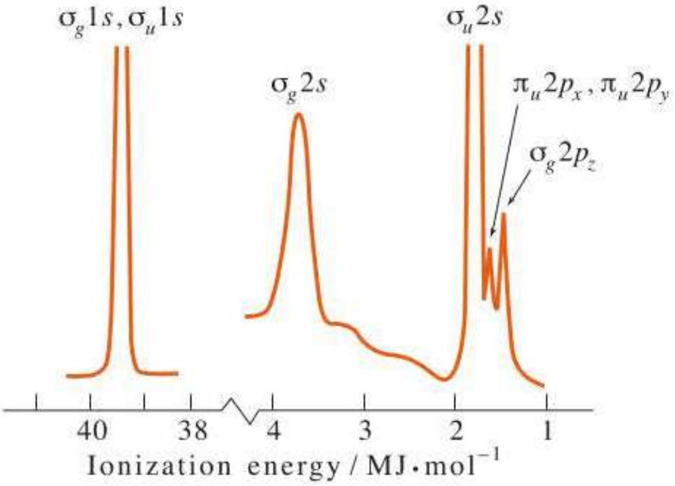


Figure 5: *The photoelectron spectrum ofN2. The peaks in this plot are caused by electrons being ejected from various molecular orbitals.*

According to **Figure 5**, the ground-state configuration of N_2 is $KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\sigma_g 2p_z)^2$. The peaks in the photoelectron spectrum correspond to the energies of occupied molecular orbitals. Photoelectron spectra provide striking experimental support for the molecular orbital picture being developed here.

The Electronic States of Molecules Are Designated by Molecular Term Symbols

The electronic states of molecules are designated by term symbols similar to atomic term symbols. However, molecular term symbols happen to be easier to deduce than atomic term symbols. The primary reason for this is that we deal with the *z* component of the total orbital angular momentum for molecules, whereas we deal with the total orbital angular momentum for atoms. In the molecular case, we deal with scalar quantities, while in the atomic case, we have to deal with vector quantities.

In order to determine molecular term symbols, we first calculate the possible values for the *z* component of the total orbital angular momentum, M_L which is the sum of the *z* components of the orbital angular momenta of the electrons occupying the molecular orbitals:

$$M_L = m_{l1} + m_{l2} + m_{l3} + \cdots$$

where $m_l = 0$ for a σ orbital, $m_l = \pm 1$ for a π orbital, and so on. The various values of $|M_L|$ are associated with capital Greek letters according to the following:

$\boldsymbol{|M_L|}$	0	1	2	3	4
Letter	Σ	Π	Δ	Φ	Γ

Once M_L has been determined, we then determine the possible values for the total *z* component of the spin angular momentum, M_S:

$$M_S = m_{s1} + m_{s2} + m_{s3} + \cdots$$

For $S = 0$, $M_S = O$; for $S = 1/2$, $M_S = \pm 1/2$; for $S = 1$, $M_S = \pm 1, 0$, and so on. For a particular set of M_L and S, the molecular term symbol is then represented by

$$^{2S+1}|M_L|^{+/-}$$

The superscript $2S + 1$ is the spin multiplicity and indicates the number of values of M_S for a particular value of S.

Besides, the overall symmetry of a state to inversion is obtained by multiplying all the symmetries of the individual electrons according to the scheme

$$g \times g = g \qquad u \times u = g \qquad g \times u = u$$

In addition to the g/u designation on the term symbols for homonuclear diatomic molecules, Σ electronic states are labelled with a + or – right superscript to indicate the behaviour of the molecular wave function when it is reflected through a plane containing the nuclei.

Consider the **H_2 molecule** first. The ground-state electron configuration of H_2 is $(\sigma_g 1s)^2$, so $m_l = 0$ for each electron in the occupied σ orbitals. Therefore,

$$M_L = 0 + 0 = 0$$

The spins of the two electrons must be paired to satisfy the Pauli exclusion principle,

So

$$M_S = +\frac{1}{2} - \frac{1}{2} = 0$$

Because the only value of M_S is 0, S must equal zero. Therefore, the term symbol for the ground-state electron configuration of H_2 is ${}^1\Sigma_g{}^+$(a singlet sigma state).

Consider now He_2^+. The ground-state electron configuration is $(\sigma_g 1s)^2(\sigma_u 1s)^1$. We need to consider the values of m_l and m_s, for all three electrons. The possible values are listed below.

$$m_{l1} = 0 \qquad m_{s1} = +1/2$$
$$m_{l2} = 0 \qquad m_{s1} = -1/2$$
$$m_{l3} = 0 \qquad m_{s1} = \pm 1/2$$
$$M_L = 0 \qquad M_S = \pm 1/2$$

The fact that $M_L = 0$ says that we have a Σ state. The $M_S = \pm 1/2$ corresponds to the two projections of $S = 1/2$, so the term symbol for the ground state of He_2^+ is ${}^1\Sigma_u{}^+$ (a doublet sigma state).

He_2: The ground-state electron configuration is $(\sigma_g 1s)^2(\sigma_u 1s)^2$. In this case, $M_L = 0$ and $M_S = 0$. Therefore, the term symbol for the ground state of He_2 is ${}^1\Sigma_g{}^+$.

Table 2: The Ground-State Electron Configuration and Term Symbols for the First-Row Homonuclear Diatomic Molecules

Molecules	Electronic configuration	Ground state term symbols
H_2^+	$(\sigma_g 1s)^1$	${}^2\Sigma_g{}^+$
H_2	$(\sigma_g 1s)^2$	${}^1\Sigma_g{}^+$

He_2^+	$(\sigma_g 1s)^2(\sigma_u 1s)1$	$^2\Sigma_u^+$
He_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2$	$^1\Sigma_g^+$
Li_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2$	$^1\Sigma_g^+$
Be_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2$	$^1\Sigma_g^+$
B_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^1(\pi_u 2p)^1$	$^3\Sigma_g^-$
C_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2(\pi_u 2p)^2$	$^1\Sigma_g^+$
N_2^+	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2(\pi_u 2p)^2(\sigma_g 2p)^1$	$^2\Sigma_g^+$
N_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2(\pi_u 2p)^2(\sigma_g 2p)^2$	$^1\Sigma_g^+$
O_2^+	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2(\pi_u 2p)^2(\sigma_g 2p)^2(\pi_g 2p)^1$	$^2\Pi_g$
O_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2(\pi_u 2p)^2(\sigma_g 2p)^2(\pi_g 2p)^2$	$^3\Sigma_g^+$
F_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2(\pi_u 2p)^2(\sigma_g 2p)^2(\pi_g 2p)^2(\pi_g 2p)^2$	$^1\Sigma_g^+$

The term symbols for heteronuclear diatomic molecules do not have a g or u designation because these molecules do not possess inversion symmetry.

Molecular Orbitals of the Heteronuclear Diatomic Molecules:

The treatment of heteronuclear diatomic molecule is similar to that of homonuclear diatomic molecules. However, in case of homonuclear diatomic molecule two similar atomic orbitals (A.O.) is involved in the formation of molecular orbitals (M.O.). Whereas, in case of heteronuclear diatomic molecules two dissimilar A.O. may involved in the formation of a M.O. For example, 1*s* orbital of H and $2p_z$ orbital of F in HF.

However, A.O. characterised by same value of '*m*' can only combine to form a M.O. in a heteronuclear diatomic molecule. For example, a 2*s* orbital on atom A can combine with $2p_z$ ($m = 0$) orbital on B to form a M.O. if z is chosen the direction of molecular axis. Thus

$$\psi = c_1 2s_A + c_2 2p_{z,B}$$

where c_1 and c_2 are the LCAO coefficients. A $2p_x$ or $2p_y$ ($m = \pm 1$) orbital cannot combine with an *s*-atomic orbital to form a bond because the overlap between the two such orbitals is zero (**Figure 6**).

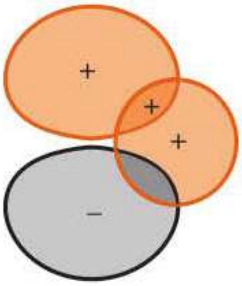


Figure 6: *The overlap between an s-type orbital and p_x (or p_y) orbital. Because of the change in sign of the p_x (or p_y) orbital, the net overlap between the p_x (or p_y) orbital and s orbital is zero for all internuclear distances.*

Since c_1 and c_2 cannot be determined by symmetry in a heteronuclear diatomic they are to be determined by a method based on the variation method.

Lithium Hydride (LiH):

Li in the ground state has the electronic configuration $1s^2\,2s$ and hydrogen has an electron in a $1s$ orbital. So, we can anticipate that the bond is formed between the $2s$-orbital of Li and the $1s$-orbital of H. LiH has the electronic configuration $1\sigma^2\,2\sigma^2$, where the 1σ-molecular orbital is mainly localised on the 1s-orbital of the Li-atom and the 2σ-orbital is given by

$$\Psi = c_1 1s_H + c_2 2s_{Li} \qquad (1)$$

Thus, we can assume that LiH is a two-electron problem and the corresponding secular determinant is

$$\begin{vmatrix} H_{11} - E & H_{12} - SE \\ H_{12} - SE & H_{22} - E \end{vmatrix} = 0$$

where

$$H_{11} = \langle 1s_H | H_e | 1s_H \rangle$$
$$H_{22} = \langle 2s_{Li} | H_e | 2s_{Li} \rangle$$
$$H_{12} = \langle 1s_H | H_e | 2s_{Li} \rangle$$
$$S = \langle 1s_H | 2s_{Li} \rangle \qquad (2)$$

and H_e is the effective electronic Hamiltonian of the molecule.

At the equilibrium bond length of 3 a.u. (1.6 Å) S = 0.5 and from ionisation potential value H_{11} = -13.6 eV = -0.5 a.u.; H_{22} = -5.44 eV = -0.2 a.u.

According to Mulliken

$$H_{12} \approx KS(H_{11} + H_{22})/2$$
$$\approx 2 * 0.5(-0.5 - 0.2)/2$$
$$= -0.35$$

[The value of K for the $2s$-$1s$ atomic orbital overlap is ~ 2]

So, $$\begin{vmatrix} 0.5 + E & 0.35 + 0.5E \\ 0.35 + 0.5E & 0.2 + E \end{vmatrix} = 0$$

$$0.75E^2 + 0.35E - 0.023 = 0$$
$$E = -0.526, +0.06$$

The lowest root (i.e. -0.526) corresponds to the energy of the lowest molecular orbital.

Substituting the value of E into one of the secular equations, we get

$$c_1(0.50 - 0.526) + c_2(0.35 + 0.5 \times -0.526) = 0$$
$$c_1/c_2 = 3.3 \qquad (3)$$

Again, the normalization condition gives,

$$\langle\psi_1|\psi_1\rangle = c_1^2\langle 1s_H|1s_H\rangle + c_2^2\langle 2s_{Li}|2s_{Li}\rangle + 2c_1c_2\langle 1s_H|2s_{Li}\rangle = 1$$
$$c_1^2 + c_2^2 + 2c_1c_2S = 1 \qquad (4)$$

Combining Eqs. 3 and 4 and S = 0.5, we get

$$c_1 = 0.8465, \quad c_2 = 0.2565$$

So, the lowest molecular orbital is

$$\psi_1 = 0.84651s_H + 0.25652s_{Li}$$

And the electron density in the 2σ-molecular orbital of LiH is

$$\rho = 2\psi_1^2 = 2[(0.8465)^2 1s_H^2 + (0.2565)^2 2s_{Li}^2 + 2 \times 0.8465 \times 02565(1s_H 2s_{Li})]$$

[According to Mulliken the overlap density of two atomic orbitals are equally divided between the orbitals according to the following approximate formula

$$\phi_a\phi_b = \frac{1}{2}S_{ab}(\phi_a^2 + \phi_b^2)$$

where S_{ab} is the overlap integral.]

$$\rho = 2[(0.8465)^2 1s_H^2 + (0.2565)^2 2s_{Li}^2 + 0.8465 \times 0.2565 \times 0.5 \times (1s_H^2 + 2s_{Li}^2)]$$
$$= 2\left[\left(0.7166 \cdot 1s_H^2 + 0.0658 \cdot 2s_{Li}^2 + 0.1085(1s_H^2 + 2s_{Li}^2)\right)\right]$$
$$= 2[0.8251 \cdot (1s_H^2) + 0.1743 \cdot (2s_{Li}^2)]$$
$$= 1.65 \cdot (1s_H^2) + 0.35 \cdot (2s_{Li}^2)$$

Since the 1σ-molecular orbital with its two electrons is localised on the Li atom, the net electron populations on the H and Li atoms in the LiH are respectively 1.65 and 2.35. So LiH is predominantly have ionic character in its ground state as

$$Li^{+0.65} - H^{-0.65}$$

The molecular orbitals corresponding to the root (+0.06) is

$$\psi_2 = -0.769 \cdot (1s_H) + 1.131 \cdot (2s_{Li})$$

Therefore

$$\psi_2^2 = (0.7691)^2 \cdot (1s_H^2) + (1.131)^2 \cdot (2s_{Li}^2) - 2 \times 0.7691 \times 1.131 \times (1s_H 2s_{Li})$$
$$= 0.5915 \cdot (1s_H^2) + 1.2792 \cdot (2s_{Li}^2) - 0.4349 \cdot (1s_H^2 + 2s_{Li}^2)$$
$$= 0.16 \cdot (1s_H^2) + 0.84 \cdot (2s_{Li}^2)$$

The lowest excited state is obtained by prompting an electron from ψ_1 to ψ_2 . So the net atomic population on the H and Li atoms in the lowest excited state of LiH are

$$\rho' = \psi_1^2 + \psi_2^2 + 2(1\sigma)^2$$
$$= 0.98 \cdot (1s_H^2) + 3.02 \cdot (2s_{Li}^2)$$

The lowest electronic excited state of LiH may be described as

$$Li^{-0.02} - H^{+0.02}$$

Which suggests that the molecule is predominantly covalent in the lowest excited state.

Hückel MO treatment of simple and conjugated polyenes:

The unsaturated carbon compounds which consist of alternate double and single bonds are conventionally called the conjugated molecules. These molecules are generally planar and sp^2 hybridise. The electrons in sp^2 orbitals called σ-electrons, are contained in the molecular plane and do not possess any angular momentum. The orbitals formed from the unhybridized $2p_z$ orbitals are called π-orbitals and electrons in these orbitals lie above and below molecular plane. These electrons possess one unit of angular momentum about the carbon-carbon bond. Since σ- and π-electrons are contained in planes perpendicular to each other, the interaction between these two types of electrons is likely to be negligible in the planar conjugated molecules. Therefore, the molecular orbitals for π-electrons in a conjugated system may be treated independently of σ-electrons. This concept along with various extensions and modifications is referred as *Hückel molecular orbital theory*.

Let us consider a system of unsaturated hydrocarbons with alternate single and double bonds. If this system has n-carbon atoms each offering one $2p_z$-orbital with one π-electron in it then, according to LCAO approximation, the molecular orbital can be written as

$$\psi = \sum_i C_i \phi_i$$

where ϕ_i is $2p_z$-atomic orbital of atom i and the summation is over all $2p_z$ atomic orbitals. The coefficient and energies of these orbitals are obtained by solving secular equations obtained according to the variation principle (similar to H_2^+ molecule).

$$\sum_{i=1}^{n} C_i\left(H_{ij} - S_{ij}E\right) = 0 \qquad j = 1, 2, 3, \ldots\ldots\ldots, n$$

where

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle$$
$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

Hückel introduced a set of approximation which are as follows:

1. The Hamiltonian H is the sum of effective one-electron Hamiltonian where the potential of each electron is determined by its own coordinates alone.
2. The terms $H_{ii}\left(= \langle \phi_i | H | \phi_j \rangle\right)$, called Coulomb integral, represents approximately the energy of an electron in a $2p$-orbital on the ith carbon atom. Since we are dealing with carbon atoms only, all such integrals are equal and denoted by the symbol α
3. The terms $H_{ij}\left(= \langle \phi_i | H | \phi_j \rangle\right)$, called resonance integrals, represent the energy of interaction of two atomic orbitals. For atoms i and j not being directly bonded $H_{ij} = 0$. When atoms i and j are bonded, H_{ij} is finite. All such integrals are assumed equal and they denoted by the symbol β.
4. The integrals S_{ii} = 1, because they are the normalisation integrals. The overlap integrals S_{ij} are neglected.

Ethylene: Let us consider the simple case of ethylene first. The σ framework of ethylene is shown in the **Figure 7**. Each carbon atom contributes a 2pz orbital to the

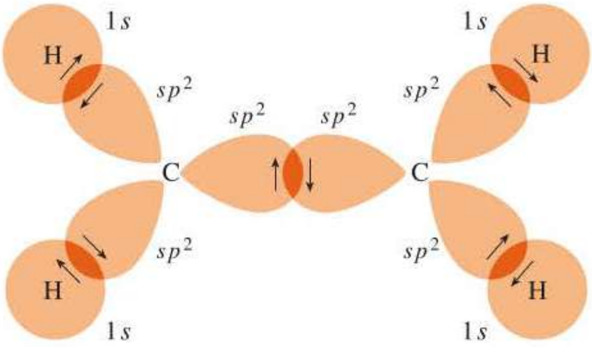


***Figure 7:** The (planar) σ-bond framework of an ethene molecule.*

delocalised π orbital, and we can write (similar to H2+ molecular orbital treatment)

$$\psi_\pi = c_1\phi_1 + c_2\phi_2$$

where ϕ_1 and ϕ_2 are the carbon 2pz orbitals.

The corresponding secular determinantal equation is

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

If we write $\frac{\alpha - E}{\beta} = x$ then above equation become

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

$$x^2 - 1 = 0$$

$$x = \pm 1$$

In other words, $E = \alpha \pm \beta$

Because β is negative, the lowest energy is $E = \alpha + \beta$. There are two π electrons in ethylene, so both the electrons occupy the orbital of lowest energy. An energy-level diagram showing the ground state of ethylene is

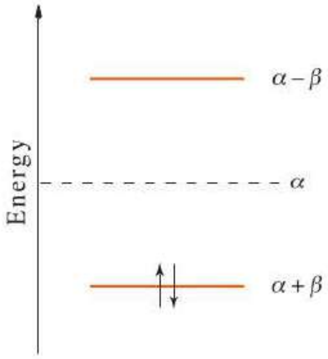


***Figure 8:** The ground-state electron configuration of the π electrons in ethene.*

The π electronic energy of ethylene is $E_n = 2\alpha + 2\beta$. Because α is essentially the energy of an electron in an isolated carbon $2p_z$ orbital, so α used to specify the zero of energy. Therefore, two energies $E = \alpha \pm \beta$ must correspond to bonding and antibonding orbitals.

Now let us determine the Hu̇ckel molecular orbitals.

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

$$c_1 x + c_2 = 0$$

$$c_1 + c_2 x = 0$$

For x = 1

$$c_1 + c_2 = 0 \quad \text{or } c_1 = -c_2 \qquad (5)$$

Since every molecular orbital is normalised, the normalisation of the molecular orbitals gives rise to

$$c_1^2 \langle \phi_1 | \phi_1 \rangle + c_2^2 \langle \phi_2 | \phi_2 \rangle + 2c_1 c_2 \langle \phi_1 | \phi_2 \rangle = 1$$

$$c_1^2 + c_2^2 = 1 \qquad (6)$$

Because we are using $S_{12} = 0$

Combining **Equation 5 and 6** we get

$$c_1 = \frac{1}{\sqrt{2}} \qquad c_2 = -\frac{1}{\sqrt{2}}$$

Hence, the molecular orbital corresponds to the energy level $E_1 = \alpha + \beta$, is

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

and the molecular orbital whose energy is $E_2 = \alpha - \beta$, is

$$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

The two orbitals ψ_1 and ψ_2 are shown schematically in **Figure 9**.

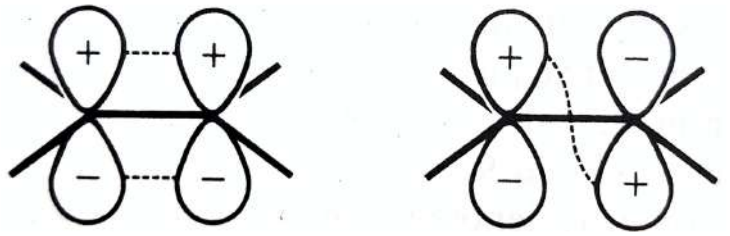


Figure 9: *the bonding and antibonding orbitals in the simple Hückel molecular orbital treatment for ethylene.*

Now we shall illustrate a few quantities of chemical interest which can be derived from the simple Hückel theory.

Electron Densities: The total electron density q_n, at an atom i is the sum of contributions from each electron in each molecular orbital.

$$q_n = \sum_i n_i \, c_{in}^2$$

where n_i is the number of electrons in the ith molecular orbital.

Bond Order: The π-bond order between the adjacent carbon atoms r and s by

$$P_{rs}^{\pi} = \sum_i n_i c_{ir} c_{is}$$

where n_i is the number of electrons in the ith molecular orbital.

So, for ethylene, we have

$$q_1 = 2 * \left({}^{1}/_{\sqrt{2}}\right)^2 + 0 * \left({}^{1}/_{\sqrt{2}}\right)^2 = 1$$

$$q_2 = 1$$

$$P_{12} = 2 * {}^{1}/_{\sqrt{2}} * {}^{1}/_{\sqrt{2}} = 1$$

Butadiene:

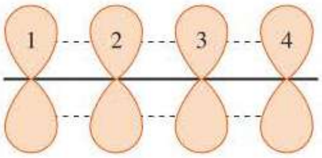


Figure 10: A schematic representation of the $2p_z$ orbitals of each of the carbon atoms in the butadiene molecule.

So, the determinantal form of secular equation is

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

Expansion of this determinant gives the following polynomial

$$x^4 - 3x^2 + 1 = 0$$

with the following roots:

$$x = \pm\, 1.618, \pm\, 0.618$$

There are four π electrons in butadiene and in the ground state these π electrons occupy the two orbitals of lowest energy as in

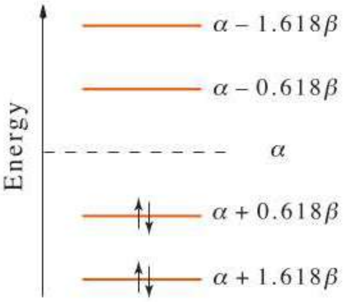


Figure 11: *The ground-state electron configuration of the 7r electrons in butadiene.*

The total π-electronic energy of butadiene is

$$E_\pi = 2\,(\alpha + 1.618\beta\,) + 2\,(\alpha + 0.618\beta)$$

$$= 4\alpha + 4.472\beta$$

We can make an interesting comparison of the energy given by above Equation with that predicted for a localized structure in which two π-electrons are localized between carbon atoms 1 and 2 and between carbon atoms 3 and 4, respectively. This localized structure is equivalent to two isolated ethene molecules. We found that the energy of the π- electrons in ethene is $2\alpha + 2\beta$. If we compare the energy of two ethene molecules with that obtained for the delocalized orbitals of butadiene, we see there is an energy stabilization that results from delocalization, known as delocalization energy (delocalization energy is defined as the difference in energy of the π-electrons in a molecule and sum of the energies of the isolated double bonds present in the classical structure of the same molecule)

$$DE = E_\pi\,(butadiene) - 2E_\pi\,(ethylene)$$

$$= 0.0472\beta$$

The DE is a measure of the stability of the molecule. The higher the value of DE more stable is the molecule. Thus, butadiene is more stable than two ethylene molecules by an energy of 0.472β.

The four molecular orbitals for butadiene are obtained by the usual procedure are as follows

$$\psi_1 = 0.3717\phi_1 + 0.6015\phi_2 + 0.6015\phi_3 + 0.3717\phi_4$$

$$\psi_2 = 0.6015\phi_1 + 0.3717\phi_2 - 0.3717\phi_3 - 0.6015\phi_4$$

$$\psi_3 = 0.6015\phi_1 - 0.3717\phi_2 - 0.3717\phi_3 + 0.6015\phi_4$$

$$\psi_4 = 0.3717\phi_1 - 0.6015\phi_2 + 0.6015\phi_3 - 0.3717\phi_4$$

These butadiene molecular orbitals are presented schematically in **Figure 12**.

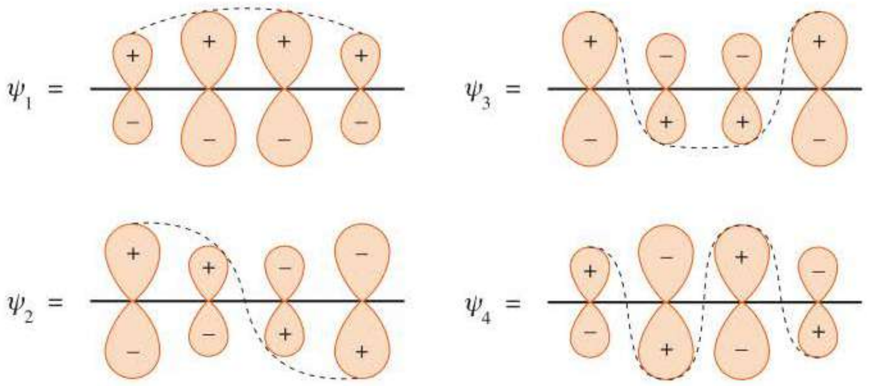


Figure 12: *A schematic representation of the π- molecular orbitals of butadiene. Note that the corresponding energy increases with the number of nodes.*

Now for butadiene the π-electronic charge on the carbon atoms are

$$q_1 = 2c_{11}^2 + 2c_{21}^2 + 0c_{31}^2 + 0c_{41}^2$$
$$= 2(0.3717)^2 + 2(0.6015)^2$$
$$= 1.000$$

The other q's are also unity, indicating that the π-electrons in butadiene are uniformly distributed over the molecule.

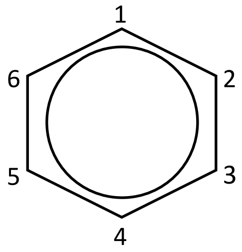
Now the bond order

$$P_{12}^{\pi} = 2c_{11}c_{12} + 2c_{21}c_{22} + 0c_{31}c_{32} + 0c_{41}c_{42}$$
$$= 2(0.3717)(0.6015) + 2(0.6015)(0.3717)$$
$$= 0.8942$$
$$P_{23}^{\pi} = 2c_{12}c_{13} + 2c_{22}c_{23} + 0c_{32}c_{33} + 0c_{42}c_{43}$$
$$= 2(0.6015)(0.6015) + 2(0.3717)(-0.3717)$$
$$= 0.4473$$

Clearly $P_{12}^{\pi} = P_{34}^{\pi}$ by symmetry. If we recall that there is a σ bond between each carbon atom, then we can define a total bond order

$$P_{rs}^{total} = 1\ (for\ \sigma\ bond) + P_{rs}^{\pi}$$
$$P_{12}^{total} = P_{34}^{total} = 1.894$$
$$P_{23}^{total} = 1.447$$

Example 3: The Hückel secular determinant for benzene



$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

The resulting determinant can be expanded to give

$$x^6 - 6x^4 + 9x^2 - 4 = 0$$

The six roots of the polynomial are $x = \pm 1, \pm 1, \pm 2$, giving the following energies for the six molecular orbitals:

$$E_1 = \alpha + 2\beta$$

$$E_2 = E_3 = \alpha + \beta$$

$$E_4 = E5 = \alpha - \beta$$

$$E_6 = \alpha - 2\beta$$

The total π-electron energy in benzene is given by

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 6\beta$$

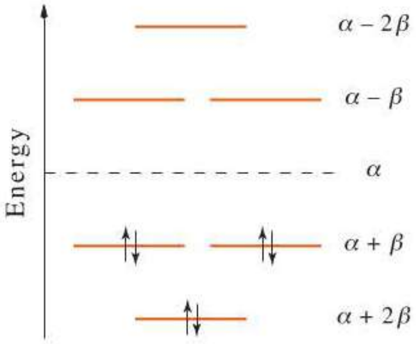


Figure 13: *The ground-state electron configuration of the π-electrons in benzene.*

The resulting six π-molecular orbitals of benzene are given by

$$\psi_1 = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\psi_2 = \frac{1}{\sqrt{4}}(\phi_2 + \phi_3 - \phi_5 - \phi_6)$$

$$\psi_3 = \frac{1}{\sqrt{3}}\left(\phi_1 + \frac{1}{2}\phi_2 - \frac{1}{2}\phi_3 - \phi_4 - \frac{1}{2}\phi_5 + \frac{1}{2}\phi_6\right)$$

$$\psi_4 = \frac{1}{\sqrt{4}}(\phi_2 - \phi_3 + \phi_5 - \phi_6)$$

$$\psi_5 = \frac{1}{\sqrt{3}}\left(\phi_1 - \frac{1}{2}\phi_2 - \frac{1}{2}\phi_3 + \phi_4 - \frac{1}{2}\phi_5 - \frac{1}{2}\phi_6\right)$$

$$\psi_6 = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

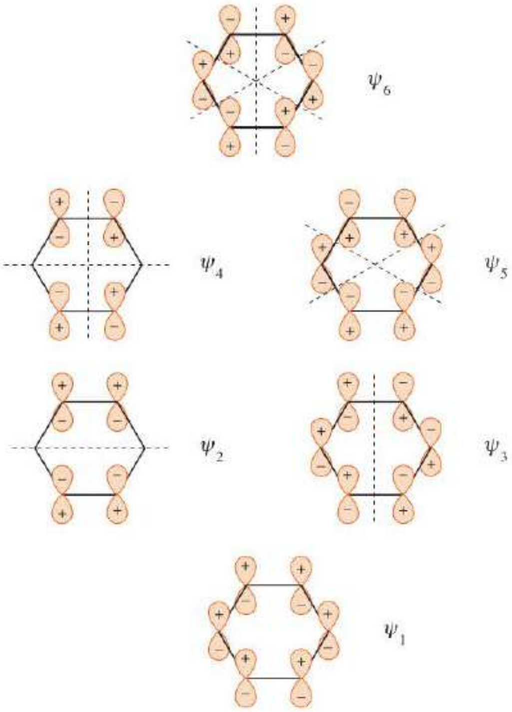


Figure 14: *A schematic representation of the π- molecular orbitals of benzene.*