Teacher: DR. SUBHANKAR SARDAR
Class : Semester-4
Paper: C8T: Physical Chemistry
Topic : Quantum Chemistry
(LCAO and HF-SCF)

Comments: This portion is not important for final examination and thus not marked. Read as much as you can. Paragraph 11.4 & 11.5 are out of syllabus, still need to know as they are involved in inorganic chemistry. Read only the concept of Hartree-Fock method and SCF method not details.

Reference: Atkins' Physical Chemistry (Oxford University Press)

11

Molecular structure

The concepts developed in Chapter 10, particularly those of orbitals, can be extended to a description of the electronic structures of molecules. There are two principal quantum mechanical theories of molecular electronic structure. In valence-bond theory, the starting point is the concept of the shared electron pair. We see how to write the wavefunction for such a pair, and how it may be extended to account for the structures of a wide variety of molecules. The theory introduces the concepts of σ and π bonds, promotion, and hybridization that are used widely in chemistry. In molecular orbital theory (with which the bulk of the chapter is concerned), the concept of atomic orbital is extended to that of molecular orbital, which is a wavefunction that spreads over all the atoms in a molecule.

In this chapter we consider the origin of the strengths, numbers, and three-dimensional arrangement of chemical bonds between atoms. The quantum mechanical description of chemical bonding has become highly developed through the use of computers, and it is now possible to consider the structures of molecules of almost any complexity. We shall concentrate on the quantum mechanical description of the **covalent bond**, which was identified by G.N. Lewis (in 1916, before quantum mechanics was fully established) as an electron pair shared between two neighbouring atoms. We shall see, however, that the other principal type of bond, an **ionic bond**, in which the cohesion arises from the Coulombic attraction between ions of opposite charge, is also captured as a limiting case of a covalent bond between dissimilar atoms. In fact, although the Schrödinger equation might shroud the fact in mystery, all chemical bonding can be traced to the interplay between the attraction of opposite charges, the repulsion of like charges, and the effect of changing kinetic energy as the electrons are confined to various regions when bonds form.

There are two major approaches to the calculation of molecular structure, **valence-bond theory** (VB theory) and **molecular orbital theory** (MO theory). Almost all modern computational work makes use of MO theory, and we concentrate on that theory in this chapter. Valence-bond theory, though, has left its imprint on the language of chemistry, and it is important to know the significance of terms that chemists use every day. Therefore, our discussion is organized as follows. First, we set out the concepts common to all levels of description. Then we present VB theory, which gives us a simple qualitative understanding of bond formation. Next, we present the basic ideas of MO theory. Finally, we see how computational techniques pervade all current discussions of molecular structure, including the prediction of chemical reactivity.

The Born–Oppenheimer approximation

All theories of molecular structure make the same simplification at the outset. Whereas the Schrödinger equation for a hydrogen atom can be solved exactly, an exact solution is not possible for any molecule because the simplest molecule consists of three particles (two nuclei and one electron). We therefore adopt the **Born–Oppenheimer approximation** in which it is supposed that the nuclei, being so much heavier than an electron, move relatively slowly and may be treated as stationary while the electrons move in their field. We can therefore think of the nuclei as being fixed at arbitrary locations, and then solve the Schrödinger equation for the wavefunction of the electrons alone.

The approximation is quite good for ground-state molecules, for calculations suggest that the nuclei in H_2 move through only about 1 pm while the electron speeds through 1000 pm, so the error of assuming that the nuclei are stationary is small. Exceptions to the approximation's validity include certain excited states of polyatomic molecules and the ground states of cations; both types of species are important when considering photoelectron spectroscopy (Section 11.4) and mass spectrometry.

The Born–Oppenheimer approximation allows us to select an internuclear separation in a diatomic molecule and then to solve the Schrödinger equation for the electrons at that nuclear separation. Then we choose a different separation and repeat the calculation, and so on. In this way we can explore how the energy of the molecule varies with bond length (in polyatomic molecules, with angles too) and obtain a **molecular potential energy curve** (Fig. 11.1). When more than one molecular parameter is changed in a polyatomic molecule, we obtain a potential energy surface. It is called a *potential* energy curve because the kinetic energy of the stationary nuclei is zero. Once the curve has been calculated or determined experimentally (by using the spectroscopic techniques described in Chapters 13 and 14), we can identify the **equilibrium bond length**, R_e, the internuclear separation at the minimum of the curve, and the **bond dissociation energy**, D_0, which is closely related to the depth, D_e, of the minimum below the energy of the infinitely widely separated and stationary atoms.

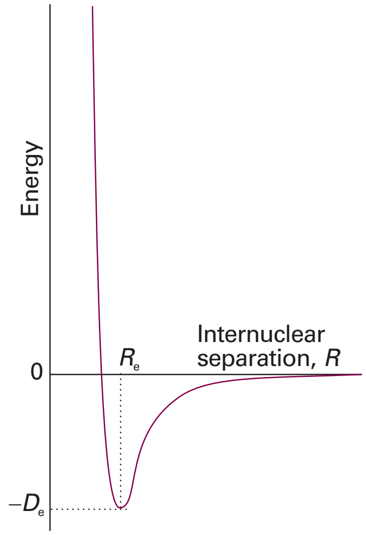


Fig. 11.1 A molecular potential energy curve. The equilibrium bond length corresponds to the energy minimum.

Comment 11.1

The dissociation energy differs from the depth of the well by an energy equal to the zero-point vibrational energy of the bonded atoms: $D_0 = D_e - \frac{1}{2}\hbar\omega$, where ω is the vibrational frequency of the bond (Section 13.9).

Valence-bond theory

Valence-bond theory was the first quantum mechanical theory of bonding to be developed. The language it introduced, which includes concepts such as spin pairing, orbital overlap, σ and π bonds, and hybridization, is widely used throughout chemistry, especially in the description of the properties and reactions of organic compounds. Here we summarize essential topics of VB theory that are familiar from introductory chemistry and set the stage for the development of MO theory.

11.1 Homonuclear diatomic molecules

In VB theory, a bond is regarded as forming when an electron in an atomic orbital on one atom pairs its spin with that of an electron in an atomic orbital on another atom. To understand why this pairing leads to bonding, we have to examine the wavefunction for the two electrons that form the bond. We begin by considering the simplest possible chemical bond, the one in molecular hydrogen, H_2.

The spatial wavefunction for an electron on each of two widely separated H atoms is

$$\psi = \chi_{\mathrm{H1}s_\mathrm{A}}(\boldsymbol{r}_1)\chi_{\mathrm{H1}s_\mathrm{B}}(\boldsymbol{r}_2)$$

if electron 1 is on atom A and electron 2 is on atom B; in this chapter we use χ (chi) to denote atomic orbitals. For simplicity, we shall write this wavefunction as $\psi = A(1)B(2)$. When the atoms are close, it is not possible to know whether it is electron 1 that is on A or electron 2. An equally valid description is therefore $\psi = A(2)B(1)$, in which electron 2 is on A and electron 1 is on B. When two outcomes are equally probable, quantum mechanics instructs us to describe the true state of the system as a superposition of the wavefunctions for each possibility (Section 8.5d), so a better description of the molecule than either wavefunction alone is the (unnormalized) linear combination

$$\psi = A(1)B(2) \pm A(2)B(1) \qquad (11.1)$$

It turns out that the combination with lower energy is the one with a + sign, so the valence-bond wavefunction of the H_2 molecule is

$$\psi = A(1)B(2) + A(2)B(1) \qquad (11.2)$$

The formation of the bond in H_2 can be pictured as due to the high probability that the two electrons will be found between the two nuclei and hence will bind them together. More formally, the wave pattern represented by the term $A(1)B(2)$ interferes constructively with the wave pattern represented by the contribution $A(2)B(1)$, and there is an enhancement in the value of the wavefunction in the internuclear region (Fig. 11.2).

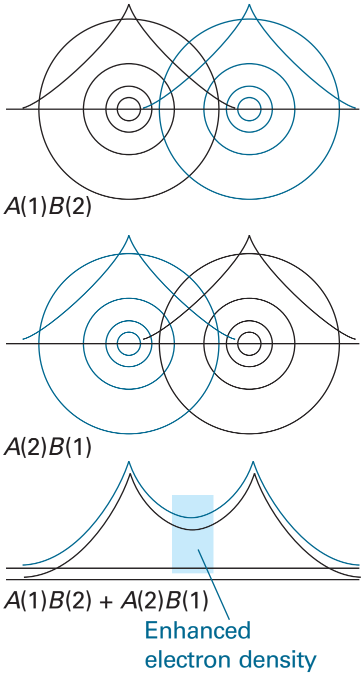


Fig. 11.2 It is very difficult to represent valence-bond wavefunctions because they refer to two electrons simultaneously. However, this illustration is an attempt. The atomic orbital for electron 1 is represented by the black contours, and that of electron 2 is represented by the blue contours. The top illustration represents $A(1)B(2)$, and the middle illustration represents the contribution $A(2)B(1)$. When the two contributions are superimposed, there is interference between the black contributions and between the blue contributions, resulting in an enhanced (two-electron) density in the internuclear region.

The electron distribution described by the wavefunction in eqn 11.2 is called a **σ bond**. A σ bond has cylindrical symmetry around the internuclear axis, and is so called because, when viewed along the internuclear axis, it resembles a pair of electrons in an *s* orbital (and σ is the Greek equivalent of s).

A chemist's picture of a covalent bond is one in which the spins of two electrons pair as the atomic orbitals overlap. The origin of the role of spin is that the wavefunction given in eqn 11.2 can be formed only by a pair of electrons with opposed spins. Spin pairing is not an end in itself: it is a means of achieving a wavefunction (and the probability distribution it implies) that corresponds to a low energy.

Justification 11.1 *Electron pairing in VB theory*

The Pauli principle requires the wavefunction of two electrons to change sign when the labels of the electrons are interchanged (see Section 10.4b). The total VB wavefunction for two electrons is

$$\psi(1,2) = \{A(1)B(2) + A(2)B(1)\}\sigma(1,2)$$

where σ represents the spin component of the wavefunction. When the labels 1 and 2 are interchanged, this wavefunction becomes

$$\psi(2,1) = \{A(2)B(1) + A(1)B(2)\}\sigma(2,1) = \{A(1)B(2) + A(2)B(1)\}\sigma(2,1)$$

The Pauli principle requires that $\psi(2,1) = -\psi(1,2)$, which is satisfied only if $\sigma(2,1) = -\sigma(1,2)$. The combination of two spins that has this property is

$$\sigma_{-}(1,2) = (1/2^{1/2})\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

which corresponds to paired electron spins (Section 10.7). Therefore, we conclude that the state of lower energy (and hence the formation of a chemical bond) is achieved if the electron spins are paired.

The VB description of H_2 can be applied to other homonuclear diatomic molecules, such as nitrogen, N_2. To construct the valence bond description of N_2, we consider the valence electron configuration of each atom, which is $2s^2 2p_x^1 2p_y^1 2p_z^1$. It is conventional to take the *z*-axis to be the internuclear axis, so we can imagine each atom as having a $2p_z$ orbital pointing towards a $2p_z$ orbital on the other atom (Fig. 11.3), with the $2p_x$ and $2p_y$ orbitals perpendicular to the axis. A σ bond is then formed by spin pairing between the two electrons in the two $2p_z$ orbitals. Its spatial wavefunction is given by eqn 11.2, but now *A* and *B* stand for the two $2p_z$ orbitals.

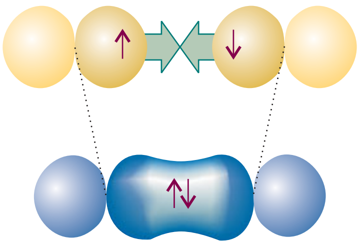


Fig. 11.3 The orbital overlap and spin pairing between electrons in two collinear *p* orbitals that results in the formation of a σ bond.

The remaining $2p$ orbitals cannot merge to give σ bonds as they do not have cylindrical symmetry around the internuclear axis. Instead, they merge to form two π bonds. A **π bond** arises from the spin pairing of electrons in two p orbitals that approach side-by-side (Fig. 11.4). It is so called because, viewed along the internuclear axis, a π bond resembles a pair of electrons in a p orbital (and π is the Greek equivalent of p).

There are two π bonds in N_2, one formed by spin pairing in two neighbouring $2p_x$ orbitals and the other by spin pairing in two neighbouring $2p_y$ orbitals. The overall bonding pattern in N_2 is therefore a σ bond plus two π bonds (Fig. 11.5), which is consistent with the Lewis structure :N≡N: for nitrogen.

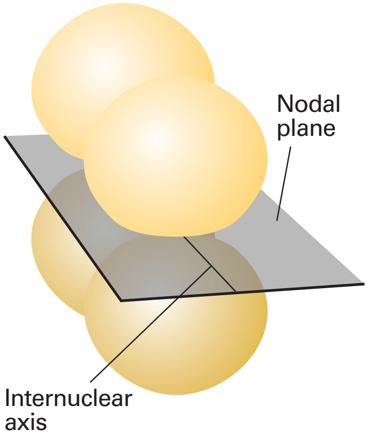


Fig. 11.4 A π bond results from orbital overlap and spin pairing between electrons in p orbitals with their axes perpendicular to the internuclear axis. The bond has two lobes of electron density separated by a nodal plane.

11.2 Polyatomic molecules

Each σ bond in a polyatomic molecule is formed by the spin pairing of electrons in atomic orbitals with cylindrical symmetry about the relevant internuclear axis. Likewise, π bonds are formed by pairing electrons that occupy atomic orbitals of the appropriate symmetry.

The VB description of H_2O will make this clear. The valence electron configuration of an O atom is $2s^22p_x^22p_y^12p_z^1$. The two unpaired electrons in the O2p orbitals can each pair with an electron in an H1s orbital, and each combination results in the formation of a σ bond (each bond has cylindrical symmetry about the respective O—H internuclear axis). Because the $2p_y$ and $2p_z$ orbitals lie at 90° to each other, the two σ bonds also lie at 90° to each other (Fig. 11.6). We can predict, therefore, that H_2O should be an angular molecule, which it is. However, the theory predicts a bond angle of 90°, whereas the actual bond angle is 104.5°.

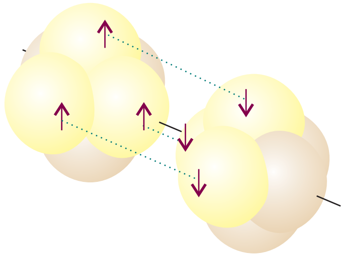


Fig. 11.5 The structure of bonds in a nitrogen molecule: there is one σ bond and two π bonds. As explained later, the overall electron density has cylindrical symmetry around the internuclear axis.

Self-test 11.1 Use valence-bond theory to suggest a shape for the ammonia molecule, NH_3.

[A trigonal pyramidal molecule with each N—H bond 90°; experimental: 107°]

Another deficiency of VB theory is its inability to account for carbon's tetravalence (its ability to form four bonds). The ground-state configuration of C is $2s^22p_x^12p_y^1$, which suggests that a carbon atom should be capable of forming only two bonds, not four. This deficiency is overcome by allowing for **promotion**, the excitation of an electron to an orbital of higher energy. In carbon, for example, the promotion of a 2s electron to a 2p orbital can be thought of as leading to the configuration $2s^12p_x^12p_y^12p_z^1$, with four unpaired electrons in separate orbitals. These electrons may pair with four electrons in orbitals provided by four other atoms (such as four H1s orbitals if the molecule is CH_4), and hence form four σ bonds. Although energy was required to promote the electron, it is more than recovered by the promoted atom's ability to form four bonds in place of the two bonds of the unpromoted atom. Promotion, and the formation of four bonds, is a characteristic feature of carbon because the promotion energy is quite small: the promoted electron leaves a doubly occupied 2s orbital and enters a vacant 2p orbital, hence significantly relieving the electron–electron repulsion it experiences in the former. However, we need to remember that promotion is not a 'real' process in which an atom somehow becomes excited and then forms bonds: it is a notional contribution to the overall energy change that occurs when bonds form.

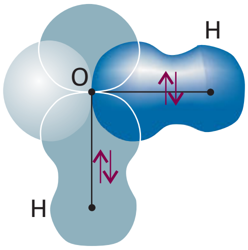


Fig. 11.6 A first approximation to the valence-bond description of bonding in an H_2O molecule. Each σ bond arises from the overlap of an H1s orbital with one of the O2p orbitals. This model suggests that the bond angle should be 90°, which is significantly different from the experimental value.

The description of the bonding in CH_4 (and other alkanes) is still incomplete because it implies the presence of three σ bonds of one type (formed from H1s and C2p

Comment 11.2

A characteristic property of waves is that they interfere with one another, resulting in a greater displacement where peaks or troughs coincide, giving rise to *constructive interference*, and a smaller displacement where peaks coincide with troughs, giving rise to *destructive interference*. The physics of waves is reviewed in *Appendix 3*.

orbitals) and a fourth σ bond of a distinctly different character (formed from H1*s* and C2*s*). This problem is overcome by realizing that the electron density distribution in the promoted atom is equivalent to the electron density in which each electron occupies a **hybrid orbital** formed by interference between the C2*s* and C2*p* orbitals. The origin of the hybridization can be appreciated by thinking of the four atomic orbitals centred on a nucleus as waves that interfere destructively and constructively in different regions, and give rise to four new shapes.

The specific linear combinations that give rise to four equivalent hybrid orbitals are

$$\begin{aligned} h_1 &= s + p_x + p_y + p_z \qquad & h_2 &= s - p_x - p_y + p_z \\ h_3 &= s - p_x + p_y - p_z \qquad & h_4 &= s + p_x - p_y - p_z \end{aligned} \tag{11.3}$$

As a result of the interference between the component orbitals, each hybrid orbital consists of a large lobe pointing in the direction of one corner of a regular tetrahedron (Fig. 11.7). The angle between the axes of the hybrid orbitals is the tetrahedral angle, 109.47°. Because each hybrid is built from one *s* orbital and three *p* orbitals, it is called an ***sp*^{3} hybrid orbital**.

It is now easy to see how the valence-bond description of the CH_4 molecule leads to a tetrahedral molecule containing four equivalent C—H bonds. Each hybrid orbital of the promoted C atom contains a single unpaired electron; an H1*s* electron can pair with each one, giving rise to a σ bond pointing in a tetrahedral direction. For example, the (un-normalized) wavefunction for the bond formed by the hybrid orbital h_1 and the $1s_A$ orbital (with wavefunction that we shall denote A) is

$$\psi = h_1(1)A(2) + h_1(2)A(1)$$

Because each sp^3 hybrid orbital has the same composition, all four σ bonds are identical apart from their orientation in space (Fig. 11.8).

A hybrid orbital has enhanced amplitude in the internuclear region, which arises from the constructive interference between the *s* orbital and the positive lobes of the *p* orbitals (Fig. 11.9). As a result, the bond strength is greater than for a bond formed

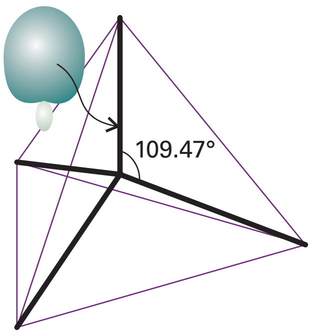


Fig. 11.7 An sp^3 hybrid orbital formed from the superposition of *s* and *p* orbitals on the same atom. There are four such hybrids: each one points towards the corner of a regular tetrahedron. The overall electron density remains spherically symmetrical.

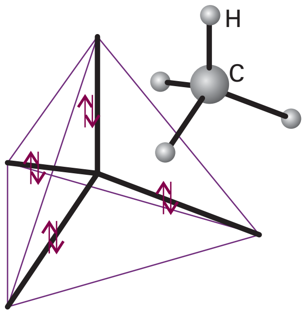


Fig. 11.8 Each sp^3 hybrid orbital forms a σ bond by overlap with an H1*s* orbital located at the corner of the tetrahedron. This model accounts for the equivalence of the four bonds in CH_4.

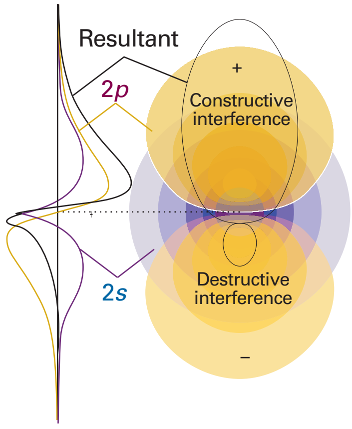


Fig. 11.9 A more detailed representation of the formation of an sp^3 hybrid by interference between wavefunctions centred on the same atomic nucleus. (To simplify the representation, we have ignored the radial node of the 2*s* orbital.)

from an *s* or *p* orbital alone. This increased bond strength is another factor that helps to repay the promotion energy.

Hybridization can also be used to describe the structure of an ethene molecule, $H_2C{=}CH_2$, and the torsional rigidity of double bonds. An ethene molecule is planar, with HCH and HCC bond angles close to 120°. To reproduce the σ bonding structure, we promote each C atom to a $2s^12p^3$ configuration. However, instead of using all four orbitals to form hybrids, we form ***sp*²** **hybrid orbitals**:

$$h_1 = s + 2^{1/2}p_y \qquad h_2 = s + \left(\tfrac{3}{2}\right)^{1/2}p_x - \left(\tfrac{1}{2}\right)^{1/2}p_y \qquad h_3 = s - \left(\tfrac{3}{2}\right)^{1/2}p_x - \left(\tfrac{1}{2}\right)^{1/2}p_y \qquad (11.4)$$

that lie in a plane and point towards the corners of an equilateral triangle (Fig. 11.10). The third 2*p* orbital ($2p_z$) is not included in the hybridization; its axis is perpendicular to the plane in which the hybrids lie. As always in superpositions, the proportion of each orbital in the mixture is given by the *square* of the corresponding coefficient. Thus, in the first of these hybrids the ratio of *s* to *p* contributions is 1:2. Similarly, the total *p* contribution in each of h_2 and h_3 is $\frac{3}{2}+\frac{1}{2}=2$, so the ratio for these orbitals is also 1:2. The different signs of the coefficients ensure that constructive interference takes place in different regions of space, so giving the patterns in the illustration.

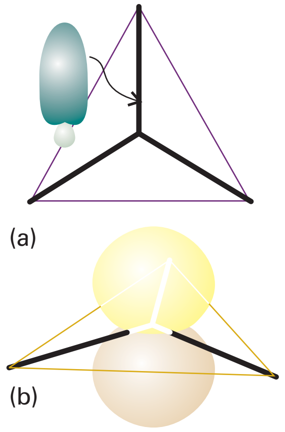


Fig. 11.10 (a) An *s* orbital and two *p* orbitals can be hybridized to form three equivalent orbitals that point towards the corners of an equilateral triangle. (b) The remaining, unhybridized *p* orbital is perpendicular to the plane.

We can now describe the structure of $CH_2{=}CH_2$ as follows. The sp^2-hybridized C atoms each form three σ bonds by spin pairing with either the h_1 hybrid of the other C atom or with H1*s* orbitals. The σ framework therefore consists of C—H and C—C σ bonds at 120° to each other. When the two CH_2 groups lie in the same plane, the two electrons in the unhybridized *p* orbitals can pair and form a π bond (Fig. 11.11). The formation of this π bond locks the framework into the planar arrangement, for any rotation of one CH_2 group relative to the other leads to a weakening of the π bond (and consequently an increase in energy of the molecule).

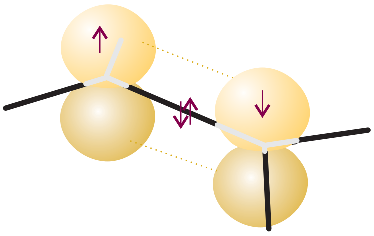


Fig. 11.11 A representation of the structure of a double bond in ethene; only the π bond is shown explicitly.

A similar description applies to ethyne, HC≡CH, a linear molecule. Now the C atoms are ***sp*** **hybridized**, and the σ bonds are formed using hybrid atomic orbitals of the form

$$h_1 = s + p_z \qquad h_2 = s - p_z \qquad (11.5)$$

These two orbitals lie along the internuclear axis. The electrons in them pair either with an electron in the corresponding hybrid orbital on the other C atom or with an electron in one of the H1*s* orbitals. Electrons in the two remaining *p* orbitals on each atom, which are perpendicular to the molecular axis, pair to form two perpendicular π bonds (Fig. 11.12).

Self-test 11.2 Hybrid orbitals do not always form bonds. They may also contain lone pairs of electrons. Use valence-bond theory to suggest possible shapes for the hydrogen peroxide molecule, H_2O_2.

[Each H—O—O bond angle is predicted to be approximately 109° (experimental: 94.8°); rotation around the O—O bond is possible, so the molecule interconverts between planar and non-planar geometries at high temperatures.]

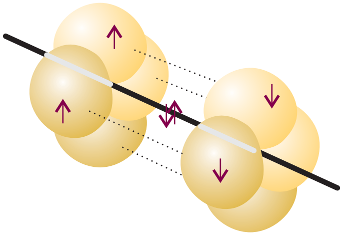


Fig. 11.12 A representation of the structure of a triple bond in ethyne; only the π bonds are shown explicitly. The overall electron density has cylindrical symmetry around the axis of the molecule.

Other hybridization schemes, particularly those involving *d* orbitals, are often invoked in elementary work to be consistent with other molecular geometries (Table 11.1). The hybridization of *N* atomic orbitals always results in the formation of *N* hybrid orbitals, which may either form bonds or may contain lone pairs of electrons. For example, sp^3d^2 hybridization results in six equivalent hybrid orbitals pointing towards the corners of a regular octahedron and is sometimes invoked to account for the structure of octahedral molecules, such as SF_6.

Table 11.1* Some hybridization schemes

Coordination number	Arrangement	Composition
2	Linear	*sp*, *pd*, *sd*
	Angular	*sd*
3	Trigonal planar	sp^2, p^2d
	Unsymmetrical planar	*spd*
	Trigonal pyramidal	pd^2
4	Tetrahedral	sp^3, sd^3
	Irregular tetrahedral	spd^2, p^3d, dp^3
	Square planar	p^2d^2, sp^2d
5	Trigonal bipyramidal	sp^3d, spd^2
	Tetragonal pyramidal	sp^2d^2, sd^4, pd^4, p^3d^2
	Pentagonal planar	p^2d^3
6	Octahedral	sp^3d^2
	Trigonal prismatic	spd^4, pd^5
	Trigonal antiprismatic	p^3d^2

* Source: H. Eyring, J. Walter, and G.E. Kimball, *Quantum chemistry*, Wiley (1944).

Molecular orbital theory

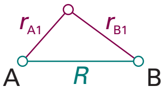
In MO theory, it is accepted that electrons should not be regarded as belonging to particular bonds but should be treated as spreading throughout the entire molecule. This theory has been more fully developed than VB theory and provides the language that is widely used in modern discussions of bonding. To introduce it, we follow the same strategy as in Chapter 10, where the one-electron H atom was taken as the fundamental species for discussing atomic structure and then developed into a description of many-electron atoms. In this chapter we use the simplest molecular species of all, the hydrogen molecule-ion, H_2^+, to introduce the essential features of bonding, and then use it as a guide to the structures of more complex systems. To that end, we will progress to **homonuclear diatomic molecules**, which, like the H_2^+ molecule-ion, are formed from two atoms of the same element, then describe **heteronuclear diatomic molecules**, which are diatomic molecules formed from atoms of two different elements (such as CO and HCl), and end with a treatment of polyatomic molecules that forms the basis for modern computational models of molecular structure and chemical reactivity.

11.3 The hydrogen molecule-ion

The hamiltonian for the single electron in H_2^+ is

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 + V \qquad V = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R}\right) \tag{11.6}$$

where r_{A1} and r_{B1} are the distances of the electron from the two nuclei (**1**) and R is the distance between the two nuclei. In the expression for V, the first two terms in parentheses are the attractive contribution from the interaction between the electron and the nuclei; the remaining term is the repulsive interaction between the nuclei.



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The one-electron wavefunctions obtained by solving the Schrödinger equation $H\psi = E\psi$ are called **molecular orbitals** (MO). A molecular orbital ψ gives, through the value of $|\psi|^2$, the distribution of the electron in the molecule. A molecular orbital is like an atomic orbital, but spreads throughout the molecule.

The Schrödinger equation can be solved analytically for H_2^+ (within the Born–Oppenheimer approximation), but the wavefunctions are very complicated functions; moreover, the solution cannot be extended to polyatomic systems. Therefore, we adopt a simpler procedure that, while more approximate, can be extended readily to other molecules.

(a) Linear combinations of atomic orbitals

If an electron can be found in an atomic orbital belonging to atom A and also in an atomic orbital belonging to atom B, then the overall wavefunction is a superposition of the two atomic orbitals:

$$\psi_{\pm} = N(A \pm B) \qquad (11.7)$$

where, for H_2^+, A denotes χ_{H1s_A}, B denotes χ_{H1s_B}, and N is a normalization factor. The technical term for the superposition in eqn 11.7 is a **linear combination of atomic orbitals** (LCAO). An approximate molecular orbital formed from a linear combination of atomic orbitals is called an **LCAO-MO**. A molecular orbital that has cylindrical symmetry around the internuclear axis, such as the one we are discussing, is called a **σ orbital** because it resembles an s orbital when viewed along the axis and, more precisely, because it has zero orbital angular momentum around the internuclear axis.

Example 11.1 *Normalizing a molecular orbital*

Normalize the molecular orbital ψ_+ in eqn 11.7.

Method We need to find the factor N such that

$$\int \psi^* \psi \, d\tau = 1$$

To proceed, substitute the LCAO into this integral, and make use of the fact that the atomic orbitals are individually normalized.

Answer When we substitute the wavefunction, we find

$$\int \psi^* \psi \, d\tau = N^2 \left\{ \int A^2 d\tau + \int B^2 d\tau + 2\int AB \, d\tau \right\} = N^2(1+1+2S)$$

where $S = \int AB \, d\tau$. For the integral to be equal to 1, we require

$$N = \frac{1}{\{2(1+S)\}^{1/2}}$$

In H_2^+, $S \approx 0.59$, so $N = 0.56$.

Self-test 11.3 Normalize the orbital ψ_- in eqn 11.7.

$[N = 1/\{2(1-S)\}^{1/2}$, so $N = 1.10]$

Figure 11.13 shows the contours of constant amplitude for the two molecular orbitals in eqn 11.7, and Fig. 11.14 shows their boundary surfaces. Plots like these are readily obtained using commercially available software. The calculation is quite straightforward, because all we need do is feed in the mathematical forms of the two atomic orbitals and then let the program do the rest. In this case, we use

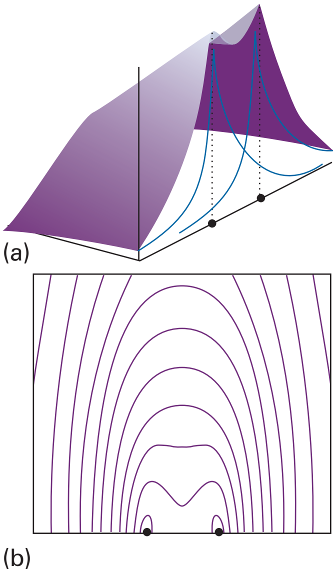


Fig. 11.13 (a) The amplitude of the bonding molecular orbital in a hydrogen molecule-ion in a plane containing the two nuclei and (b) a contour representation of the amplitude.

Exploration Plot the 1σ orbital for different values of the internuclear distance. Point to the features of the 1σ orbital that lead to bonding.

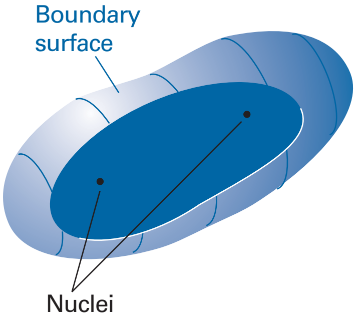
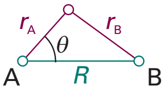


Fig. 11.14 A general indication of the shape of the boundary surface of a σ orbital.

Comment 11.3

The *law of cosines* states that for a triangle such as that shown in (**2**) with sides r_A, r_B, and R, and angle θ facing side r_B we may write: $r_B^2 = r_A^2 + R^2 - 2r_AR\cos\theta$.



2

$$A = \frac{e^{-r_A/a_0}}{(\pi a_0^3)^{1/2}} \qquad B = \frac{e^{-r_B/a_0}}{(\pi a_0^3)^{1/2}} \tag{11.8}$$

and note that r_A and r_B are not independent (**2**), but related by the *law of cosines* (see *Comment 11.3*):

$$r_B = \{r_A^2 + R^2 - 2r_AR\cos\theta\}^{1/2} \tag{11.9}$$

To make this plot, we have taken $N^2 = 0.31$ (Example 11.1).

(b) Bonding orbitals

According to the Born interpretation, the probability density of the electron in H_2^+ is proportional to the square modulus of its wavefunction. The probability density corresponding to the (real) wavefunction ψ_+ in eqn 11.7 is

$$\psi_+^2 = N^2(A^2 + B^2 + 2AB) \tag{11.10}$$

This probability density is plotted in Fig. 11.15.

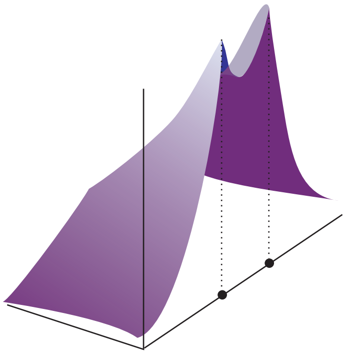


Fig. 11.15 The electron density calculated by forming the square of the wavefunction used to construct Fig. 11.13. Note the accumulation of electron density in the internuclear region.

An important feature of the probability density becomes apparent when we examine the internuclear region, where both atomic orbitals have similar amplitudes. According to eqn 11.10, the total probability density is proportional to the sum of

1 A^2, the probability density if the electron were confined to the atomic orbital A.

2 B^2, the probability density if the electron were confined to the atomic orbital B.

3 $2AB$, an extra contribution to the density.

This last contribution, the **overlap density**, is crucial, because it represents an enhancement of the probability of finding the electron in the internuclear region. The enhancement can be traced to the constructive interference of the two atomic orbitals: each has a positive amplitude in the internuclear region, so the total amplitude is greater there than if the electron were confined to a single atomic orbital.

We shall frequently make use of the result that *electrons accumulate in regions where atomic orbitals overlap and interfere constructively*. The conventional explanation is based on the notion that accumulation of electron density between the nuclei puts the electron in a position where it interacts strongly with both nuclei. Hence, the energy of the molecule is lower than that of the separate atoms, where each electron can interact strongly with only one nucleus. This conventional explanation, however, has been called into question, because shifting an electron away from a nucleus into the internuclear region *raises* its potential energy. The modern (and still controversial) explanation does not emerge from the simple LCAO treatment given here. It seems that, at the same time as the electron shifts into the internuclear region, the atomic orbitals shrink. This orbital shrinkage improves the electron–nucleus attraction more than it is decreased by the migration to the internuclear region, so there is a net lowering of potential energy. The kinetic energy of the electron is also modified because the curvature of the wavefunction is changed, but the change in kinetic energy is dominated by the change in potential energy. Throughout the following discussion we ascribe the strength of chemical bonds to the accumulation of electron density in the internuclear region. We leave open the question whether in molecules more complicated than H_2^+ the true source of energy lowering is that accumulation itself or some indirect but related effect.

The σ orbital we have described is an example of a **bonding orbital**, an orbital which, if occupied, helps to bind two atoms together. Specifically, we label it 1σ as it is the σ orbital of lowest energy. An electron that occupies a σ orbital is called a **σ electron**, and if that is the only electron present in the molecule (as in the ground state of H_2^+), then we report the configuration of the molecule as $1\sigma^1$.

The energy $E_{1\sigma}$ of the 1σ orbital is (see Problem 11.23):

$$E_{1\sigma} = E_{\mathrm{H}1s} + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{j+k}{1+S} \tag{11.11}$$

where

$$S = \int AB\,\mathrm{d}\tau = \left\{1 + \frac{R}{a_0} + \frac{1}{3}\left(\frac{R}{a_0}\right)^2\right\}\mathrm{e}^{-R/a_0} \tag{11.12a}$$

$$j = \frac{e^2}{4\pi\varepsilon_0}\int \frac{A^2}{r_\mathrm{B}}\mathrm{d}\tau = \frac{e^2}{4\pi\varepsilon_0 R}\left\{1 - \left(1 + \frac{R}{a_0}\right)\mathrm{e}^{-2R/a_0}\right\} \tag{11.12b}$$

$$k = \frac{e^2}{4\pi\varepsilon_0}\int \frac{AB}{r_\mathrm{B}}\mathrm{d}\tau = \frac{e^2}{4\pi\varepsilon_0 a_0}\left(1 + \frac{R}{a_0}\right)\mathrm{e}^{-R/a_0} \tag{11.12c}$$

We can interpret the preceding integrals as follows:

1 All three integrals are positive and decline towards zero at large internuclear separations (S and k on account of the exponential term, j on account of the factor $1/R$).

2 The integral j is a measure of the interaction between a nucleus and electron density centred on the other nucleus.

3 The integral k is a measure of the interaction between a nucleus and the excess probability in the internuclear region arising from overlap.

Figure 11.16 is a plot of $E_{1\sigma}$ against R relative to the energy of the separated atoms. The energy of the 1σ orbital decreases as the internuclear separation decreases from large values because electron density accumulates in the internuclear region as the constructive interference between the atomic orbitals increases (Fig. 11.17). However, at small separations there is too little space between the nuclei for significant accumulation of electron density there. In addition, the nucleus–nucleus repulsion (which is proportional to $1/R$) becomes large. As a result, the energy of the molecule rises at short distances, and there is a minimum in the potential energy curve. Calculations on H_2^+ give $R_\mathrm{e} = 130$ pm and $D_\mathrm{e} = 1.77$ eV (171 kJ mol^{-1}); the experimental values are 106 pm and 2.6 eV, so this simple LCAO-MO description of the molecule, while inaccurate, is not absurdly wrong.

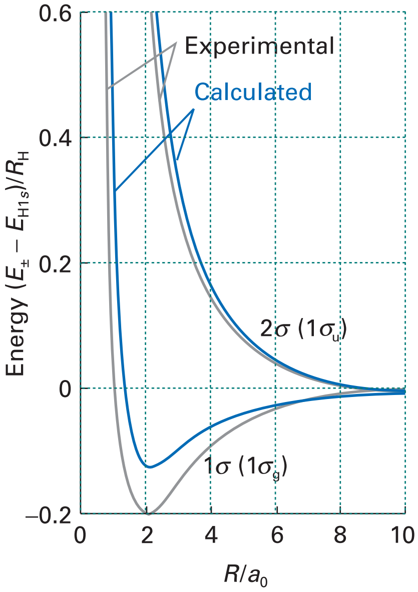


Fig. 11.16 The calculated and experimental molecular potential energy curves for a hydrogen molecule-ion showing the variation of the energy of the molecule as the bond length is changed. The alternative g,u notation is introduced in Section 11.3c.

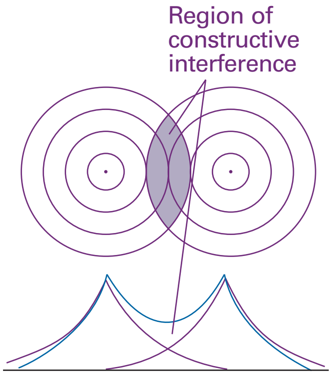


Fig. 11.17 A representation of the constructive interference that occurs when two H1s orbitals overlap and form a bonding σ orbital.

(c) Antibonding orbitals

The linear combination ψ_- in eqn 11.7 corresponds to a higher energy than that of ψ_+. Because it is also a σ orbital we label it 2σ. This orbital has an internuclear nodal plane where A and B cancel exactly (Figs. 11.18 and 11.19). The probability density is

$$\psi_-^2 = N^2(A^2 + B^2 - 2AB) \tag{11.13}$$

There is a reduction in probability density between the nuclei due to the $-2AB$ term (Fig. 11.20); in physical terms, there is destructive interference where the two atomic orbitals overlap. The 2σ orbital is an example of an **antibonding orbital**, an orbital that, if occupied, contributes to a reduction in the cohesion between two atoms and helps to raise the energy of the molecule relative to the separated atoms.

The energy $E_{2\sigma}$ of the 2σ antibonding orbital is given by (see Problem 11.23)

$$E_{2\sigma} = E_{\mathrm{H}1s} + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{j-k}{1-S} \tag{11.14}$$

where the integrals S, j, and k are given by eqn 11.12. The variation of $E_{2\sigma}$ with R is shown in Fig. 11.16, where we see the destabilizing effect of an antibonding electron.

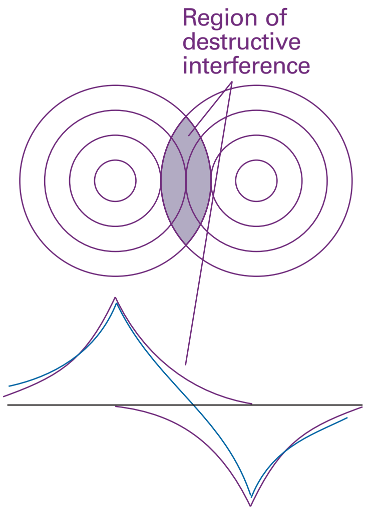


Fig. 11.18 A representation of the destructive interference that occurs when two H1*s* orbitals overlap and form an antibonding 2σ orbital.

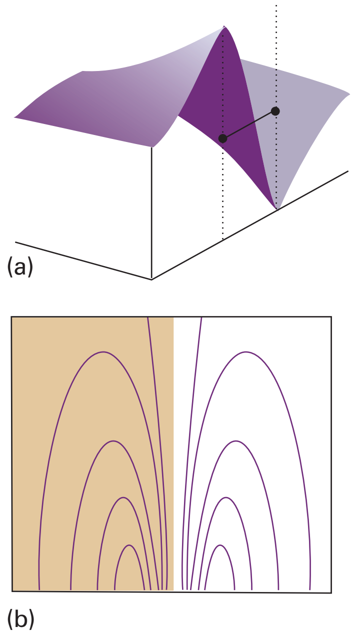


Fig. 11.19 (a) The amplitude of the antibonding molecular orbital in a hydrogen molecule-ion in a plane containing the two nuclei and (b) a contour representation of the amplitude. Note the internuclear node.

Exploration Plot the 2σ orbital for different values of the internuclear distance. Point to the features of the 2σ orbital that lead to antibonding.

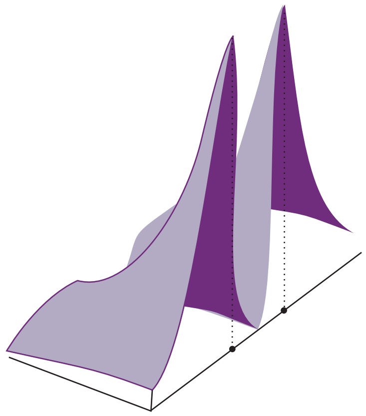


Fig. 11.20 The electron density calculated by forming the square of the wavefunction used to construct Fig. 11.19. Note the elimination of electron density from the internuclear region.

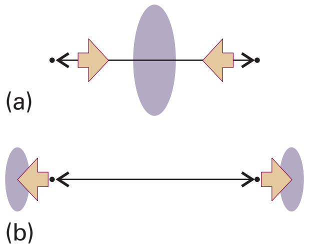


Fig. 11.21 A partial explanation of the origin of bonding and antibonding effects. (a) In a bonding orbital, the nuclei are attracted to the accumulation of electron density in the internuclear region. (b) In an antibonding orbital, the nuclei are attracted to an accumulation of electron density outside the internuclear region.

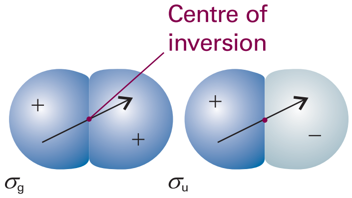


Fig. 11.22 The parity of an orbital is even (g) if its wavefunction is unchanged under inversion through the centre of symmetry of the molecule, but odd (u) if the wavefunction changes sign. Heteronuclear diatomic molecules do not have a centre of inversion, so for them the g, u classification is irrelevant.

The effect is partly due to the fact that an antibonding electron is excluded from the internuclear region, and hence is distributed largely outside the bonding region. In effect, whereas a bonding electron pulls two nuclei together, an antibonding electron pulls the nuclei apart (Fig. 11.21). Figure 11.16 also shows another feature that we draw on later: $|E_- - E_{\mathrm{H1}s}| > |E_+ - E_{\mathrm{H1}s}|$, which indicates that *the antibonding orbital is more antibonding than the bonding orbital is bonding*. This important conclusion stems in part from the presence of the nucleus–nucleus repulsion ($e^2/4\pi\varepsilon_0R$): this contribution raises the energy of both molecular orbitals. Antibonding orbitals are often labelled with an asterisk (*), so the 2σ orbital could also be denoted 2σ* (and read '2 sigma star').

For homonuclear diatomic molecules, it is helpful to describe a molecular orbital by identifying its **inversion symmetry**, the behaviour of the wavefunction when it is inverted through the centre (more formally, the centre of inversion) of the molecule. Thus, if we consider any point on the bonding σ orbital, and then project it through the centre of the molecule and out an equal distance on the other side, then we arrive at an identical value of the wavefunction (Fig. 11.22). This so-called **gerade symmetry** (from the German word for 'even') is denoted by a subscript g, as in σ_g. On the other hand, the same procedure applied to the antibonding 2σ orbital results in the same size but opposite sign of the wavefunction. This **ungerade symmetry** ('odd symmetry') is denoted by a subscript u, as in σ_u. This inversion symmetry classification is not applicable to diatomic molecules formed by atoms from two different elements (such as CO) because these molecules do not have a centre of inversion. When using the g,u notation, each set of orbitals of the same inversion symmetry are labelled separately so, whereas 1σ becomes $1\sigma_g$, its antibonding partner, which so far we have called 2σ, is the first orbital of a different symmetry, and is denoted $1\sigma_u$. The general rule is that *each set of orbitals of the same symmetry designation is labelled separately*.

Comment 11.4

When treating homonuclear diatomic molecules, we shall favour the more modern notation that focuses attention on the symmetry properties of the orbital. For all other molecules, we shall use asterisks from time to time to denote antibonding orbitals.

11.4 Homonuclear diatomic molecules

In Chapter 10 we used the hydrogenic atomic orbitals and the building-up principle to deduce the ground electronic configurations of many-electron atoms. We now do the same for many-electron diatomic molecules by using the H_2^+ molecular orbitals. The general procedure is to construct molecular orbitals by combining the available atomic orbitals. The electrons supplied by the atoms are then accommodated in the orbitals so as to achieve the lowest overall energy subject to the constraint of the Pauli exclusion principle, that no more than two electrons may occupy a single orbital (and then must be paired). As in the case of atoms, if several degenerate molecular orbitals are available, we add the electrons singly to each individual orbital before doubly occupying any one orbital (because that minimizes electron–electron repulsions). We also take note of Hund's maximum multiplicity rule (Section 10.4) that, if electrons do occupy different degenerate orbitals, then a lower energy is obtained if they do so with parallel spins.

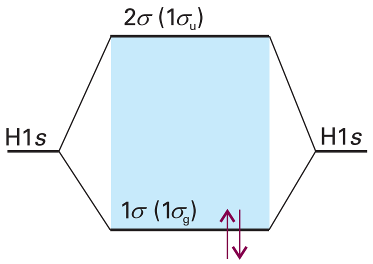


Fig. 11.23 A molecular orbital energy level diagram for orbitals constructed from the overlap of H1*s* orbitals; the separation of the levels corresponds to that found at the equilibrium bond length. The ground electronic configuration of H_2 is obtained by accommodating the two electrons in the lowest available orbital (the bonding orbital).

(a) σ orbitals

Consider H_2, the simplest many-electron diatomic molecule. Each H atom contributes a 1*s* orbital (as in H_2^+), so we can form the $1\sigma_g$ and $1\sigma_u$ orbitals from them, as we have seen already. At the experimental internuclear separation these orbitals will have the energies shown in Fig. 11.23, which is called a **molecular orbital energy level diagram**. Note that from two atomic orbitals we can build two molecular orbitals. In general, from *N* atomic orbitals we can build *N* molecular orbitals.

There are two electrons to accommodate, and both can enter $1\sigma_g$ by pairing their spins, as required by the Pauli principle (see the following *Justification*). The ground-state configuration is therefore $1\sigma_g^2$ and the atoms are joined by a bond consisting of an electron pair in a bonding σ orbital. This approach shows that an electron pair, which was the focus of Lewis's account of chemical bonding, represents the maximum number of electrons that can enter a bonding molecular orbital.

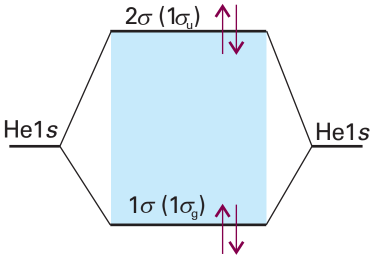


Fig. 11.24 The ground electronic configuration of the hypothetical four-electron molecule He_2 has two bonding electrons and two antibonding electrons. It has a higher energy than the separated atoms, and so is unstable.

Justification 11.2 *Electron pairing in MO theory*

The spatial wavefunction for two electrons in a bonding molecular orbital ψ such as the bonding orbital in eqn 11.7, is $\psi(1)\psi(2)$. This two-electron wavefunction is obviously symmetric under interchange of the electron labels. To satisfy the Pauli principle, it must be multiplied by the antisymmetric spin state $\alpha(1)\beta(2)-\beta(1)\alpha(2)$ to give the overall antisymmetric state

$$\psi(1,2)=\psi(1)\psi(2)\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}$$

Because $\alpha(1)\beta(2)-\beta(1)\alpha(2)$ corresponds to paired electron spins, we see that two electrons can occupy the same molecular orbital (in this case, the bonding orbital) only if their spins are paired.

Comment 11.5

Diatomic helium 'molecules' have been prepared: they consist of pairs of atoms held together by weak van der Waals forces of the type described in Chapter 18.

The same argument shows why He does not form diatomic molecules. Each He atom contributes a 1*s* orbital, so $1\sigma_g$ and $1\sigma_u$ molecular orbitals can be constructed. Although these orbitals differ in detail from those in H_2, the general shape is the same, and we can use the same qualitative energy level diagram in the discussion. There are four electrons to accommodate. Two can enter the $1\sigma_g$ orbital, but then it is full, and the next two must enter the $1\sigma_u$ orbital (Fig. 11.24). The ground electronic configuration of He_2 is therefore $1\sigma_g^2 1\sigma_u^2$. We see that there is one bond and one antibond. Because an antibond is slightly more antibonding than a bond is bonding, an He_2 molecule has a higher energy than the separated atoms, so it is unstable relative to the individual atoms.

We shall now see how the concepts we have introduced apply to homonuclear diatomic molecules in general. In elementary treatments, only the orbitals of the valence shell are used to form molecular orbitals so, for molecules formed with atoms from Period 2 elements, only the 2*s* and 2*p* atomic orbitals are considered.

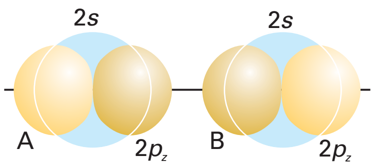


Fig. 11.25 According to molecular orbital theory, σ orbitals are built from all orbitals that have the appropriate symmetry. In homonuclear diatomic molecules of Period 2, that means that two 2*s* and two $2p_z$ orbitals should be used. From these four orbitals, four molecular orbitals can be built.

A general principle of molecular orbital theory is that *all orbitals of the appropriate symmetry contribute to a molecular orbital.* Thus, to build σ orbitals, we form linear combinations of all atomic orbitals that have cylindrical symmetry about the internuclear axis. These orbitals include the 2*s* orbitals on each atom and the $2p_z$ orbitals on the two atoms (Fig. 11.25). The general form of the σ orbitals that may be formed is therefore

$$\psi = c_{A2s}\chi_{A2s} + c_{B2s}\chi_{B2s} + c_{A2p_z}\chi_{A2p_z} + c_{B2p_z}\chi_{B2p_z} \tag{11.15}$$

From these four atomic orbitals we can form four molecular orbitals of σ symmetry by an appropriate choice of the coefficients *c*.

The procedure for calculating the coefficients will be described in Section 11.6. At this stage we adopt a simpler route, and suppose that, because the 2*s* and $2p_z$ orbitals have distinctly different energies, they may be treated separately. That is, the four σ orbitals fall approximately into two sets, one consisting of two molecular orbitals of the form

$$\psi = c_{A2s}\chi_{A2s} + c_{B2s}\chi_{B2s} \tag{11.16a}$$

and another consisting of two orbitals of the form

$$\psi = c_{A2p_z}\chi_{A2p_z} + c_{B2p_z}\chi_{B2p_z} \tag{11.16b}$$

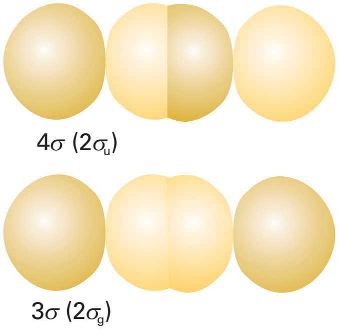


Fig. 11.26 A representation of the composition of bonding and antibonding σ orbitals built from the overlap of *p* orbitals. These illustrations are schematic.

Because atoms A and B are identical, the energies of their 2*s* orbitals are the same, so the coefficients are equal (apart from a possible difference in sign); the same is true of the $2p_z$ orbitals. Therefore, the two sets of orbitals have the form $\chi_{A2s} \pm \chi_{B2s}$ and $\chi_{A2p_z} \pm \chi_{B2p_z}$.

Comment 11.6

Note that we number only the molecular orbitals formed from atomic orbitals in the valence shell. In an alternative system of notation, $1\sigma_g$ and $1\sigma_u$ are used to designate the molecular orbitals formed from the core 1*s* orbitals of the atoms; the orbitals we are considering would then be labelled starting from 2.

The 2*s* orbitals on the two atoms overlap to give a bonding and an antibonding σ orbital ($1\sigma_g$ and $1\sigma_u$, respectively) in exactly the same way as we have already seen for 1*s* orbitals. The two $2p_z$ orbitals directed along the internuclear axis overlap strongly. They may interfere either constructively or destructively, and give a bonding or antibonding σ orbital, respectively (Fig. 11.26). These two σ orbitals are labelled $2\sigma_g$ and $2\sigma_u$, respectively. In general, note how the numbering follows the order of increasing energy.

(b) π orbitals

Now consider the $2p_x$ and $2p_y$ orbitals of each atom. These orbitals are perpendicular to the internuclear axis and may overlap broadside-on. This overlap may be constructive or destructive, and results in a bonding or an antibonding **π orbital** (Fig. 11.27). The notation π is the analogue of *p* in atoms, for when viewed along the axis of the molecule, a π orbital looks like a *p* orbital, and has one unit of orbital angular momentum around the internuclear axis. The two $2p_x$ orbitals overlap to give a bonding and antibonding π_x orbital, and the two $2p_y$ orbitals overlap to give two π_y orbitals. The π_x and π_y bonding orbitals are degenerate; so too are their antibonding partners. We also see from Fig. 11.27 that a bonding π orbital has odd parity and is denoted π_u and an antibonding π orbital has even parity, denoted π_g.

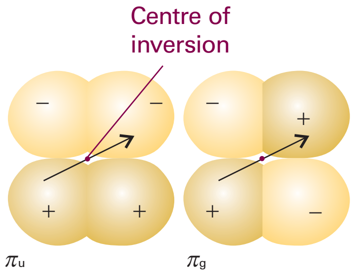


Fig. 11.27 A schematic representation of the structure of π bonding and antibonding molecular orbitals. The figure also shows that the bonding π orbital has odd parity, whereas the antiboding π orbital has even parity.

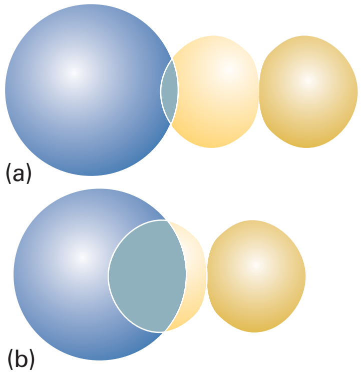


Fig. 11.28 (a) When two orbitals are on atoms that are far apart, the wavefunctions are small where they overlap, so S is small. (b) When the atoms are closer, both orbitals have significant amplitudes where they overlap, and S may approach 1. Note that S will decrease again as the two atoms approach more closely than shown here, because the region of negative amplitude of the p orbital starts to overlap the positive overlap of the s orbital. When the centres of the atoms coincide, $S = 0$.

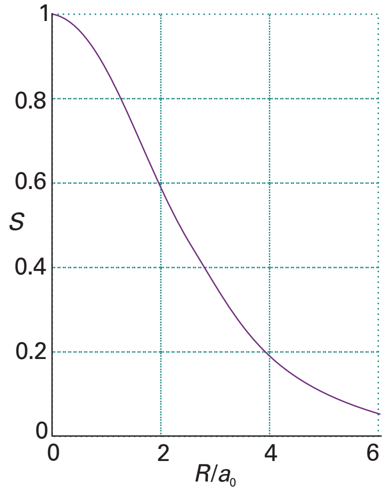


Fig. 11.29 The overlap integral, S, between two H1s orbitals as a function of their separation R.

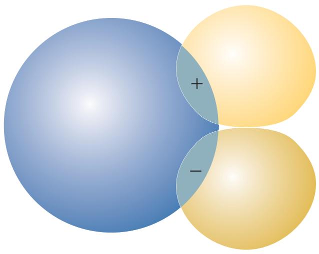


Fig. 11.30 A p orbital in the orientation shown here has zero net overlap ($S = 0$) with the s orbital at all internuclear separations.

(c) The overlap integral

The extent to which two atomic orbitals on different atoms overlap is measured by the **overlap integral**, S:

$$S = \int \chi_A^* \chi_B \, d\tau \tag*{[11.17]}$$

If the atomic orbital χ_A on A is small wherever the orbital χ_B on B is large, or vice versa, then the product of their amplitudes is everywhere small and the integral—the sum of these products—is small (Fig. 11.28). If χ_A and χ_B are simultaneously large in some region of space, then S may be large. If the two normalized atomic orbitals are identical (for instance, 1s orbitals on the same nucleus), then $S = 1$. In some cases, simple formulas can be given for overlap integrals and the variation of S with bond length plotted (Fig. 11.29). It follows that $S = 0.59$ for two H1s orbitals at the equilibrium bond length in H_2^+, which is an unusually large value. Typical values for orbitals with $n = 2$ are in the range 0.2 to 0.3.

Now consider the arrangement in which an s orbital is superimposed on a p_x orbital of a different atom (Fig. 11.30). The integral over the region where the product of orbitals is positive exactly cancels the integral over the region where the product of orbitals is negative, so overall $S = 0$ exactly. Therefore, there is no net overlap between the s and p orbitals in this arrangement.

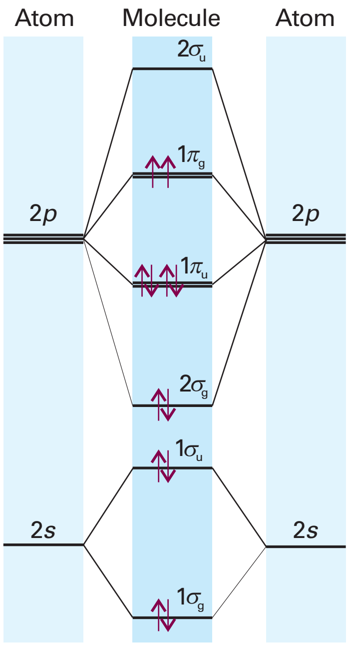


Fig. 11.31 The molecular orbital energy level diagram for homonuclear diatomic molecules. The lines in the middle are an indication of the energies of the molecular orbitals that can be formed by overlap of atomic orbitals. As remarked in the text, this diagram should be used for O_2 (the configuration shown) and F_2.

(d) The electronic structures of homonuclear diatomic molecules

To construct the molecular orbital energy level diagram for Period 2 homonuclear diatomic molecules, we form eight molecular orbitals from the eight valence shell orbitals (four from each atom). In some cases, π orbitals are less strongly bonding than σ orbitals because their maximum overlap occurs off-axis. This relative weakness suggests that the molecular orbital energy level diagram ought to be as shown in Fig. 11.31. However, we must remember that we have assumed that 2s and 2p_z orbitals

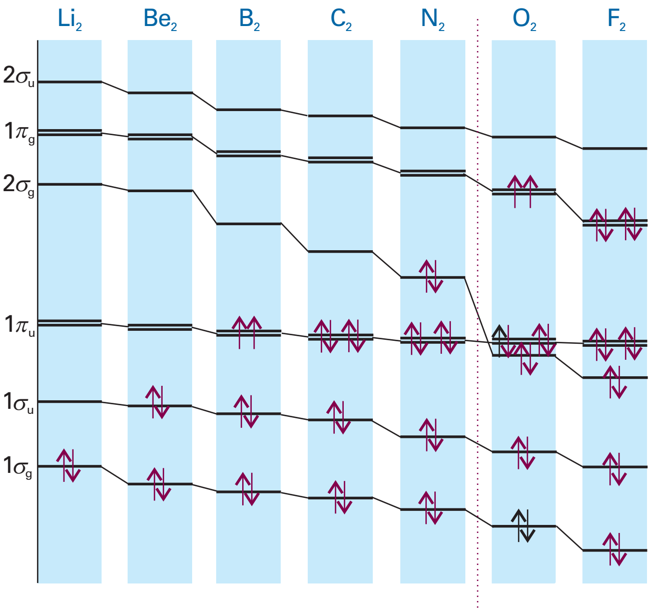


Fig. 11.32 The variation of the orbital energies of Period 2 homonuclear diatomics.

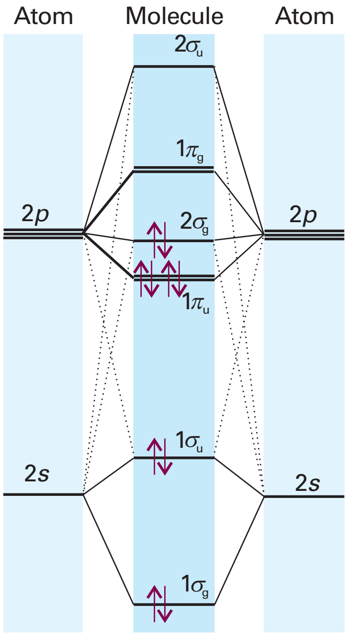


Fig. 11.33 An alternative molecular orbital energy level diagram for homonuclear diatomic molecules. As remarked in the text, this diagram should be used for diatomics up to and including N_2 (the configuration shown).

contribute to different sets of molecular orbitals whereas in fact all four atomic orbitals contribute jointly to the four σ orbitals. Hence, there is no guarantee that this order of energies should prevail, and it is found experimentally (by spectroscopy) and by detailed calculation that the order varies along Period 2 (Fig. 11.32). The order shown in Fig. 11.33 is appropriate as far as N_2, and Fig. 11.31 applies for O_2 and F_2. The relative order is controlled by the separation of the 2*s* and 2*p* orbitals in the atoms, which increases across the group. The consequent switch in order occurs at about N_2.

With the orbitals established, we can deduce the ground configurations of the molecules by adding the appropriate number of electrons to the orbitals and following the building-up rules. Anionic species (such as the peroxide ion, O_2^{2-}) need more electrons than the parent neutral molecules; cationic species (such as O_2^+) need fewer.

Consider N_2, which has 10 valence electrons. Two electrons pair, occupy, and fill the $1\sigma_g$ orbital; the next two occupy and fill the $1\sigma_u$ orbital. Six electrons remain. There are two $1\pi_u$ orbitals, so four electrons can be accommodated in them. The last two enter the $2\sigma_g$ orbital. Therefore, the ground-state configuration of N_2 is $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2$.

A measure of the net bonding in a diatomic molecule is its **bond order**, *b*:

$$b = \tfrac{1}{2}(n - n^*) \qquad [11.18]$$

where *n* is the number of electrons in bonding orbitals and n^* is the number of electrons in antibonding orbitals. Thus each electron pair in a bonding orbital increases the bond order by 1 and each pair in an antibonding orbital decreases *b* by 1. For H_2, $b = 1$, corresponding to a single bond, H—H, between the two atoms. In He_2, $b = 0$, and there is no bond. In N_2, $b = \tfrac{1}{2}(8 - 2) = 3$. This bond order accords with the Lewis structure of the molecule (:N≡N:).

The ground-state electron configuration of O_2, with 12 valence electrons, is based on Fig. 11.31, and is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$. Its bond order is 2. According to the building-up principle, however, the two $1\pi_g$ electrons occupy different orbitals: one will enter $1\pi_{u,x}$ and the other will enter $1\pi_{u,y}$. Because the electrons are in different orbitals, they will have parallel spins. Therefore, we can predict that an O_2 molecule will have a net spin angular momentum $S = 1$ and, in the language introduced in Section 10.7, be in a triplet state. Because electron spin is the source of a magnetic moment, we can go on to predict that oxygen should be paramagnetic. This prediction, which VB theory does not make, is confirmed by experiment.

Synoptic table 11.2* Bond lengths

Bond	Order	R_e/pm
HH	1	74.14
NN	3	109.76
HCl	1	127.45
CH	1	114
CC	1	*154*
CC	2	*134*
CC	3	*120*

* More values will be found in the *Data section*. Numbers in italics are mean values for polyatomic molecules.

Synoptic table 11.3* Bond dissociation energies

Bond	Order	D_0/(kJ mol^{-1})
HH	1	432.1
NN	3	941.7
HCl	1	427.7
CH	1	*435*
CC	1	*368*
CC	2	*720*
CC	3	*962*

* More values will be found in the *Data section*. Numbers in italics are mean values for polyatomic molecules.

Comment 11.7

A paramagnetic substance tends to move into a magnetic field; a diamagnetic substance tends to move out of one. Paramagnetism, the rarer property, arises when the molecules have unpaired electron spins. Both properties are discussed in more detail in Chapter 20.

An F_2 molecule has two more electrons than an O_2 molecule. Its configuration is therefore $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^4$ and $b = 1$. We conclude that F_2 is a singly-bonded molecule, in agreement with its Lewis structure. The hypothetical molecule dineon, Ne_2, has two further electrons: its configuration is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2 2\sigma_u^2$ and $b = 0$. The zero bond order is consistent with the monatomic nature of Ne.

The bond order is a useful parameter for discussing the characteristics of bonds, because it correlates with bond length and bond strength. For bonds between atoms of a given pair of elements:

1 The greater the bond order, the shorter the bond.

2 The greater the bond order, the greater the bond strength.

Table 11.2 lists some typical bond lengths in diatomic and polyatomic molecules. The strength of a bond is measured by its bond dissociation energy, D_e, the energy required to separate the atoms to infinity. Table 11.3 lists some experimental values of dissociation energies.

Comment 11.8

Bond dissociation energies are commonly used in thermodynamic cycles, where bond enthalpies, $\Delta_{\text{bond}}H^{\ominus}$, should be used instead. It follows from the same kind of argument used in *Justification 10.7* concerning ionization enthalpies, that

$$X_2(g) \rightarrow 2\,X(g) \qquad \Delta_{\text{bond}}H^{\ominus}(T) = D_e + \tfrac{3}{2}RT$$

To derive this relation, we have supposed that the molar constant-pressure heat capacity of X_2 is $\frac{7}{2}R$ (*Molecular interpretation 2.2*) for there is a contribution from two rotational modes as well as three translational modes.

Example 11.2 *Judging the relative bond strengths of molecules and ions*

Judge whether N_2^+ is likely to have a larger or smaller dissociation energy than N_2.

Method Because the molecule with the larger bond order is likely to have the larger dissociation energy, compare their electronic configurations and assess their bond orders.

Answer From Fig. 11.33, the electron configurations and bond orders are

$$\begin{array}{lll} N_2 & 1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2 & b = 3 \\ N_2^+ & 1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^1 & b = 2\frac{1}{2} \end{array}$$

Because the cation has the smaller bond order, we expect it to have the smaller dissociation energy. The experimental dissociation energies are 945 kJ mol^{-1} for N_2 and 842 kJ mol^{-1} for N_2^+.

Self-test 11.4 Which can be expected to have the higher dissociation energy, F_2 or F_2^+? [F_2^+]

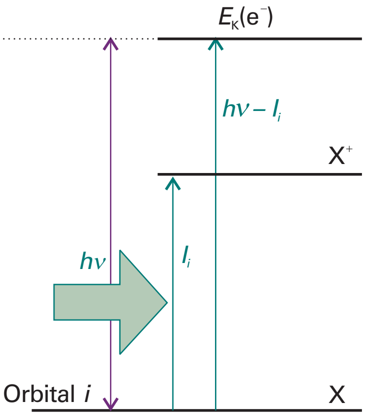


Fig. 11.34 An incoming photon carries an energy $h\nu$; an energy I_i is needed to remove an electron from an orbital i, and the difference appears as the kinetic energy of the electron.

(e) Photoelectron spectroscopy

So far we have treated molecular orbitals as purely theoretical constructs, but is there experimental evidence for their existence? **Photoelectron spectroscopy** (PES) measures the ionization energies of molecules when electrons are ejected from different orbitals by absorption of a photon of the proper energy, and uses the information to infer the energies of molecular orbitals. The technique is also used to study solids, and in Chapter 25 we shall see the important information that it gives about species at or on surfaces.

Because energy is conserved when a photon ionizes a sample, the energy of the incident photon $h\nu$ must be equal to the sum of the ionization energy, I, of the sample and the kinetic energy of the **photoelectron**, the ejected electron (Fig. 11.34):

$$h\nu = \tfrac{1}{2}m_e v^2 + I \tag{11.19}$$

This equation (which is like the one used for the photoelectric effect, Section 8.2a) can be refined in two ways. First, photoelectrons may originate from one of a number of different orbitals, and each one has a different ionization energy. Hence, a series of different kinetic energies of the photoelectrons will be obtained, each one satisfying

$$h\nu = \tfrac{1}{2}m_e v^2 + I_i \tag{11.20}$$

where I_i is the ionization energy for ejection of an electron from an orbital i. Therefore, by measuring the kinetic energies of the photoelectrons, and knowing ν, these ionization energies can be determined. Photoelectron spectra are interpreted in terms of an approximation called **Koopmans' theorem**, which states that the ionization energy I_i is equal to the orbital energy of the ejected electron (formally: $I_i = -\varepsilon_i$). That is, we can identify the ionization energy with the energy of the orbital from which it is ejected. Similarly, the energy of unfilled ('virtual orbitals') is related to the electron affinity. The theorem is only an approximation because it ignores the fact that the remaining electrons adjust their distributions when ionization occurs.

The ionization energies of molecules are several electronvolts even for valence electrons, so it is essential to work in at least the ultraviolet region of the spectrum and with wavelengths of less than about 200 nm. Much work has been done with radiation generated by a discharge through helium: the He(I) line ($1s^12p^1 \rightarrow 1s^2$) lies at 58.43 nm, corresponding to a photon energy of 21.22 eV. Its use gives rise to the technique of **ultraviolet photoelectron spectroscopy** (UPS). When core electrons are being studied, photons of even higher energy are needed to expel them: X–rays are used, and the technique is denoted XPS.

The kinetic energies of the photoelectrons are measured using an electrostatic deflector that produces different deflections in the paths of the photoelectrons as they pass between charged plates (Fig. 11.35). As the field strength is increased, electrons of different speeds, and therefore kinetic energies, reach the detector. The electron flux can be recorded and plotted against kinetic energy to obtain the photoelectron spectrum.

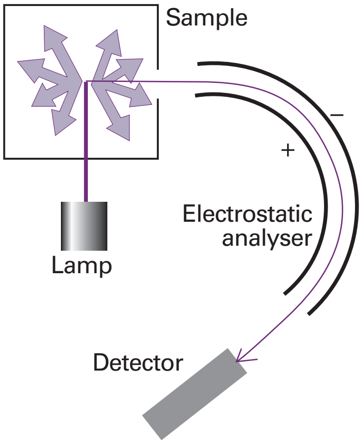


Fig. 11.35 A photoelectron spectrometer consists of a source of ionizing radiation (such as a helium discharge lamp for UPS and an X-ray source for XPS), an electrostatic analyser, and an electron detector. The deflection of the electron path caused by the analyser depends on their speed.

Illustration 11.1 *Interpreting a photoelectron spectrum*

Photoelectrons ejected from N_2 with He(I) radiation had kinetic energies of 5.63 eV (1 eV = 8065.5 cm^{-1}). Helium(I) radiation of wavelength 58.43 nm has wavenumber $1.711 \times 10^5\ cm^{-1}$ and therefore corresponds to an energy of 21.22 eV. Then, from eqn 11.20, 21.22 eV = 5.63 eV + I_i, so I_i = 15.59 eV. This ionization energy is the energy needed to remove an electron from the occupied molecular orbital with the highest energy of the N_2 molecule, the $2\sigma_g$ bonding orbital (see Fig. 11.33).

Self-test 11.5 Under the same circumstances, photoelectrons are also detected at 4.53 eV. To what ionization energy does that correspond? Suggest an origin.

[16.7 eV, $1\pi_u$]

11.5 Heteronuclear diatomic molecules

The electron distribution in the covalent bond between the atoms in a heteronuclear diatomic molecule is not shared evenly because it is energetically favourable for the electron pair to be found closer to one atom than the other. This imbalance results in a **polar bond**, a covalent bond in which the electron pair is shared unequally by the two atoms. The bond in HF, for instance, is polar, with the electron pair closer to the F atom. The accumulation of the electron pair near the F atom results in that atom having a net negative charge, which is called a **partial negative charge** and denoted $\delta-$. There is a matching **partial positive charge**, $\delta+$, on the H atom.

(a) Polar bonds

A polar bond consists of two electrons in an orbital of the form

$$\psi = c_A A + c_B B \qquad (11.21)$$

with unequal coefficients. The proportion of the atomic orbital A in the bond is $|c_A|^2$ and that of B is $|c_B|^2$. A nonpolar bond has $|c_A|^2 = |c_B|^2$ and a pure ionic bond has one coefficient zero (so the species A^+B^- would have $c_A = 0$ and $c_B = 1$). The atomic orbital with the lower energy makes the larger contribution to the bonding molecular orbital. The opposite is true of the antibonding orbital, for which the dominant component comes from the atomic orbital with higher energy.

These points can be illustrated by considering HF, and judging the energies of the atomic orbitals from the ionization energies of the atoms. The general form of the molecular orbitals is

$$\psi = c_H \chi_H + c_F \chi_F \qquad (11.22)$$

where χ_H is an H1s orbital and χ_F is an F2p orbital. The H1s orbital lies 13.6 eV below the zero of energy (the separated proton and electron) and the F2p orbital lies at 18.6 eV (Fig. 11.36). Hence, the bonding σ orbital in HF is mainly F2p and the antibonding σ orbital is mainly H1s orbital in character. The two electrons in the bonding orbital are most likely to be found in the F2p orbital, so there is a partial negative charge on the F atom and a partial positive charge on the H atom.

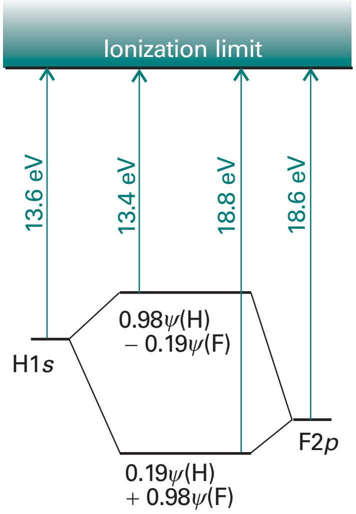


Fig. 11.36 The atomic orbital energy levels of H and F atoms and the molecular orbitals they form.

(b) Electronegativity

The charge distribution in bonds is commonly discussed in terms of the **electronegativity**, χ, of the elements involved (there should be little danger of confusing this use of χ with its use to denote an atomic orbital, which is another common convention). The electronegativity is a parameter introduced by Linus Pauling as a measure of the power of an atom to attract electrons to itself when it is part of a compound. Pauling used valence-bond arguments to suggest that an appropriate numerical scale of electronegativities could be defined in terms of bond dissociation energies, D, in electronvolts and proposed that the difference in electronegativities could be expressed as

$$|\chi_A - \chi_B| = 0.102\{D(\text{A—B}) - \tfrac{1}{2}[D(\text{A—A}) + D(\text{B—B})]\}^{1/2} \qquad [11.23]$$

Electronegativities based on this definition are called **Pauling electronegativities**. A list of Pauling electronegativities is given in Table 11.4. The most electronegative

Synoptic table 11.4* Pauling electronegativities

Element	χ_P
H	2.2
C	2.6
N	3.0
O	3.4
F	4.0
Cl	3.2
Cs	0.79

* More values will be found in the *Data section*.

elements are those close to fluorine; the least are those close to caesium. It is found that the greater the difference in electronegativities, the greater the polar character of the bond. The difference for HF, for instance, is 1.78; a C—H bond, which is commonly regarded as almost nonpolar, has an electronegativity difference of 0.51.

The spectroscopist Robert Mulliken proposed an alternative definition of electronegativity. He argued that an element is likely to be highly electronegative if it has a high ionization energy (so it will not release electrons readily) and a high electron affinity (so it is energetically favorable to acquire electrons). The **Mulliken electronegativity scale** is therefore based on the definition

$$\chi_M = \tfrac{1}{2}(I + E_{ea}) \qquad [11.24]$$

where I is the ionization energy of the element and E_{ea} is its electron affinity (both in electronvolts, Section 10.4e). The Mulliken and Pauling scales are approximately in line with each other. A reasonably reliable conversion between the two is $\chi_P = 1.35\chi_M^{1/2} - 1.37$.

(c) The variation principle

A more systematic way of discussing bond polarity and finding the coefficients in the linear combinations used to build molecular orbitals is provided by the **variation principle**:

> If an arbitrary wavefunction is used to calculate the energy, the value calculated is never less than the true energy.

This principle is the basis of all modern molecular structure calculations (Section 11.7). The arbitrary wavefunction is called the **trial wavefunction**. The principle implies that, if we vary the coefficients in the trial wavefunction until the lowest energy is achieved (by evaluating the expectation value of the hamiltonian for each wavefunction), then those coefficients will be the best. We might get a lower energy if we use a more complicated wavefunction (for example, by taking a linear combination of several atomic orbitals on each atom), but we shall have the optimum (minimum energy) molecular orbital that can be built from the chosen **basis set**, the given set of atomic orbitals.

Comment 11.9
The name ‘secular’ is derived from the Latin word for age or generation. The term comes via astronomy, where the same equations appear in connection with slowly accumulating modifications of planetary orbits.

The method can be illustrated by the trial wavefunction in eqn 11.21. We show in the *Justification* below that the coefficients are given by the solutions of the two **secular equations**

$$(\alpha_A - E)c_A + (\beta - ES)c_B = 0 \qquad (11.25a)$$

$$(\beta - ES)c_A + (\alpha_B - E)c_B = 0 \qquad (11.25b)$$

The parameter α is called a **Coulomb integral**. It is negative and can be interpreted as the energy of the electron when it occupies A (for α_A) or B (for α_B). In a homonuclear diatomic molecule, $\alpha_A = \alpha_B$. The parameter β is called a **resonance integral** (for classical reasons). It vanishes when the orbitals do not overlap, and at equilibrium bond lengths it is normally negative.

Justification 11.3 *The variation principle applied to a heteronuclear diatomic molecule*

The trial wavefunction in eqn 11.21 is real but not normalized because at this stage the coefficients can take arbitrary values. Therefore, we can write $\psi^* = \psi$ but do not assume that $\int\psi^2 d\tau = 1$. The energy of the trial wavefunction is the expectation value of the energy operator (the hamiltonian, $\hat{H}$, Section 8.5):

$$E=\frac{\displaystyle\int\psi^{\star}\hat{H}\psi\,\mathrm{d}\tau}{\displaystyle\int\psi^{\star}\psi\,\mathrm{d}\tau} \tag{11.26}$$

We must search for values of the coefficients in the trial function that minimize the value of E. This is a standard problem in calculus, and is solved by finding the coefficients for which

$$\frac{\partial E}{\partial c_{\mathrm{A}}}=0 \qquad \frac{\partial E}{\partial c_{\mathrm{B}}}=0$$

The first step is to express the two integrals in terms of the coefficients. The denominator is

$$\begin{aligned}\int\psi^2\,\mathrm{d}\tau&=\int(c_{\mathrm{A}}A+c_{\mathrm{B}}B)^2\,\mathrm{d}\tau\\&=c_{\mathrm{A}}^2\int A^2\,\mathrm{d}\tau+c_{\mathrm{B}}^2\int B^2\,\mathrm{d}\tau+2c_{\mathrm{A}}c_{\mathrm{B}}\int AB\,\mathrm{d}\tau\\&=c_{\mathrm{A}}^2+c_{\mathrm{B}}^2+2c_{\mathrm{A}}c_{\mathrm{B}}S\end{aligned}$$

because the individual atomic orbitals are normalized and the third integral is the overlap integral S (eqn 11.17). The numerator is

$$\begin{aligned}\int\psi\hat{H}\psi\,\mathrm{d}\tau&=\int(c_{\mathrm{A}}A+c_{\mathrm{B}}B)\hat{H}(c_{\mathrm{A}}A+c_{\mathrm{B}}B)\,\mathrm{d}\tau\\&=c_{\mathrm{A}}^2\int A\hat{H}A\,\mathrm{d}\tau+c_{\mathrm{B}}^2\int B\hat{H}B\,\mathrm{d}\tau+c_{\mathrm{A}}c_{\mathrm{B}}\int A\hat{H}B\,\mathrm{d}\tau+c_{\mathrm{A}}c_{\mathrm{B}}\int B\hat{H}A\,\mathrm{d}\tau\end{aligned}$$

There are some complicated integrals in this expression, but we can combine them all into the parameters

$$\alpha_{\mathrm{A}}=\int A\hat{H}A\,\mathrm{d}\tau \qquad \alpha_{\mathrm{B}}=\int B\hat{H}B\,\mathrm{d}\tau \tag*{[11.27]}$$

$$\beta=\int A\hat{H}B\,\mathrm{d}\tau=\int B\hat{H}A\,\mathrm{d}\tau\ \text{(by the hermiticity of }\hat{H}\text{)}$$

Then

$$\int\psi\hat{H}\psi\,\mathrm{d}\tau=c_{\mathrm{A}}^2\alpha_{\mathrm{A}}+c_{\mathrm{B}}^2\alpha_{\mathrm{B}}+2c_{\mathrm{A}}c_{\mathrm{B}}\beta$$

The complete expression for E is

$$E=\frac{c_{\mathrm{A}}^2\alpha_{\mathrm{A}}+c_{\mathrm{B}}^2\alpha_{\mathrm{B}}+2c_{\mathrm{A}}c_{\mathrm{B}}\beta}{c_{\mathrm{A}}^2+c_{\mathrm{B}}^2+2c_{\mathrm{A}}c_{\mathrm{B}}S} \tag{11.28}$$

Its minimum is found by differentiation with respect to the two coefficients and setting the results equal to 0. After a bit of work, we obtain

$$\frac{\partial E}{\partial c_{\mathrm{A}}}=\frac{2\times(c_{\mathrm{A}}\alpha_{\mathrm{A}}-c_{\mathrm{A}}E+c_{\mathrm{B}}\beta-c_{\mathrm{B}}SE)}{c_{\mathrm{A}}^2+c_{\mathrm{B}}^2+2c_{\mathrm{A}}c_{\mathrm{B}}S}=0$$

$$\frac{\partial E}{\partial c_{\mathrm{B}}}=\frac{2\times(c_{\mathrm{B}}\alpha_{\mathrm{B}}-c_{\mathrm{B}}E+c_{\mathrm{A}}\beta-c_{\mathrm{A}}SE)}{c_{\mathrm{A}}^2+c_{\mathrm{B}}^2+2c_{\mathrm{A}}c_{\mathrm{B}}S}=0$$

For the derivatives to vanish, the numerators of the expressions above must vanish. That is, we must find values of c_A and c_B that satisfy the conditions

$$c_A\alpha_A - c_AE + c_B\beta - c_BSE = (\alpha_A - E)c_A + (\beta - ES)c_B = 0$$
$$c_A\beta - c_ASE + c_B\alpha_B - c_BE = (\beta - ES)c_A + (\alpha_B - E)c_B = 0$$

which are the secular equations (eqn 11.25).

To solve the secular equations for the coefficients we need to know the energy E of the orbital. As for any set of simultaneous equations, the secular equations have a solution if the **secular determinant**, the determinant of the coefficients, is zero; that is, if

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha_B - E \end{vmatrix} = 0 \tag{11.29}$$

Comment 11.10
We need to know that a 2 × 2 determinant expands as follows:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

This determinant expands to a quadratic equation in E (see *Illustration 11.2*). Its two roots give the energies of the bonding and antibonding molecular orbitals formed from the atomic orbitals and, according to the variation principle, the lower root is the best energy achievable with the given basis set.

Illustration 11.2 *Using the variation principle (1)*

To find the energies E of the bonding and antibonding orbitals of a homonuclear diatomic molecule set with $\alpha_A = \alpha_B = \alpha$ in eqn 11.29 and get

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0$$

The solutions of this equation are

$$E_\pm = \frac{\alpha \pm \beta}{1 \pm S}$$

The values of the coefficients in the linear combination are obtained by solving the secular equations using the two energies obtained from the secular determinant. The lower energy (E_+ in the *Illustration*) gives the coefficients for the bonding molecular orbital, the upper energy (E_-) the coefficients for the antibonding molecular orbital. The secular equations give expressions for the ratio of the coefficients in each case, so we need a further equation in order to find their individual values. This equation is obtained by demanding that the best wavefunction should also be normalized. This condition means that, at this final stage, we must also ensure that

$$\int \psi^2 \, d\tau = c_A^2 + c_B^2 + 2c_Ac_BS = 1 \tag{11.30}$$

Illustration 11.3 *Using the variation principle (2)*

To find the values of the coefficients c_A and c_B in the linear combination that corresponds to the energy E_+ from *Illustration 11.2*, we use eqn 11.28 (with $\alpha_A = \alpha_B = \alpha$) to write

$$E_+ = \frac{\alpha + \beta}{1 + S} = \frac{c_A^2\alpha + c_B^2\alpha + 2c_Ac_B\beta}{c_A^2 + c_B^2 + 2c_Ac_BS}$$

Now we use the normalization condition, eqn 11.30, to set $c_A^2 + c_B^2 + 2c_Ac_BS = 1$, and so write

$$\frac{\alpha+\beta}{1+S} = (c_A^2 + c_B^2)\alpha + 2c_Ac_B\beta$$

This expression implies that

$$c_A^2 + c_B^2 = 2c_Ac_B = \frac{1}{1+S} \qquad \text{and} \qquad |c_A| = \frac{1}{\{2(1+S)\}^{1/2}} \qquad c_B = c_A$$

Proceeding in a similar way to find the coefficients in the linear combination that corresponds to the energy E_-,we write

$$E_- = \frac{\alpha-\beta}{1-S} = (c_A^2 + c_B^2)\alpha + 2c_Ac_B\beta$$

which implies that

$$c_A^2 + c_B^2 = -2c_Ac_B = \frac{1}{1-S} \qquad \text{and} \qquad |c_A| = \frac{1}{\{2(1-S)\}^{1/2}} \qquad c_B = -c_A$$

(d) Two simple cases

The complete solutions of the secular equations are very cumbersome, even for 2×2 determinants, but there are two cases where the roots can be written down very simply.

We saw in *Illustrations* 11.2 and 11.3 that, when the two atoms are the same, and we can write $\alpha_A = \alpha_B = \alpha$, the solutions are

$$E_+ = \frac{\alpha+\beta}{1+S} \qquad c_A = \frac{1}{\{2(1+S)\}^{1/2}} \qquad c_B = c_A \tag{11.31a}$$

$$E_- = \frac{\alpha-\beta}{1-S} \qquad c_A = \frac{1}{\{2(1-S)\}^{1/2}} \qquad c_B = -c_A \tag{11.31b}$$

In this case, the bonding orbital has the form

$$\psi_+ = \frac{A+B}{\{2(1+S)\}^{1/2}} \tag{11.32a}$$

and the corresponding antibonding orbital is

$$\psi_- = \frac{A-B}{\{2(1-S)\}^{1/2}} \tag{11.32b}$$

in agreement with the discussion of homonuclear diatomics we have already given, but now with the normalization constant in place.

The second simple case is for a heteronuclear diatomic molecule but with $S = 0$ (a common approximation in elementary work). The secular determinant is then

$$\begin{vmatrix} \alpha_A - E & \beta \\ \beta & \alpha_B - E \end{vmatrix} = (\alpha_A - E)(\alpha_B - E) - \beta^2 = 0$$

The solutions can be expressed in terms of the parameter ζ (zeta), with

$$\zeta = \tfrac{1}{2}\arctan\frac{2|\beta|}{\alpha_B - \alpha_A} \tag{11.33}$$

and are

$$E_- = \alpha_B - \beta \tan \zeta \qquad \psi_- = -A \sin \zeta + B \cos \zeta \tag{11.34a}$$

$$E_+ = \alpha_A + \beta \tan \zeta \qquad \psi_+ = A \cos \zeta + B \sin \zeta \tag{11.34b}$$

An important feature revealed by these solutions is that as the energy difference $|\alpha_B - \alpha_A|$ between the interacting atomic orbitals increases, the value of ζ decreases. We show in the following *Justification* that, when the energy difference is very large, in the sense that $|\alpha_B - \alpha_A| \gg 2|\beta|$, the energies of the resulting molecular orbitals differ only slightly from those of the atomic orbitals, which implies in turn that the bonding and antibonding effects are small. That is, the strongest bonding and antibonding effects are obtained when the two contributing orbitals have closely similar energies. The difference in energy between core and valence orbitals is the justification for neglecting the contribution of core orbitals to bonding. The core orbitals of one atom have a similar energy to the core orbitals of the other atom; but core–core interaction is largely negligible because the overlap between them (and hence the value of β) is so small.

Comment 11.11

For $x \ll 1$, we can write: $\sin x \approx x$, $\cos x \approx 1$, $\tan x \approx x$, and $\arctan x = \tan^{-1} x \approx x$.

Justification 11.4 *Bonding and antibonding effects in heteronuclear diatomic molecules*

When $|\alpha_B - \alpha_A| \gg 2|\beta|$ and $2|\beta|/|\alpha_B - \alpha_A| \ll 1$, we can write $\arctan 2|\beta|/|\alpha_B - \alpha_A| \approx 2|\beta|/|\alpha_B - \alpha_A|$ and, from eqn 11.33, $\zeta \approx |\beta|/(\alpha_B - \alpha_A)$. It follows that $\tan \zeta \approx |\beta|/(\alpha_B - \alpha_A)$. Noting that β is normally a negative number, so that $\beta/|\beta| = -1$, we can use eqn 11.34 to write

$$E_- = \alpha_B + \frac{\beta^2}{\alpha_B - \alpha_A} \qquad E_+ = \alpha_A - \frac{\beta^2}{\alpha_B - \alpha_A}$$

(In Problem 11.25 you are invited to derive these expressions via a different route.) It follows that, when the energy difference between the atomic orbitals is so large that $|\alpha_B - \alpha_A| \gg 2|\beta|$, the energies of the two molecular orbitals are $E_- \approx \alpha_B$ and $E_+ \approx \alpha_A$.

Now we consider the behaviour of the wavefunctions in the limit of large $|\alpha_B - \alpha_A|$, when $\zeta \ll 1$. In this case, $\sin \zeta \approx \zeta$ and $\cos \zeta \approx 1$ and, from eqn 11.34, we write $\psi_- \approx B$ and $\psi_+ \approx A$. That is, the molecular orbitals are respectively almost pure B and almost pure A.

Example 11.3 *Calculating the molecular orbitals of HF*

Calculate the wavefunctions and energies of the σ orbitals in the HF molecule, taking $\beta = -1.0$ eV and the following ionization energies: H1*s*: 13.6 eV, F2*s*: 40.2 eV, F2*p*: 17.4 eV.

Method Because the F2*p* and H1*s* orbitals are much closer in energy than the F2*s* and H1*s* orbitals, to a first approximation neglect the contribution of the F2*s* orbital. To use eqn 11.34, we need to know the values of the Coulomb integrals α_H and α_F. Because these integrals represent the energies of the H1*s* and F2*p* electrons, respectively, they are approximately equal to (the negative of) the ionization energies of the atoms. Calculate ζ from eqn 11.33 (with A identified as F and B as H), and then write the wavefunctions by using eqn 11.34.

Answer Setting $\alpha_H = -13.6$ eV and $\alpha_F = -17.4$ eV gives $\tan 2\zeta = 0.58$; so $\zeta = 13.9°$. Then

$$E_- = -13.4\text{ eV} \qquad \psi_- = 0.97\chi_{\mathrm{H}} - 0.24\chi_{\mathrm{F}}$$
$$E_+ = -17.6\text{ eV} \qquad \psi_+ = 0.24\chi_{\mathrm{H}} + 0.97\chi_{\mathrm{F}}$$

Notice how the lower energy orbital (the one with energy −17.6 eV) has a composition that is more F2*p* orbital than H1*s*, and that the opposite is true of the higher energy, antibonding orbital.

Self-test 11.6 The ionization energy of Cl is 13.1 eV; find the form and energies of the σ orbitals in the HCl molecule using $\beta = -1.0$ eV.

$[E_- = -12.8\text{ eV}, \psi_- = -0.62\chi_{\mathrm{H}} + 0.79\chi_{\mathrm{Cl}}; E_+ = -13.9\text{ eV}, \psi_+ = 0.79\chi_{\mathrm{H}} + 0.62\chi_{\mathrm{Cl}}]$

IMPACT ON BIOCHEMISTRY

I11.1 The biochemical reactivity of O_2, N_2, and NO

We can now see how some of these concepts are applied to diatomic molecules that play a vital biochemical role. At sea level, air contains approximately 23.1 per cent O_2 and 75.5 per cent N_2 by mass. Molecular orbital theory predicts—correctly—that O_2 has unpaired electron spins and, consequently, is a reactive component of the Earth's atmosphere; its most important biological role is as an oxidizing agent. By contrast N_2, the major component of the air we breathe, is so stable (on account of the triple bond connecting the atoms) and unreactive that *nitrogen fixation*, the reduction of atmospheric N_2 to NH_3, is among the most thermodynamically demanding of biochemical reactions, in the sense that it requires a great deal of energy derived from metabolism. So taxing is the process that only certain bacteria and archaea are capable of carrying it out, making nitrogen available first to plants and other microorganisms in the form of ammonia. Only after incorporation into amino acids by plants does nitrogen adopt a chemical form that, when consumed, can be used by animals in the synthesis of proteins and other nitrogen-containing molecules.

The reactivity of O_2, while important for biological energy conversion, also poses serious physiological problems. During the course of metabolism, some electrons escape from complexes I, II, and III of the respiratory chain and reduce O_2 to superoxide ion, O_2^-. The ground-state electronic configuration of O_2^- is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^3$, so the ion is a radical with a bond order $b = \frac{3}{2}$. We predict that the superoxide ion is a reactive species that must be scavenged to prevent damage to cellular components. The enzyme superoxide dismutase protects cells by catalysing the disproportionation (or dismutation) of O_2^- into O_2 and H_2O_2:

$$2\,O_2^- + 2\,H^+ \rightarrow H_2O_2 + O_2$$

However, H_2O_2 (hydrogen peroxide), formed by the reaction above and by leakage of electrons out of the respiratory chain, is a powerful oxidizing agent and also harmful to cells. It is metabolized further by catalases and peroxidases. A catalase catalyses the reaction

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

and a peroxidase reduces hydrogen peroxide to water by oxidizing an organic molecule. For example, the enzyme glutathione peroxidase catalyses the reaction

$$2\,\text{glutathione}_{\text{red}} + H_2O_2 \rightarrow \text{glutathione}_{\text{ox}} + 2\,H_2O$$

There is growing evidence for the involvement of the damage caused by reactive oxygen species (ROS), such as O_2^-, H_2O_2, and ·OH (the hydroxyl radical), in the mechanism of ageing and in the development of cardiovascular disease, cancer,

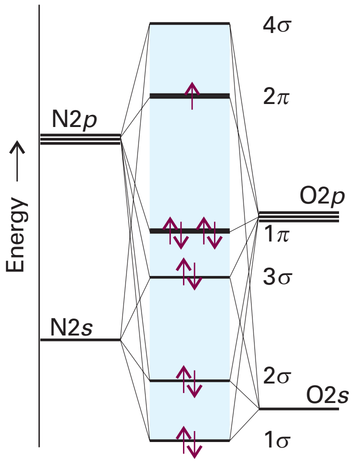


Fig. 11.37 The molecular orbital energy level diagram for NO.

stroke, inflammatory disease, and other conditions. For this reason, much effort has been expended on studies of the biochemistry of *antioxidants*, substances that can either deactivate ROS directly (as glutathione does) or halt the progress of cellular damage through reactions with radicals formed by processes initiated by ROS. Important examples of antioxidants are vitamin C (ascorbic acid), vitamin E (α-tocopherol), and uric acid.

Nitric oxide (nitrogen monoxide, NO) is a small molecule that diffuses quickly between cells, carrying chemical messages that help initiate a variety of processes, such as regulation of blood pressure, inhibition of platelet aggregation, and defence against inflammation and attacks to the immune system. The molecule is synthesized from the amino acid arginine in a series of reactions catalysed by nitric oxide synthase and requiring O_2 and NADPH.

Figure 11.37 shows the bonding scheme in NO and illustrates a number of points we have made about heteronuclear diatomic molecules. The ground configuration is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 2\pi^1$. The 3σ and 1π orbitals are predominantly of O character as that is the more electronegative element. The highest-energy occupied orbital is 2π, contains one electron, and has more N character than O character. It follows that NO is a radical with an unpaired electron that can be regarded as localized more on the N atom than on the O atom. The lowest-energy occupied orbital is 4σ, which is also localized predominantly on N.

Because NO is a radical, we expect it to be reactive. Its half-life is estimated at approximately 1–5 s, so it needs to be synthesized often in the cell. As we saw above, there is a biochemical price to be paid for the reactivity of biological radicals. Like O_2, NO participates in some reactions that are not beneficial to the cell. Indeed, the radicals O_2^- and NO combine to form the peroxynitrite ion:

$$\mathrm{NO}\cdot + \mathrm{O}_2^-\cdot \rightarrow \mathrm{ONOO}^-$$

where we have shown the unpaired electrons explicitly. The peroxynitrite ion is a reactive oxygen species that damages proteins, DNA, and lipids, possibly leading to heart disease, amyotrophic lateral sclerosis (Lou Gehrig's disease), Alzheimer's disease, and multiple sclerosis. Note that the structure of the ion is consistent with the bonding scheme in Fig. 11.37: because the unpaired electron in NO is slightly more localized on the N atom, we expect that atom to form a bond with an O atom from the O_2^- ion.

Molecular orbitals for polyatomic systems

The molecular orbitals of polyatomic molecules are built in the same way as in diatomic molecules, the only difference being that we use more atomic orbitals to construct them. As for diatomic molecules, polyatomic molecular orbitals spread over the entire molecule. A molecular orbital has the general form

$$\psi = \sum_i c_i \chi_i \qquad (11.35)$$

where χ_i is an atomic orbital and the sum extends over all the valence orbitals of all the atoms in the molecule. To find the coefficients, we set up the secular equations and the secular determinant, just as for diatomic molecules, solve the latter for the energies, and then use these energies in the secular equations to find the coefficients of the atomic orbitals for each molecular orbital.

The principal difference between diatomic and polyatomic molecules lies in the greater range of shapes that are possible: a diatomic molecule is necessarily linear, but a triatomic molecule, for instance, may be either linear or angular with a characteristic bond angle. The shape of a polyatomic molecule—the specification of its bond lengths and its bond angles—can be predicted by calculating the total energy of the molecule for a variety of nuclear positions, and then identifying the conformation that corresponds to the lowest energy.

11.6 The Hückel approximation

Molecular orbital theory takes large molecules and extended aggregates of atoms, such as solid materials, in its stride. First we shall consider conjugated molecules, in which there is an alternation of single and double bonds along a chain of carbon atoms. Although the classification of an orbital as σ or π is strictly valid only in linear molecules, as will be familiar from introductory chemistry courses, it is also used to denote the local symmetry with respect to a given A—B bond axis.

The π molecular orbital energy level diagrams of conjugated molecules can be constructed using a set of approximations suggested by Erich Hückel in 1931. In his approach, the π orbitals are treated separately from the σ orbitals, and the latter form a rigid framework that determines the general shape of the molecule. All the C atoms are treated identically, so all the Coulomb integrals α for the atomic orbitals that contribute to the π orbitals are set equal. For example, in ethene, we take the σ bonds as fixed, and concentrate on finding the energies of the single π bond and its companion antibond.

(a) Ethene and frontier orbitals

We express the π orbitals as LCAOs of the C2*p* orbitals that lie perpendicular to the molecular plane. In ethene, for instance, we would write

$$\psi = c_A A + c_B B \tag{11.36}$$

where the *A* is a C2*p* orbital on atom A, and so on. Next, the optimum coefficients and energies are found by the variation principle as explained in Section 11.5. That is, we have to solve the secular determinant, which in the case of ethene is eqn 11.29 with $\alpha_A = \alpha_B = \alpha$:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \tag{11.37}$$

The roots of this determinant can be found very easily (they are the same as those in *Illustration 11.2*). In a modern computation all the resonance integrals and overlap integrals would be included, but an indication of the molecular orbital energy level diagram can be obtained very readily if we make the following additional **Hückel approximations**:

1 All overlap integrals are set equal to zero.

2 All resonance integrals between non-neighbours are set equal to zero.

3 All remaining resonance integrals are set equal (to β).

These approximations are obviously very severe, but they let us calculate at least a general picture of the molecular orbital energy levels with very little work. The assumptions result in the following structure of the secular determinant:

1 All diagonal elements: $\alpha - E$.

2 Off-diagonal elements between neighbouring atoms: β.

3 All other elements: 0.

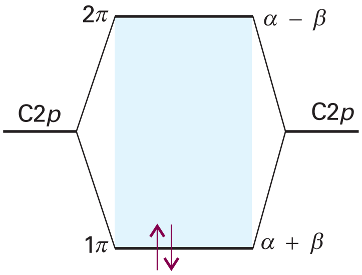


Fig. 11.38 The Hückel molecular orbital energy levels of ethene. Two electrons occupy the lower π orbital.

These approximations lead to

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0 \tag{11.38}$$

The roots of the equation are

$$E_{\pm} = \alpha \pm \beta \tag{11.39}$$

The + sign corresponds to the bonding combination (β is negative) and the − sign corresponds to the antibonding combination (Fig. 11.38). We see the effect of neglecting overlap by comparing this result with eqn 11.31.

The building-up principle leads to the configuration $1\pi^2$, because each carbon atom supplies one electron to the π system. The **highest occupied molecular orbital** in ethene, its HOMO, is the 1π orbital; the **lowest unfilled molecular orbital**, its LUMO, is the 2π orbital (or, as it is sometimes denoted, the $2\pi^*$ orbital). These two orbitals jointly form the **frontier orbitals** of the molecule. The frontier orbitals are important because they are largely responsible for many of the chemical and spectroscopic properties of the molecule. For example, we can estimate that $2|\beta|$ is the $\pi^* \leftarrow \pi$ excitation energy of ethene, the energy required to excite an electron from the 1π to the 2π orbital. The constant β is often left as an adjustable parameter; an approximate value for π bonds formed from overlap of two C2p atomic orbitals is about −2.4 eV (−230 kJ mol^{-1}).

(b) The matrix formulation of the Hückel method

In preparation for making Hückel theory more sophisticated and readily applicable to bigger molecules, we need to reformulate it in terms of matrices and vectors (see *Appendix 2*). We have seen that the secular equations that we have to solve for a two-atom system have the form

$$(H_{\mathrm{AA}} - E_i S_{\mathrm{AA}})c_{i,\mathrm{A}} + (H_{\mathrm{AB}} - E_i S_{\mathrm{AB}})c_{i,\mathrm{B}} = 0 \tag{11.40a}$$

$$(H_{\mathrm{BA}} - E_i S_{\mathrm{BA}})c_{i,\mathrm{A}} + (H_{\mathrm{BB}} - E_i S_{\mathrm{BB}})c_{i,\mathrm{B}} = 0 \tag{11.40b}$$

where the eigenvalue E_i corresponds to a wavefunction of the form $\psi_i = c_{i,\mathrm{A}}A + c_{i,\mathrm{B}}B$. (These expressions generalize eqn 11.25). There are two atomic orbitals, two eigenvalues, and two wavefunctions, so there are two pairs of secular equations, with the first corresponding to E_1 and ψ_1:

$$(H_{\mathrm{AA}} - E_1 S_{\mathrm{AA}})c_{1,\mathrm{A}} + (H_{\mathrm{AB}} - E_1 S_{\mathrm{AB}})c_{1,\mathrm{B}} = 0 \tag{11.41a}$$

$$(H_{\mathrm{BA}} - E_1 S_{\mathrm{BA}})c_{1,\mathrm{A}} + (H_{\mathrm{BB}} - E_1 S_{\mathrm{BB}})c_{1,\mathrm{B}} = 0 \tag{11.41b}$$

and another corresponding to E_2 and ψ_2:

$$(H_{\mathrm{AA}} - E_2 S_{\mathrm{AA}})c_{2,\mathrm{A}} + (H_{\mathrm{AB}} - E_2 S_{\mathrm{AB}})c_{2,\mathrm{B}} = 0 \tag{11.41c}$$

$$(H_{\mathrm{BA}} - E_2 S_{\mathrm{BA}})c_{2,\mathrm{A}} + (H_{\mathrm{BB}} - E_2 S_{\mathrm{BB}})c_{2,\mathrm{B}} = 0 \tag{11.41d}$$

If we introduce the following matrices and column vectors

$$\boldsymbol{H} = \begin{pmatrix} H_{\mathrm{AA}} & H_{\mathrm{AB}} \\ H_{\mathrm{BA}} & H_{\mathrm{BB}} \end{pmatrix} \qquad \boldsymbol{S} = \begin{pmatrix} S_{\mathrm{AA}} & S_{\mathrm{AB}} \\ S_{\mathrm{BA}} & S_{\mathrm{BB}} \end{pmatrix} \qquad \boldsymbol{c}_i = \begin{pmatrix} c_{i,\mathrm{A}} \\ c_{i,\mathrm{B}} \end{pmatrix} \tag{11.42}$$

then each pair of equations may be written more succinctly as

$$(\boldsymbol{H} - E_i \boldsymbol{S})\boldsymbol{c}_i = 0 \qquad \text{or} \qquad \boldsymbol{H}\boldsymbol{c}_i = \boldsymbol{S}\boldsymbol{c}_i E_i \tag{11.43}$$

where $\boldsymbol{H}$ is the hamiltonian matrix and $\boldsymbol{S}$ is the overlap matrix. To proceed with the calculation of the eigenvalues and coefficients, we introduce the matrices

$$\boldsymbol{C} = (\boldsymbol{c}_1 \quad \boldsymbol{c}_2) = \begin{pmatrix} c_{1,\mathrm{A}} & c_{2,\mathrm{A}} \\ c_{1,\mathrm{B}} & c_{2,\mathrm{B}} \end{pmatrix} \qquad \boldsymbol{E} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \qquad [11.44]$$

for then the entire set of equations we have to solve can be expressed as

$$\boldsymbol{HC} = \boldsymbol{SCE} \tag{11.45}$$

Self-test 11.7 Show by carrying out the necessary matrix operations that eqn 11.45 is a representation of the system of equations consisting of eqns 11.41(a)–(d).

In the Hückel approximation, $H_{AA} = H_{BB} = \alpha$, $H_{AB} = H_{BA} = \beta$, and we neglect overlap, setting $\boldsymbol{S} = \boldsymbol{1}$, the unit matrix (with 1 on the diagonal and 0 elsewhere). Then

$$\boldsymbol{HC} = \boldsymbol{CE}$$

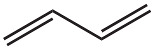
At this point, we multiply from the left by the inverse matrix $\boldsymbol{C}^{-1}$, and find

$$\boldsymbol{C}^{-1}\boldsymbol{HC} = \boldsymbol{E} \tag{11.46}$$

where we have used $\boldsymbol{C}^{-1}\boldsymbol{C} = \boldsymbol{1}$. In other words, to find the eigenvalues E_i, we have to find a transformation of $\boldsymbol{H}$ that makes it diagonal. This procedure is called **matrix diagonalization**. The diagonal elements then correspond to the eigenvalues E_i and the columns of the matrix $\boldsymbol{C}$ that brings about this diagonalization are the coefficients of the members of the **basis set**, the set of atomic orbitals used in the calculation, and hence give us the composition of the molecular orbitals. If there are N orbitals in the basis set (there are only two in our example), then there are N eigenvalues E_i and N corresponding column vectors $\boldsymbol{c}_i$. As a result, we have to solve N equations of the form $\boldsymbol{Hc}_i = \boldsymbol{Sc}_iE_i$ by diagonalization of the $N \times N$ matrix $\boldsymbol{H}$, as directed by eqn 11.46.

Example 11.4 *Finding the molecular orbitals by matrix diagonalization*

Set up and solve the matrix equations within the Hückel approximation for the π-orbitals of butadiene (**3**).



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Method The matrices will be four-dimensional for this four-atom system. Ignore overlap, and construct the matrix $\boldsymbol{H}$ by using the Hückel values α and β. Find the matrix $\boldsymbol{C}$ that diagonalizes $\boldsymbol{H}$: for this step, use mathematical software. Full details are given in *Appendix 2*.

Solution

$$\boldsymbol{H} = \begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{pmatrix} = \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}$$

Mathematical software then diagonalizes this matrix to

$$\boldsymbol{E} = \begin{pmatrix} \alpha + 1.62\beta & 0 & 0 & 0 \\ 0 & \alpha + 0.62\beta & 0 & 0 \\ 0 & 0 & \alpha - 0.62\beta & 0 \\ 0 & 0 & 0 & \alpha - 1.62\beta \end{pmatrix}$$

and the matrix that achieves the diagonalization is

$$\boldsymbol{C} = \begin{pmatrix} 0.372 & 0.602 & 0.602 & -0.372 \\ 0.602 & 0.372 & -0.372 & 0.602 \\ 0.602 & -0.372 & -0.372 & -0.602 \\ 0.372 & -0.602 & 0.602 & 0.372 \end{pmatrix}$$

We can conclude that the energies and molecular orbitals are

$$\begin{aligned}
&E_1 = \alpha + 1.62\beta && \psi_1 = 0.372\chi_A + 0.602\chi_B + 0.602\chi_C + 0.372\chi_D\\
&E_2 = \alpha + 0.62\beta && \psi_2 = 0.602\chi_A + 0.372\chi_B - 0.372\chi_C - 0.602\chi_D\\
&E_3 = \alpha - 0.62\beta && \psi_3 = 0.602\chi_A - 0.372\chi_B - 0.372\chi_C + 0.602\chi_D\\
&E_4 = \alpha - 1.62\beta && \psi_4 = -0.372\chi_A + 0.602\chi_B - 0.602\chi_C - 0.372\chi_D
\end{aligned}$$

where the C2*p* atomic orbitals are denoted by $\chi_A, \ldots, \chi_D$. Note that the orbitals are mutually orthogonal and, with overlap neglected, normalized.

Self-test 11.8 Repeat the exercise for the allyl radical, $\cdot CH_2{-}CH{=}CH_2$.

$[E = \alpha + 2^{1/2}\beta, \alpha, \alpha - 2^{1/2}\beta; \psi_1 = \tfrac{1}{2}\chi_A + (\tfrac{1}{2})^{1/2}\chi_B + \tfrac{1}{2}\chi_C,$
$\psi_2 = (\tfrac{1}{2})^{1/2}\chi_A - (\tfrac{1}{2})^{1/2}\chi_C, \psi_3 = \tfrac{1}{2}\chi_A - (\tfrac{1}{2})^{1/2}\chi_B + \tfrac{1}{2}\chi_C$

(c) Butadiene and π-electron binding energy

As we saw in the preceding example, the energies of the four LCAO-MOs for butadiene are

$$E = \alpha \pm 1.62\beta, \qquad \alpha \pm 0.62\beta \tag{11.47}$$

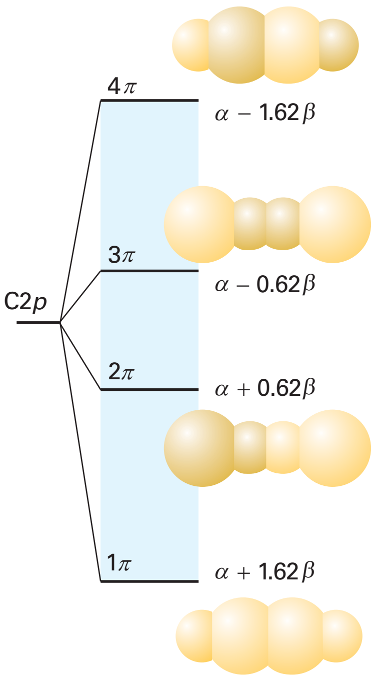


Fig. 11.39 The Hückel molecular orbital energy levels of butadiene and the top view of the corresponding π orbitals. The four *p* electrons (one supplied by each C) occupy the two lower π orbitals. Note that the orbitals are delocalized.

These orbitals and their energies are drawn in Fig. 11.39. Note that the greater the number of internuclear nodes, the higher the energy of the orbital. There are four electrons to accommodate, so the ground-state configuration is $1\pi^2 2\pi^2$. The frontier orbitals of butadiene are the 2π orbital (the HOMO, which is largely bonding) and the 3π orbital (the LUMO, which is largely antibonding). 'Largely' bonding means that an orbital has both bonding and antibonding interactions between various neighbours, but the bonding effects dominate. 'Largely antibonding' indicates that the antibonding effects dominate.

An important point emerges when we calculate the total **π-electron binding energy**, E_π, the sum of the energies of each π electron, and compare it with what we find in ethene. In ethene the total energy is

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

In butadiene it is

$$E_\pi = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = 4\alpha + 4.48\beta$$

Therefore, the energy of the butadiene molecule lies lower by 0.48β (about 110 kJ mol^{-1}) than the sum of two individual π bonds. This extra stabilization of a conjugated system is called the **delocalization energy**. A closely related quantity is the **π-bond formation energy**, the energy released when a π bond is formed. Because the contribution of α is the same in the molecule as in the atoms, we can find the π-bond formation energy from the π-electron binding energy by writing

$$E_{bf} = E_\pi - N\alpha \tag{11.48}$$

where *N* is the number of carbon atoms in the molecule. The π-bond formation energy in butadiene, for instance, is 4.48β.

Example 11.5 *Estimating the delocalization energy*

Use the Hückel approximation to find the energies of the π orbitals of cyclobutadiene, and estimate the delocalization energy.

Method Set up the secular determinant using the same basis as for butadiene, but note that atoms A and D are also now neighbours. Then solve for the roots of the secular equation and assess the total π-bond energy. For the delocalization energy, subtract from the total π-bond energy the energy of two π-bonds.

Answer The hamiltonian matrix is

$$\boldsymbol{H}=\begin{pmatrix}\alpha & \beta & 0 & \beta\\ \beta & \alpha & \beta & 0\\ 0 & \beta & \alpha & \beta\\ \beta & 0 & \beta & \alpha\end{pmatrix}$$

Diagonalization gives the energies of the orbitals as

$$E=\alpha+2\beta, \qquad \alpha, \qquad \alpha, \qquad \alpha-2\beta$$

Four electrons must be accommodated. Two occupy the lowest orbital (of energy $\alpha+2\beta$), and two occupy the doubly degenerate orbitals (of energy α). The total energy is therefore $4\alpha+4\beta$. Two isolated π bonds would have an energy $4\alpha+4\beta$; therefore, in this case, the delocalization energy is zero.

Self-test 11.9 Repeat the calculation for benzene. [See next subsection]

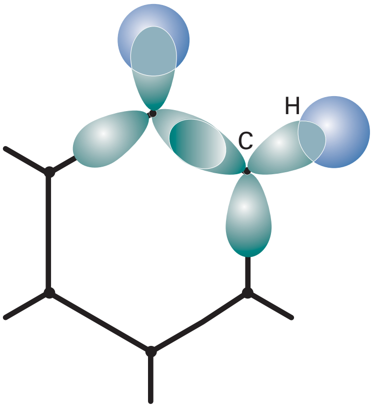


Fig. 11.40 The σ framework of benzene is formed by the overlap of Csp^2 hybrids, which fit without strain into a hexagonal arrangement.

(d) Benzene and aromatic stability

The most notable example of delocalization conferring extra stability is benzene and the aromatic molecules based on its structure. Benzene is often expressed in a mixture of valence-bond and molecular orbital terms, with typically valence-bond language used for its σ framework and molecular orbital language used to describe its π electrons.

First, the valence-bond component. The six C atoms are regarded as sp^2 hybridized, with a single unhydridized perpendicular $2p$ orbital. One H atom is bonded by (Csp^2,H1s) overlap to each C carbon, and the remaining hybrids overlap to give a regular hexagon of atoms (Fig. 11.40). The internal angle of a regular hexagon is 120°, so sp^2 hybridization is ideally suited for forming σ bonds. We see that benzene's hexagonal shape permits strain-free σ bonding.

Now consider the molecular orbital component of the description. The six C2p orbitals overlap to give six π orbitals that spread all round the ring. Their energies are calculated within the Hückel approximation by diagonalizing the hamiltonian matrix

$$\boldsymbol{H}=\begin{pmatrix}\alpha & \beta & 0 & 0 & 0 & \beta\\ \beta & \alpha & \beta & 0 & 0 & 0\\ 0 & \beta & \alpha & \beta & 0 & 0\\ 0 & 0 & \beta & \alpha & \beta & 0\\ 0 & 0 & 0 & \beta & \alpha & \beta\\ \beta & 0 & 0 & 0 & \beta & \alpha\end{pmatrix}$$

The MO energies, the eigenvalues of this matrix, are simply

$$E=\alpha\pm 2\beta, \alpha\pm\beta, \alpha\pm\beta \tag{11.49}$$

as shown in Fig. 11.41. The orbitals there have been given symmetry labels that we explain in Chapter 12. Note that the lowest energy orbital is bonding between all neighbouring atoms, the highest energy orbital is antibonding between each pair of neighbours, and the intermediate orbitals are a mixture of bonding, nonbonding, and antibonding character between adjacent atoms.

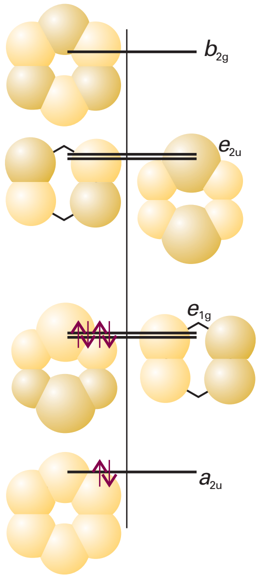


Fig. 11.41 The Hückel orbitals of benzene and the corresponding energy levels. The symmetry labels are explained in Chapter 12. The bonding and antibonding character of the delocalized orbitals reflects the numbers of nodes between the atoms. In the ground state, only the bonding orbitals are occupied.

We now apply the building-up principle to the π system. There are six electrons to accommodate (one from each C atom), so the three lowest orbitals (a_{2u} and the doubly-degenerate pair e_{1g}) are fully occupied, giving the ground-state configuration $a_{2u}^2 e_{1g}^4$. A significant point is that the only molecular orbitals occupied are those with net bonding character.

The π-electron energy of benzene is

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

If we ignored delocalization and thought of the molecule as having three isolated π bonds, it would be ascribed a π-electron energy of only $3(2\alpha + 2\beta) = 6\alpha + 6\beta$. The delocalization energy is therefore $2\beta \approx -460$ kJ mol^{-1}, which is considerably more than for butadiene. The π-bond formation energy in benzene is 8β.

This discussion suggests that aromatic stability can be traced to two main contributions. First, the shape of the regular hexagon is ideal for the formation of strong σ bonds: the σ framework is relaxed and without strain. Second, the π orbitals are such as to be able to accommodate all the electrons in bonding orbitals, and the delocalization energy is large.

11.7 Computational chemistry

The difficulties arising from the severe assumptions of Hückel method have been overcome by more sophisticated theories that not only calculate the shapes and energies of molecular orbitals but also predict with reasonable accuracy the structure and reactivity of molecules. The full treatment of molecular electronic structure is quite easy to formulate but difficult to implement. However, it has received an enormous amount of attention by chemists, and has become a keystone of modern chemical research. John Pople and Walter Kohn were awarded the Nobel Prize in Chemistry for 1998 for their contributions to the development of computational techniques for the elucidation of molecular structure and reactivity.

Comment 11.12
The web site contains links to sites where you may perform semi-empirical and *ab initio* calculations on simple molecules directly from your web browser.

(a) The Hartree–Fock equations

The starting point is to write down the many-electron wavefunction as a product of one-electron wavefunctions:

$$\Psi = \psi_{a,\alpha}(1)\psi_{a,\beta}(2)\ldots\psi_{z,\beta}(N)$$

This is the wavefunction for an N-electron closed-shell molecule in which electron 1 occupies molecular orbital ψ_a with spin α, electron 2 occupies molecular orbital ψ_a with spin β, and so on. However, the wavefunction must satisfy the Pauli principle and change sign under the permutation of any pair of electrons. To achieve this behaviour, we write the wavefunction as a sum of all possible permutations with the appropriate sign:

$$\Psi = \psi_{a,\alpha}(1)\psi_{a,\beta}(2)\ldots\psi_{z,\beta}(N) - \psi_{a,\alpha}(2)\psi_{a,\beta}(1)\ldots\psi_{z,\beta}(N) + \cdots$$

There are $N!$ terms in this sum, and the entire sum can be written as a determinant:

$$\Psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{a,\alpha}(1) & \psi_{a,\beta}(1) & \cdots & \cdots & \psi_{z,\beta}(1) \\ \psi_{a,\alpha}(2) & \psi_{a,\beta}(2) & \cdots & \cdots & \psi_{z,\beta}(2) \\ \vdots & \vdots & & & \vdots \\ \vdots & \vdots & & & \vdots \\ \psi_{a,\alpha}(N) & \psi_{a,\beta}(N) & \cdots & \cdots & \psi_{z,\beta}(N) \end{vmatrix} \qquad (11.50a)$$

The initial factor ensures that the wavefunction is normalized if the component molecular orbitals are normalized. To save the tedium of writing out large determinants, the wavefunction is normally written simply as

$$\Psi = (1/N!)^{1/2}\det|\psi_{a,\alpha}(1)\psi_{a,\beta}(2)\ldots\psi_{z,\beta}(N)| \qquad (11.50\text{b})$$

When the determinantal wavefunction is combined with the variation principle (Section 11.5c), the optimum wavefunctions, in the sense of corresponding to the lowest total energy, must satisfy the **Hartree–Fock equations**:

$$f_1\psi_{a,\sigma}(1) = \varepsilon\psi_{a,\sigma}(1) \qquad (11.51)$$

where σ is either α or β. The **Fock operator** f_1 is

$$f_1 = h_1 + \Sigma_j\{2J_j(1) - K_j(1)\} \qquad (11.52)$$

The three terms in this expression are the **core hamiltonian**

$$h_1 = -\frac{\hbar^2}{2m_\mathrm{e}}\nabla_1^2 - \sum_n \frac{Z_n e^2}{4\pi\varepsilon_0 r_{ni}} \qquad [11.53\text{a}]$$

the **Coulomb operator** J, where

$$J_j(1)\psi_a(1) = \int \psi_j^*(2)\psi_j(2)\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi_a(1)\mathrm{d}\tau_2 \qquad [11.53\text{b}]$$

and the **exchange operator**, K, where

$$K_j(1)\psi_a(1) = \int \psi_j^*(2)\psi_a(2)\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi_j(1)\mathrm{d}\tau_2 \qquad [11.53\text{c}]$$

Although the Hartree–Fock equations look deceptively simple, with the Fock operator looking like a hamiltonian, we see from these definitions that f actually depends on the wavefunctions of all the electrons. To proceed, we have to guess the initial form of the wavefunctions, use them in the definition of the Coulomb and exchange operators, and solve the Hartree–Fock equations. That process is then continued using the newly found wavefunctions until each cycle of calculation leaves the energies and wavefunctions unchanged to within a chosen criterion. This is the origin of the term **self-consistent field** (SCF) for this type of procedure.

The difficulty in this procedure is in the solution of the Hartree–Fock equations. To make progress, we have to express the wavefunctions as linear combinations of M atomic orbitals χ_i, and write

$$\psi_a = \sum_{i=1}^{M} c_{ia}\chi_i$$

As we show in the *Justification* below, the use of a linear combination like this leads to a set of equations that can be expressed in a matrix form known as the **Roothaan equations**:

$$\boldsymbol{FC} = \boldsymbol{SC\varepsilon} \qquad (11.54)$$

where $\boldsymbol{F}$ is the matrix formed from the Fock operator:

$$F_{ij} = \int \chi_i^*(1)f_1\chi_j(1)\mathrm{d}\tau \qquad (11.55\text{a})$$

and $\boldsymbol{S}$ is the matrix of overlap integrals

$$S_{ij} = \int \chi_i^*(1)\chi_j(1)\mathrm{d}\tau \qquad (11.55\text{b})$$

Justification 11.5 *The Roothaan equations*

To construct the Roothaan equations we substitute the linear combination of atomic orbitals into eqn 11.51, which gives

$$f_1 \sum_{i=1}^{M} c_{i\alpha}\chi_i(1) = \varepsilon_\alpha \sum_{i=1}^{M} c_{i\alpha}\chi_i(1)$$

Now multiply from the left by $\chi_j^*(1)$ and integrate over the coordinates of electron 1:

$$\sum_{i=1}^{M} c_{i\alpha} \overbrace{\int \chi_j(1)^* f(1)\chi_i(1)\mathrm{d}\boldsymbol{r}_1}^{F_{ji}} = \varepsilon_\alpha \sum_{i=1}^{M} c_{i\alpha} \overbrace{\int \chi_j(1)^* \chi_i(1)\mathrm{d}\boldsymbol{r}_1}^{S_{ji}}$$

That is,

$$\sum_{i=1}^{M} F_{ji}c_{i\alpha} = \varepsilon_\alpha \sum_{i=1}^{M} S_{ji}c_{i\alpha}$$

This expression has the form of the matrix equation in eqn 11.54.

(b) Semi-empirical and *ab initio* methods

There are two main strategies for continuing the calculation from this point. In the **semi-empirical methods**, many of the integrals are estimated by appealing to spectroscopic data or physical properties such as ionization energies, and using a series of rules to set certain integrals equal to zero. In the ***ab initio* methods**, an attempt is made to calculate all the integrals that appear in the Fock and overlap matrices. Both procedures employ a great deal of computational effort and, along with cryptanalysts and meteorologists, theoretical chemists are among the heaviest users of the fastest computers.

The Fock matrix has elements that consist of integrals of the form

$$(AB|CD) = \int A(1)B(1)\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)C(2)D(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \qquad (11.56)$$

where A, B, C, and D are atomic orbitals that in general may be centred on different nuclei. It can be appreciated that, if there are several dozen atomic orbitals used to build the molecular orbitals, then there will be tens of thousands of integrals of this form to evaluate (the number of integrals increases as the fourth power of the number of atomic orbitals in the basis). One severe approximation is called **complete neglect of differential overlap** (CNDO), in which all integrals are set to zero unless A and B are the same orbitals centred on the same nucleus, and likewise for C and D. The surviving integrals are then adjusted until the energy levels are in good agreement with experiment. The more recent semi-empirical methods make less draconian decisions about which integrals are to be ignored, but they are all descendants of the early CNDO technique. These procedures are now readily available in commercial software packages and can be used with very little detailed knowledge of their mode of calculation. The packages also have sophisticated graphical output procedures, which enable one to analyse the shapes of orbitals and the distribution of electric charge in molecules. The latter is important when assessing, for instance, the likelihood that a given molecule will bind to an active site in an enzyme.

Commercial packages are also available for *ab initio* calculations. Here the problem is to evaluate as efficiently as possible thousands of integrals. This task is greatly facilitated by expressing the atomic orbitals used in the LCAOs as linear combinations of

Gaussian orbitals. A **Gaussian type orbital** (GTO) is a function of the form $e^{-\zeta r^2}$. The advantage of GTOs over the correct orbitals (which for hydrogenic systems are proportional to $e^{-\zeta r}$) is that the product of two Gaussian functions is itself a Gaussian function that lies between the centres of the two contributing functions (Fig. 11.42). In this way, the four-centre integrals like that in eqn 11.56 become two-centre integrals of the form

$$(AB|CD) = \int X(1)\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)Y(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{11.57}$$

where X is the Gaussian corresponding to the product AB and Y is the corresponding Gaussian from CD. Integrals of this form are much easier and faster to evaluate numerically than the original four-centre integrals. Although more GTOs have to be used to simulate the atomic orbitals, there is an overall increase in speed of computation.

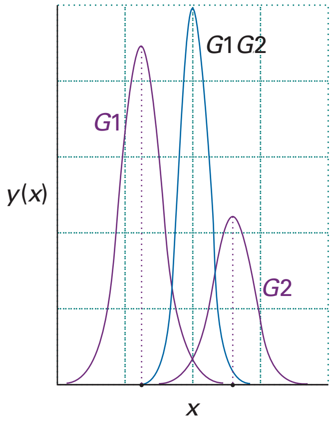


Fig. 11.42 The product of two Gaussian functions (the purple curves) is itself a Gaussian function located between the two contributing Gaussians.

(c) Density functional theory

A technique that has gained considerable ground in recent years to become one of the most widely used techniques for the calculation of molecular structure is **density functional theory** (DFT). Its advantages include less demanding computational effort, less computer time, and—in some cases (particularly *d*-metal complexes)—better agreement with experimental values than is obtained from Hartree–Fock procedures.

The central focus of DFT is the electron density, ρ, rather than the wavefunction ψ. The 'functional' part of the name comes from the fact that the energy of the molecule is a function of the electron density, written $E[\rho]$, and the electron density is itself a function of position, $\rho(\boldsymbol{r})$, and in mathematics a function of a function is called a *functional*. The exact ground-state energy of an n-electron molecule is

$$E[\rho] = E_\mathrm{K} + E_\mathrm{P;e,N} + E_\mathrm{P;e,e} + E_\mathrm{XC}[\rho] \tag{11.58}$$

where E_K is the total electron kinetic energy, $E_\mathrm{P;e,N}$ the electron–nucleus potential energy, $E_\mathrm{P;e,e}$ the electron–electron potential energy, and $E_\mathrm{XC}[\rho]$ the **exchange–correlation energy**, which takes into account all the effects due to spin. The orbitals used to construct the electron density from

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N} |\psi_i(\boldsymbol{r})|^2 \tag{11.59}$$

are calculated from the **Kohn–Sham equations**, which are found by applying the variation principle to the electron energy, and are like the Hartree–Fock equations except for a term V_XC, which is called the **exchange–correlation potential**:

$$\left\{\underbrace{-\frac{\hbar^2}{2m_\mathrm{e}}\nabla_1^2}_{\text{Kinetic energy}} - \underbrace{\sum_{j=1}^{N}\frac{Z_j e^2}{4\pi\varepsilon_0 r_{j1}}}_{\text{Electron–nucleus attraction}} + \underbrace{\int\frac{\rho(\boldsymbol{r}_2)e^2}{4\pi\varepsilon_0 r_{12}}\mathrm{d}\boldsymbol{r}_2}_{\text{Electron–electron repulsion}} + \underbrace{V_\mathrm{XC}(\boldsymbol{r}_1)}_{\text{Exchange–correlation}}\right\}\psi_i(\boldsymbol{r}_1) = \varepsilon_i\psi_i(\boldsymbol{r}_1) \tag{11.60}$$

The exchange–correlation potential is the 'functional derivative' of the exchange–correlation energy:

$$V_\mathrm{XC}[\rho] = \frac{\delta E_\mathrm{XC}[\rho]}{\delta\rho} \tag{11.61}$$

The Kohn–Sham equations are solved iteratively and self-consistently. First, we guess the electron density. For this step it is common to use a superposition of atomic

Comment 11.13

Consider the functional $G[f]$ where f is a function of x. When x changes to $x + \delta x$, the function changes to $f + \delta f$ and the functional changes to $G[f + \delta f]$. By analogy with the derivative of a function, the functional derivative is then defined as

$$\frac{\delta G}{\delta f} = \lim_{\delta f\to 0}\frac{G[f+\delta f] - G[f]}{\delta f}$$

where the manner in which δf goes to zero must be specified explicitly. See *Appendix 2* for more details and examples.

electron densities. Then the exchange–correlation potential is calculated by assuming an approximate form of the dependence of the exchange–correlation energy on the electron density and evaluating the functional derivative in eqn 11.61. For this step, the simplest approximation is the **local-density approximation** and to write

$$E_{\mathrm{XC}}[\rho] = \int \rho(\boldsymbol{r})\varepsilon_{\mathrm{XC}}[\rho(\boldsymbol{r})]\mathrm{d}\boldsymbol{r} \tag{11.62}$$

where $\varepsilon_{\mathrm{XC}}$ is the exchange–correlation energy per electron in a homogeneous gas of constant density. Next, the Kohn–Sham equations are solved to obtain an initial set of orbitals. This set of orbitals is used to obtain a better approximation to the electron density (from eqn 11.59) and the process is repeated until the density and the exchange–correlation energy are constant to within some tolerance.

11.8 The prediction of molecular properties

The results of molecular orbital calculations are only approximate, with deviations from experimental values increasing with the size of the molecule. Therefore, one goal of computational chemistry is to gain insight into trends in properties of molecules, without necessarily striving for ultimate accuracy. In the next sections we give a brief summary of strategies used by computational chemists for the prediction of molecular properties.

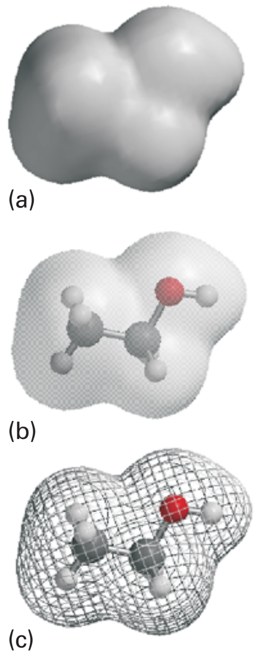


Fig. 11.43 Various representations of an isodensity surface of ethanol (a) solid surface, (b) transparent surface, and (c) mesh surface.

(a) Electron density and the electrostatic potential surfaces

One of the most significant developments in computational chemistry has been the introduction of graphical representations of molecular orbitals and electron densities. The raw output of a molecular structure calculation is a list of the coefficients of the atomic orbitals in each molecular orbital and the energies of these orbitals. The graphical representation of a molecular orbital uses stylized shapes to represent the basis set, and then scales their size to indicate the coefficient in the linear combination. Different signs of the wavefunctions are represented by different colours.

Once the coefficients are known, we can build up a representation of the electron density in the molecule by noting which orbitals are occupied and then forming the squares of those orbitals. The total electron density at any point is then the sum of the squares of the wavefunctions evaluated at that point. The outcome is commonly represented by a **isodensity surface**, a surface of constant total electron density (Fig. 11.43). As shown in the illustration, there are several styles of representing an isodensity surface, as a solid form, as a transparent form with a ball-and-stick representation of the molecule within, or as a mesh. A related representation is a **solvent-accessible surface** in which the shape represents the shape of the molecule by imagining a sphere representing a solvent molecule rolling across the surface and plotting the locations of the centre of that sphere.

One of the most important aspects of a molecule other than its geometrical shape is the distribution of charge over its surface. The net charge at each point on an isodensity surface can be calculated by subtracting the charge due to the electron density at that point form the charge due to the nuclei: the result is an **electrostatic potential surface** (an 'elpot surface') in which net positive charge is shown in one colour and net negative charge is shown in another, with intermediate gradations of colour (Fig. 11.44).

Representations such as those we have illustrated are of critical importance in a number of fields. For instance, they may be used to identify an electron-poor region of a molecule that is susceptible to association with or chemical attack by an electron-rich region of another molecule. Such considerations are important for assessing the pharmacological activity of potential drugs.

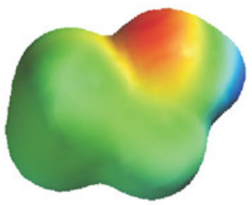
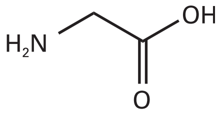


Fig. 11.44 An elpot diagram of ethanol.

(b) Thermodynamic and spectroscopic properties

We already saw in Section 2.8 that computational chemistry is becoming the technique of choice for estimating standard enthalpies of formation of molecules with complex three-dimensional structures. The computational approach also makes it possible to gain insight into the effect of solvation on the enthalpy of formation without conducting experiments. A calculation performed in the absence of solvent molecules estimates the properties of the molecule of interest in the gas phase. Computational methods are available that allow for the inclusion of several solvent molecules around a solute molecule, thereby taking into account the effect of molecular interactions with the solvent on the enthalpy of formation of the solute. Again, the numerical results are only estimates and the primary purpose of the calculation is to predict whether interactions with the solvent increase or decrease the enthalpy of formation. As an example, consider the amino acid glycine, which can exist in a neutral (**4**) or zwitterionic (**5**) form, in which the amino group is protonated and the carboxyl group is deprotonated. It is possible to show computationally that in the gas phase the neutral form has a lower enthalpy of formation than the zwitterionic form. However, in water the opposite is true because of strong interactions between the polar solvent and the charges in the zwitterion.



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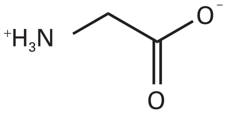
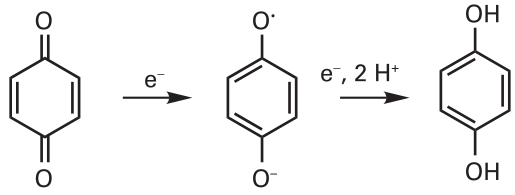


5

Molecular orbital calculations can also be used to predict trends in electrochemical properties, such as standard potentials (Chapter 7). Several experimental and computational studies of aromatic hydrocarbons indicate that decreasing the energy of the LUMO enhances the ability of a molecule to accept an electron into the LUMO, with an attendant increase in the value of the molecule's standard potential. The effect is also observed in quinones and flavins, co-factors involved in biological electron transfer reactions. For example, stepwise substitution of the hydrogen atoms in *p*-benzoquinone by methyl groups ($-CH_3$) results in a systematic increase in the energy of the LUMO and a decrease in the standard potential for formation of the semiquinone radical (**6**):

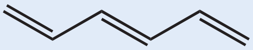


6

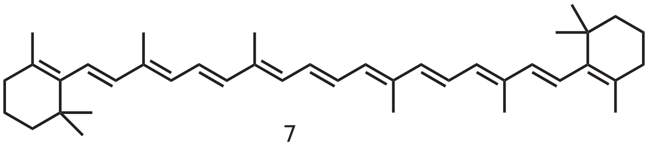
The standard potentials of naturally occurring quinones are also modified by the presence of different substituents, a strategy that imparts specific functions to specific quinones. For example, the substituents in coenzyme Q are largely responsible for poising its standard potential so that the molecule can function as an electron shuttle between specific electroactive proteins in the respiratory chain (*Impact* I17.2).

We remarked in Chapter 8 that a molecule can absorb or emit a photon of energy hc/λ, resulting in a transition between two quantized molecular energy levels. The transition of lowest energy (and longest wavelength) occurs between the HOMO and LUMO. We can use calculations based on semi-empirical, *ab initio*, and DFT methods to correlate the calculated HOMO–LUMO energy gap with the wavelength of absorption. For example, consider the linear polyenes shown in Table 11.5: ethene (C_2H_4), butadiene (C_4H_6), hexatriene (C_6H_8), and octatetraene (C_8H_{10}), all of which absorb in the ultraviolet region of the spectrum. The table also shows that, as expected, the wavelength of the lowest-energy electronic transition decreases as the energy separation between the HOMO and LUMO increases. We also see that the smallest HOMO–LUMO gap and longest transition wavelength correspond to octatetraene, the longest

Table 11.5 *Ab initio* calculations and spectroscopic data

Polyene	$\{E(\mathrm{HOMO}) - E(\mathrm{LUMO})\}/\mathrm{eV}$	λ/nm
 (C_2H_4)	18.1	163
	14.5	217
	12.7	252
	11.8	304

polyene in the group. It follows that the wavelength of the transition increases with increasing number of conjugated double bonds in linear polyenes. Extrapolation of the trend suggests that a sufficiently long linear polyene should absorb light in the visible region of the electromagnetic spectrum. This is indeed the case for β-carotene (**7**), which absorbs light with $\lambda \approx 450$ nm. The ability of β-carotene to absorb visible light is part of the strategy employed by plants to harvest solar energy for use in photosynthesis (Chapter 23).



7

Checklist of key ideas

☐ 1. In the Born–Oppenheimer approximation, nuclei are treated as stationary while electrons move around them.

☐ 2. In valence-bond theory (VB theory), a bond is regarded as forming when an electron in an atomic orbital on one atoms pairs its spin with that of an electron in an atomic orbital on another atom.

☐ 3. A valence bond wavefunction with cylindrical symmetry around the internuclear axis is a σ bond. A π bond arises from the merging of two *p* orbitals that approach side-by-side and the pairing of electrons that they contain.

☐ 4. Hybrid orbitals are mixtures or atomic orbitals on the same atom and are invoked in VB theory to explain molecular geometries.

☐ 5. In molecular orbital theory (MO theory), electrons are treated as spreading throughout the entire molecule.

☐ 6. A bonding orbital is a molecular orbital that, if occupied, contributes to the strength of a bond between two atoms. An antibonding orbital is a molecular orbital that, if occupied, decreases the strength of a bond between two atoms.

☐ 7. A σ molecular orbital has zero orbital angular momentum about the internuclear axis. A π molecular orbital has one unit of angular momentum around the internuclear axis; in a nonlinear molecule, it has a nodal plane that includes the internucelar axis.

☐ 8. The electron configurations of homonuclear diatomic molecules are shown in Figs. 11.31 and 11.33.

☐ 9. When constructing molecular orbitals, we need to consider only combinations of atomic orbitals of similar energies and of the same symmetry around the internuclear axis.

☐ 10. The bond order of a diatomic molecule is $b = \frac{1}{2}(n - n^*)$, where n and n^* are the numbers of electrons in bonding and antibonding orbitals, respectively.

☐ 11. The electronegativity, χ, of an element is the power of its atoms to draw electrons to itself when it is part of a compound.

☐ 12. In a bond between dissimilar atoms, the atomic orbital belonging to the more electronegative atom makes the larger contribution to the molecular orbital with the lowest energy. For the molecular orbital with the highest energy, the principal contribution comes from the atomic orbital belonging to the less electronegative atom.

Teacher: DR. SUBHANKAR SARDAR
Class : Semester-4
Paper: C8T: Physical Chemistry
Topic : Application of Thermodynamics-II

Reference: Physical Chemistry by P.C. Rakshit

This chapter is important and scoring for final examination. This chapter is also easy. The chapter contains many straight forward derivations.

a) Application of Thermodynamics-II

- Colligative properties: Vapour pressure of solution, Ideal solutions, ideally diluted solutions and colligative properties, Thermodynamic derivation using chemical potential to derive relations between the four colligative properties[………………..Abnormal colligative properties. ------→ For these portion thoroughly read the Chapter: "DILUTE SOLUTIONS:COLLIGATIVE PROPERTIES" of the book "Physical Chemistry" by P.C.Rakshit

- Phase rule: Definations of phase, component , degree……….. ------→ For these portion thoroughly read the Chapter: "HETEROGENEOUS EQUILIBRIA - I, The Phase rule: One component systems" of the book "Physical Chemistry" by P.C.Rakshit

- For the rest portions: "HETEROGENEOUS EQUILIBRIA - II, The Phase rule: Two component systems" of the book "Physical Chemistry" by P.C.Rakshit