

# 11

# Molecular structure

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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  $\sigma$  and  $\pi$  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  $\text{H}_2$  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.

## 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,  $\sigma$  and  $\pi$  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.

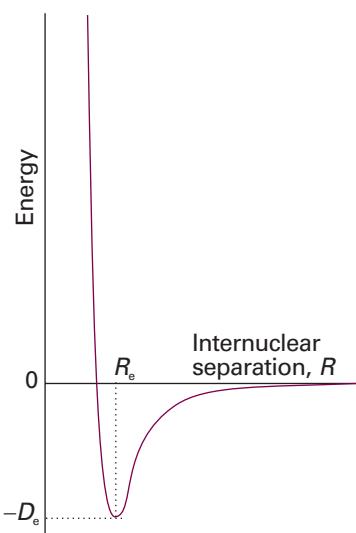
### 11.1 Homonuclear diatomic molecules

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,  $\text{H}_2$ .

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

$$\psi = \chi_{\text{H}1s_A}(\mathbf{r}_1) \chi_{\text{H}1s_B}(\mathbf{r}_2)$$

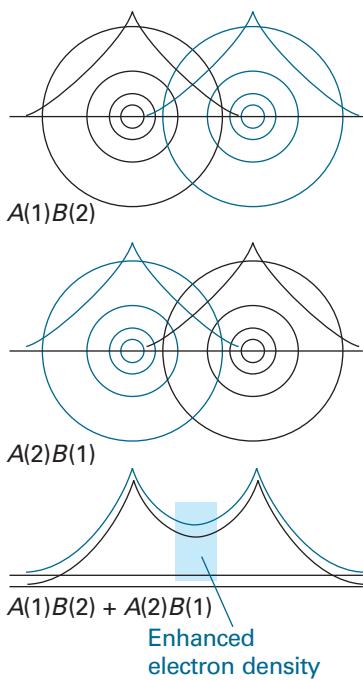
if electron 1 is on atom A and electron 2 is on atom B; in this chapter we use  $\chi$  (chi) to denote atomic orbitals. For simplicity, we shall write this wavefunction as  $\psi = A(1)B(2)$ . When the atoms are close, it is not possible to know whether it is electron 1 that is on A or electron 2. An 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,



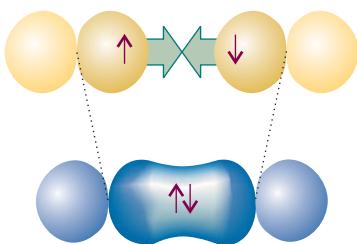
**Fig. 11.1** A molecular potential energy curve. The equilibrium bond length corresponds to the energy minimum.

#### 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  $\omega$  is the vibrational frequency of the bond (Section 13.9).



**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.



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

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

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

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

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

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).

The electron distribution described by the wavefunction in eqn 11.2 is called a  **$\sigma$  bond**. A  $\sigma$  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  $\sigma$  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  $\sigma$  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  $\sigma$  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.

The remaining  $2p$  orbitals cannot merge to give  $\sigma$  bonds as they do not have cylindrical symmetry around the internuclear axis. Instead, they merge to form two  $\pi$  bonds. A  **$\pi$  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  $\pi$  bond resembles a pair of electrons in a  $p$  orbital (and  $\pi$  is the Greek equivalent of  $p$ ).

There are two  $\pi$  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  $\sigma$  bond plus two  $\pi$  bonds (Fig. 11.5), which is consistent with the Lewis structure : $N\equiv N:$  for nitrogen.

## 11.2 Polyatomic molecules

Each  $\sigma$  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,  $\pi$  bonds are formed by pairing electrons that occupy atomic orbitals of the appropriate symmetry.

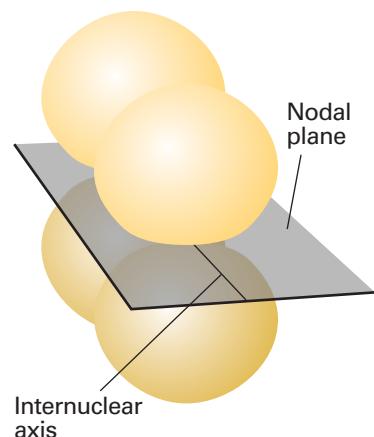
The VB description of  $H_2O$  will make this clear. The valence electron configuration of an O atom is  $2s^2 2p_x^2 2p_y^1 2p_z^1$ . The two unpaired electrons in the  $O2p$  orbitals can each pair with an electron in an  $H1s$  orbital, and each combination results in the formation of a  $\sigma$  bond (each bond has cylindrical symmetry about the respective O–H internuclear axis). Because the  $2p_y$  and  $2p_z$  orbitals lie at  $90^\circ$  to each other, the two  $\sigma$  bonds also lie at  $90^\circ$  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  $90^\circ$ , whereas the actual bond angle is  $104.5^\circ$ .

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

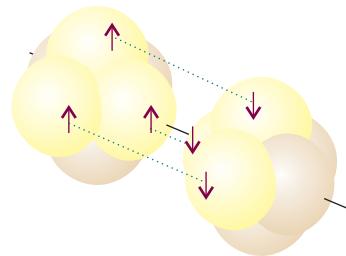
[A trigonal pyramidal molecule with each N–H bond  $90^\circ$ ; experimental:  $107^\circ$ ]

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  $2s^2 2p_x^1 2p_y^1$ , 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  $2s^1 2p_x^1 2p_y^1 2p_z^1$ , 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  $\sigma$  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.

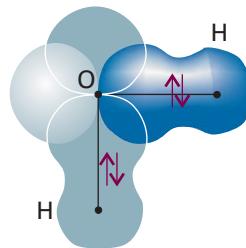
The description of the bonding in  $CH_4$  (and other alkanes) is still incomplete because it implies the presence of three  $\sigma$  bonds of one type (formed from  $H1s$  and  $C2p$



**Fig. 11.4** A  $\pi$  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.



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



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

**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  $\sigma$  bond of a distinctly different character (formed from H1s and C2s). 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 C2s and C2p 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

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

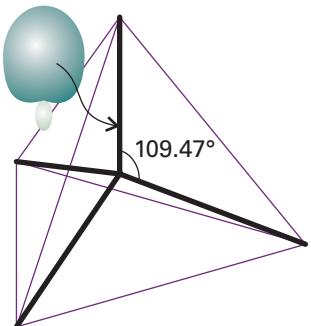
As a result of the interference between the component orbitals, each hybrid orbital consists of a large lobe pointing in the direction of one corner of a regular tetrahedron (Fig. 11.7). The angle between the axes of the hybrid orbitals is the tetrahedral angle, 109.47°. Because each hybrid is built 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<sub>4</sub> 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 H1s electron can pair with each one, giving rise to a  $\sigma$  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<sub>A</sub> orbital (with wavefunction that we shall denote A) is

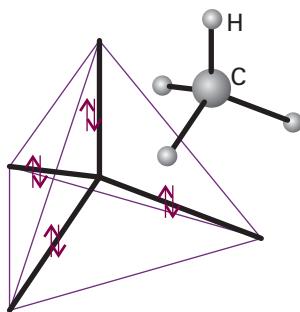
$$\psi = h_1(1)A(2) + h_1(2)A(1)$$

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

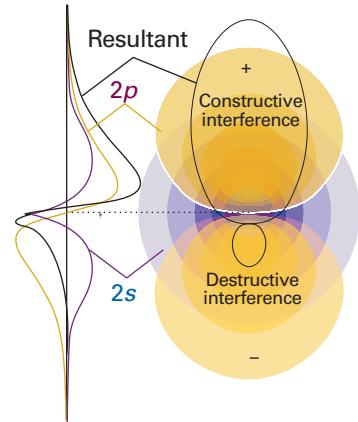
A hybrid orbital has enhanced amplitude in the internuclear region, which arises from the constructive interference between the s orbital and the positive lobes of the p orbitals (Fig. 11.9). As a result, the bond strength is greater than for a bond formed



**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  $\sigma$  bond by overlap with an H1s orbital located at the corner of the tetrahedron. This model accounts for the equivalence of the four bonds in CH<sub>4</sub>.



**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 2s 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,  $\text{H}_2\text{C}=\text{CH}_2$ , and the torsional rigidity of double bonds. An ethene molecule is planar, with HCH and HCC bond angles close to  $120^\circ$ . To reproduce the  $\sigma$  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**:

$$h_1 = s + 2^{1/2}p_y \quad h_2 = s + (\frac{3}{2})^{1/2}p_x - (\frac{1}{2})^{1/2}p_y \quad h_3 = s - (\frac{3}{2})^{1/2}p_x - (\frac{1}{2})^{1/2}p_y \quad (11.4)$$

that lie in a plane and point towards the corners of an equilateral triangle (Fig. 11.10). The third *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.

We can now describe the structure of  $\text{CH}_2=\text{CH}_2$  as follows. The  $sp^2$ -hybridized C atoms each form three  $\sigma$  bonds by spin pairing with either the  $h_1$  hybrid of the other C atom or with  $\text{H}1s$  orbitals. The  $\sigma$  framework therefore consists of C—H and C—C  $\sigma$  bonds at  $120^\circ$  to each other. When the two  $\text{CH}_2$  groups lie in the same plane, the two electrons in the unhybridized *p* orbitals can pair and form a  $\pi$  bond (Fig. 11.11). The formation of this  $\pi$  bond locks the framework into the planar arrangement, for any rotation of one  $\text{CH}_2$  group relative to the other leads to a weakening of the  $\pi$  bond (and consequently an increase in energy of the molecule).

A similar description applies to ethyne,  $\text{HC}\equiv\text{CH}$ , a linear molecule. Now the C atoms are  **$sp$  hybridized**, and the  $\sigma$  bonds are formed using hybrid atomic orbitals of the form

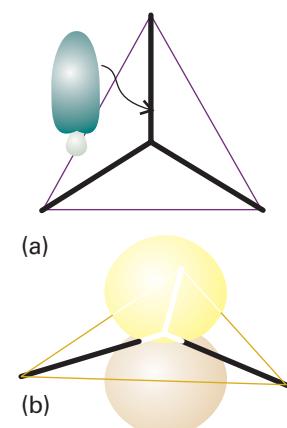
$$h_1 = s + p_z \quad h_2 = s - p_z \quad (11.5)$$

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  $\text{H}1s$  orbitals. Electrons in the two remaining *p* orbitals on each atom, which are perpendicular to the molecular axis, pair to form two perpendicular  $\pi$  bonds (Fig. 11.12).

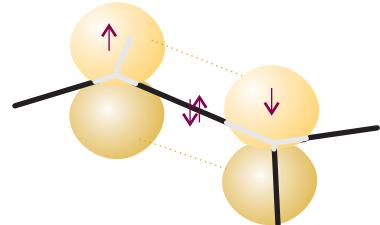
**Self-test 11.2** Hybrid orbitals do not always form bonds. They may also contain lone pairs of electrons. Use valence-bond theory to suggest possible shapes for the hydrogen peroxide molecule,  $\text{H}_2\text{O}_2$ .

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

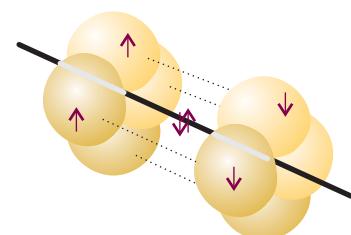
Other hybridization schemes, particularly those involving *d* orbitals, are often invoked in elementary work to be consistent with other molecular geometries (Table 11.1). The hybridization of *N* atomic orbitals always results in the formation of *N* hybrid orbitals, which may either form bonds or may 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  $\text{SF}_6$ .



**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.



**Fig. 11.11** A representation of the structure of a double bond in ethene; only the  $\pi$  bond is shown explicitly.



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

**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.

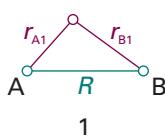
### 11.3 The hydrogen molecule-ion

The hamiltonian for the single electron in  $H_2^+$  is

$$H = -\frac{\hbar^2}{2m_e} \nabla_1^2 + V \quad V = -\frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R} \right) \quad (11.6)$$

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.

The one-electron wavefunctions obtained by solving the Schrödinger equation  $H\psi = E\psi$  are called **molecular orbitals** (MO). A molecular orbital  $\psi$  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  $\text{H}_2^+$  (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:

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

where, for  $\text{H}_2^+$ , A denotes  $\chi_{\text{H}1s_A}$ , B denotes  $\chi_{\text{H}1s_B}$ , 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  **$\sigma$  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  $\psi_+$  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

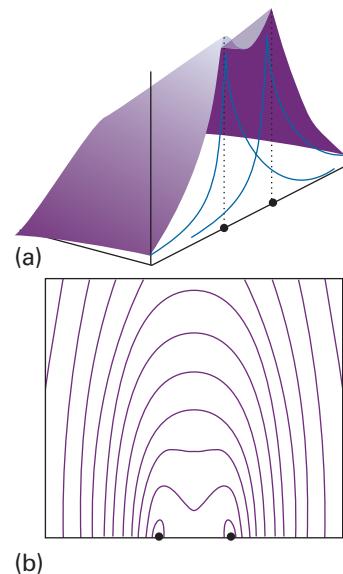
$$N = \frac{1}{\sqrt{2(1+S)}}$$

In  $\text{H}_2^+$ ,  $S \approx 0.59$ , so  $N = 0.56$ .

#### Self-test 11.3 Normalize the orbital $\psi_-$ in eqn 11.7.

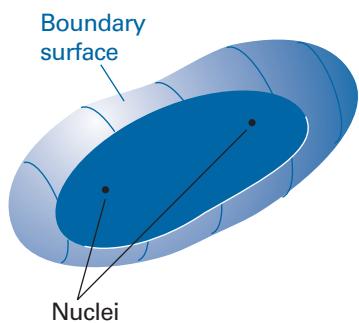
$$[N = 1/\sqrt{2(1-S)} = 1.10]$$

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.

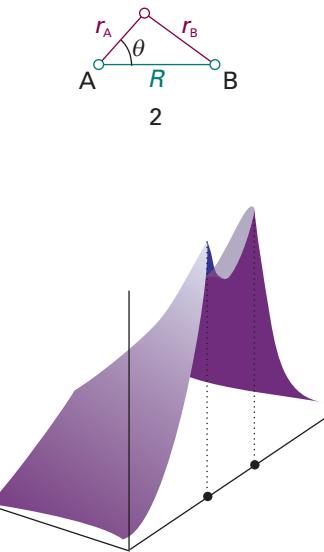
**Exploration** Plot the  $1\sigma$  orbital for different values of the internuclear distance. Point to the features of the  $1\sigma$  orbital that lead to bonding.



**Fig. 11.14** A general indication of the shape of the boundary surface of a  $\sigma$  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  $\theta$  facing side  $r_B$  we may write:  $r_B^2 = r_A^2 + R^2 - 2r_A R \cos \theta$ .



**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.

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

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

$$r_B = \{r_A^2 + R^2 - 2r_A R \cos \theta\}^{1/2} \quad (11.9)$$

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  $\psi_+$  in eqn 11.7 is

$$\psi_+^2 = N^2(A^2 + B^2 + 2AB) \quad (11.10)$$

This probability density is plotted in Fig. 11.15.

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  $\sigma$  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  $1\sigma$  as it is the  $\sigma$  orbital of lowest energy. An electron that occupies a  $\sigma$  orbital is called a  **$\sigma$  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  $1\sigma$  orbital is (see Problem 11.23):

$$E_{1\sigma} = E_{\text{H}1s} + \frac{e^2}{4\pi\epsilon_0 R} - \frac{j+k}{1+S} \quad (11.11)$$

where

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

$$j = \frac{e^2}{4\pi\epsilon_0} \int \frac{A^2}{r_B} d\tau = \frac{e^2}{4\pi\epsilon_0 R} \left\{ 1 - \left( 1 + \frac{R}{a_0} \right) e^{-2R/a_0} \right\} \quad (11.12b)$$

$$k = \frac{e^2}{4\pi\epsilon_0} \int \frac{AB}{r_B} d\tau = \frac{e^2}{4\pi\epsilon_0 a_0} \left( 1 + \frac{R}{a_0} \right) e^{-R/a_0} \quad (11.12c)$$

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  $1\sigma$  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  $\text{H}_2^+$  give  $R_e = 130 \text{ pm}$  and  $D_e = 1.77 \text{ eV}$  ( $171 \text{ kJ mol}^{-1}$ ); the experimental values are  $106 \text{ pm}$  and  $2.6 \text{ eV}$ , so this simple LCAO-MO description of the molecule, while inaccurate, is not absurdly wrong.

### (c) Antibonding orbitals

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

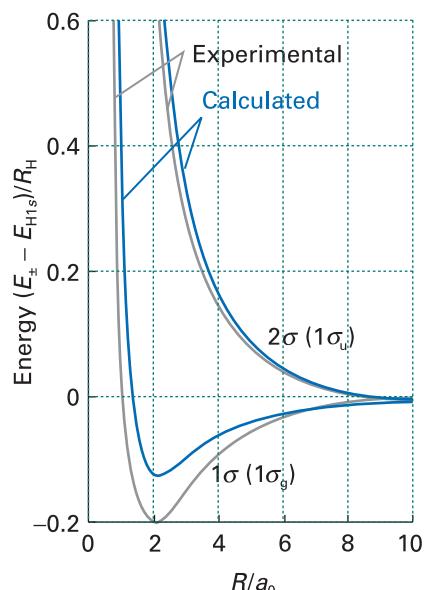
$$\psi_-^2 = N^2(A^2 + B^2 - 2AB) \quad (11.13)$$

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  $2\sigma$  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.

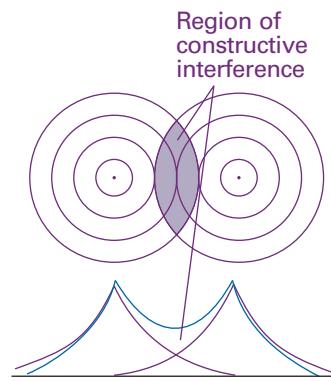
The energy  $E_{2\sigma}$  of the  $2\sigma$  antibonding orbital is given by (see Problem 11.23)

$$E_{2\sigma} = E_{\text{H}1s} + \frac{e^2}{4\pi\epsilon_0 R} - \frac{j-k}{1-S} \quad (11.14)$$

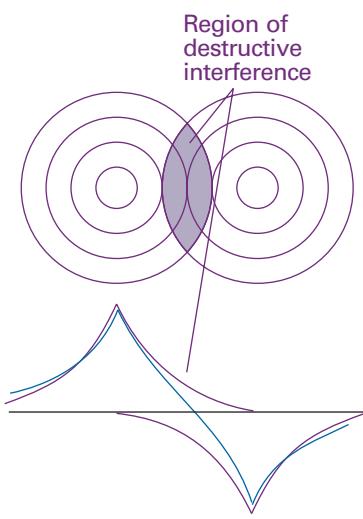
where the integrals  $S$ ,  $j$ , and  $k$  are given by eqn 11.12. The variation of  $E_{2\sigma}$  with  $R$  is shown in Fig. 11.16, where we see the destabilizing effect of an antibonding electron.



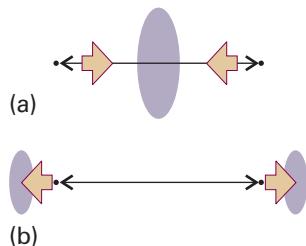
**Fig. 11.16** The calculated and experimental molecular potential energy curves for a hydrogen molecule-ion showing the variation of the energy of the molecule as the bond length is changed. The alternative g,u notation is introduced in Section 11.3c.



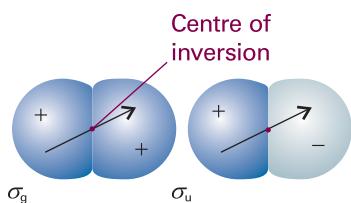
**Fig. 11.17** A representation of the constructive interference that occurs when two  $\text{H}1s$  orbitals overlap and form a bonding  $\sigma$  orbital.



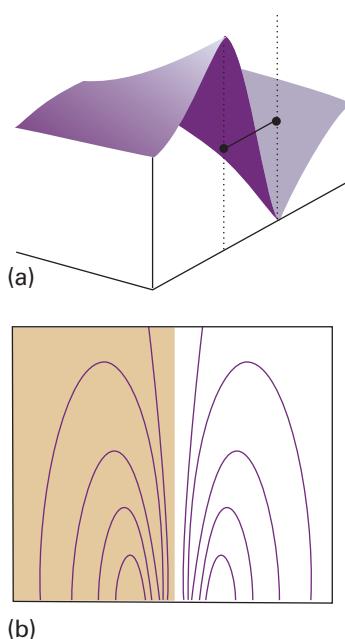
**Fig. 11.18** A representation of the destructive interference that occurs when two H<sub>1s</sub> orbitals overlap and form an antibonding 2σ orbital.



**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.

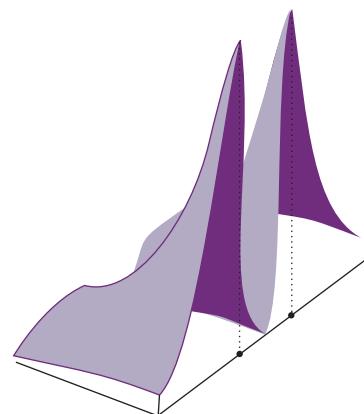


**Fig. 11.22** The parity of an orbital is even (g) if its wavefunction is unchanged under inversion through the centre of symmetry of the molecule, but odd (u) if the wavefunction changes sign. Heteronuclear diatomic molecules do not have a centre of inversion, so for them the g, u classification is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



**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.

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:  $|E_- - E_{\text{H}1s}| > |E_+ - E_{\text{H}1s}|$ , 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 ( $e^2/4\pi\epsilon_0 R$ ): 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<sub>g</sub>. 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<sub>u</sub>. 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  $1\sigma$  becomes  $1\sigma_g$ , its antibonding partner, which so far we have called  $2\sigma$ , 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*.

## 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  $\text{H}_2^+$  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.

### (a) $\sigma$ orbitals

Consider  $\text{H}_2$ , the simplest many-electron diatomic molecule. Each H atom contributes a  $1s$  orbital (as in  $\text{H}_2^+$ ), 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  $\sigma$  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.

#### Justification 11.2 Electron pairing in MO theory

The spatial wavefunction for two electrons in a bonding molecular orbital  $\psi$  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

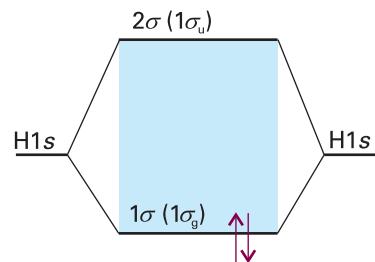
$$\psi(1,2) = \psi(1)\psi(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

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.

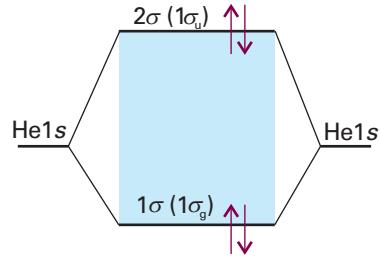
The same argument shows why He does not form diatomic molecules. Each He atom contributes a  $1s$  orbital, so  $1\sigma_g$  and  $1\sigma_u$  molecular orbitals can be constructed. Although these orbitals differ in detail from those in  $\text{H}_2$ , the general shape is the same, and we can use the 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

### 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.



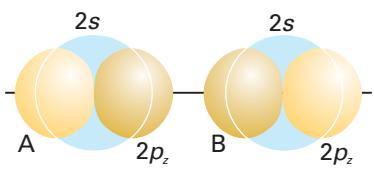
**Fig. 11.23** A molecular orbital energy level diagram for orbitals constructed from the overlap of  $\text{H}1s$  orbitals; the separation of the levels corresponds to that found at the equilibrium bond length. The ground electronic configuration of  $\text{H}_2$  is obtained by accommodating the two electrons in the lowest available orbital (the bonding orbital).



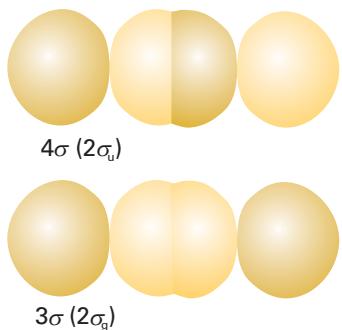
**Fig. 11.24** The ground electronic configuration of the hypothetical four-electron molecule  $\text{He}_2$  has two bonding electrons and two antibonding electrons. It has a higher energy than the separated atoms, and so is unstable.

### Comment 11.5

Diatom 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.



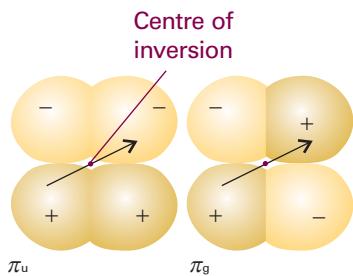
**Fig. 11.25** According to molecular orbital theory,  $\sigma$  orbitals are built from all orbitals that have the appropriate symmetry. In homonuclear diatomic molecules of Period 2, that means that two 2s and two 2p<sub>z</sub> orbitals should be used. From these four orbitals, four molecular orbitals can be built.



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

#### 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 1s orbitals of the atoms; the orbitals we are considering would then be labelled starting from 2.



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

of He<sub>2</sub> 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<sub>2</sub> 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 2s and 2p atomic orbitals are considered.

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

$$\psi = c_{A2s}\chi_{A2s} + c_{B2s}\chi_{B2s} + c_{A2p_z}\chi_{A2p_z} + c_{B2p_z}\chi_{B2p_z} \quad (11.15)$$

From these four atomic orbitals we can form four molecular orbitals of  $\sigma$  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 2s and 2p<sub>z</sub> orbitals have distinctly different energies, they may be treated separately. That is, the four  $\sigma$  orbitals fall approximately into two sets, one consisting of two molecular orbitals of the form

$$\psi = c_{A2s}\chi_{A2s} + c_{B2s}\chi_{B2s} \quad (11.16a)$$

and another consisting of two orbitals of the form

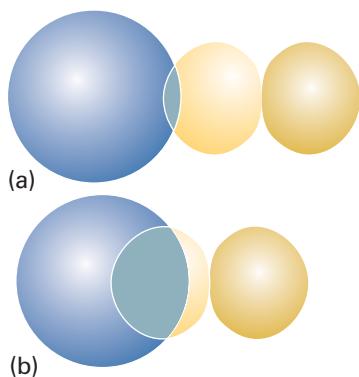
$$\psi = c_{A2p_z}\chi_{A2p_z} + c_{B2p_z}\chi_{B2p_z} \quad (11.16b)$$

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

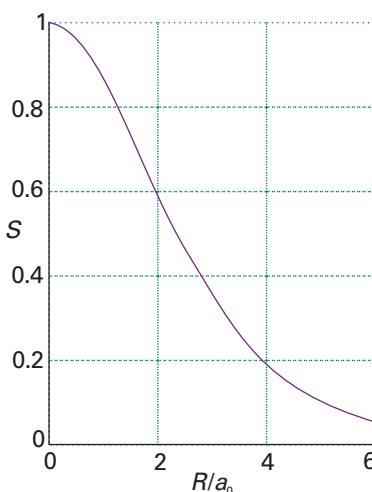
The 2s orbitals on the two atoms overlap to give a bonding and an antibonding  $\sigma$  orbital (1 $\sigma_g$  and 1 $\sigma_u$ , respectively) in exactly the same way as we have already seen for 1s orbitals. The two 2p<sub>z</sub> orbitals directed along the internuclear axis overlap strongly. They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

#### (b) $\pi$ orbitals

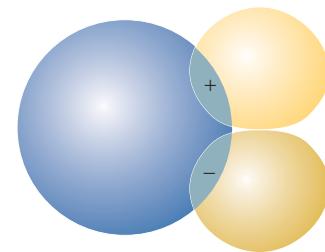
Now consider the 2p<sub>x</sub> and 2p<sub>y</sub> orbitals of each atom. These orbitals are perpendicular to the internuclear axis and may overlap broadside-on. This overlap may be constructive or destructive, and results in a bonding or an antibonding  $\pi$  orbital (Fig. 11.27). The notation  $\pi$  is the analogue of  $p$  in atoms, for when viewed along the axis of the molecule, a  $\pi$  orbital looks like a  $p$  orbital, and has one unit of orbital angular momentum around the internuclear axis. The two 2p<sub>x</sub> orbitals overlap to give a bonding and antibonding  $\pi_x$  orbital, and the two 2p<sub>y</sub> orbitals overlap to give two  $\pi_y$  orbitals. The  $\pi_x$  and  $\pi_y$  bonding orbitals are degenerate; so too are their antibonding partners. We also see from Fig. 11.27 that a bonding  $\pi$  orbital has odd parity and is denoted  $\pi_u$  and an antibonding  $\pi$  orbital has even parity, denoted  $\pi_g$ .



**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**,  $S$ :

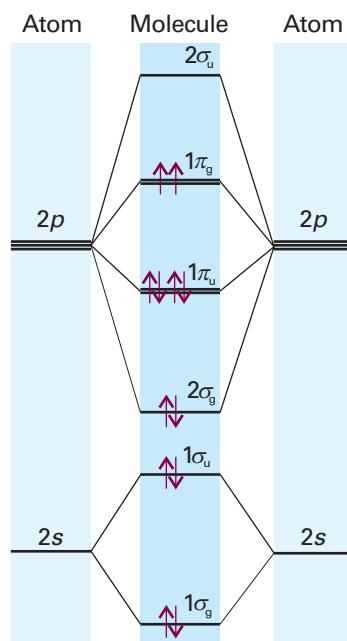
$$S = \int \chi_A^* \chi_B d\tau \quad [11.17]$$

If the atomic orbital  $\chi_A$  on A is small wherever the orbital  $\chi_B$  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  $\chi_A$  and  $\chi_B$  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.

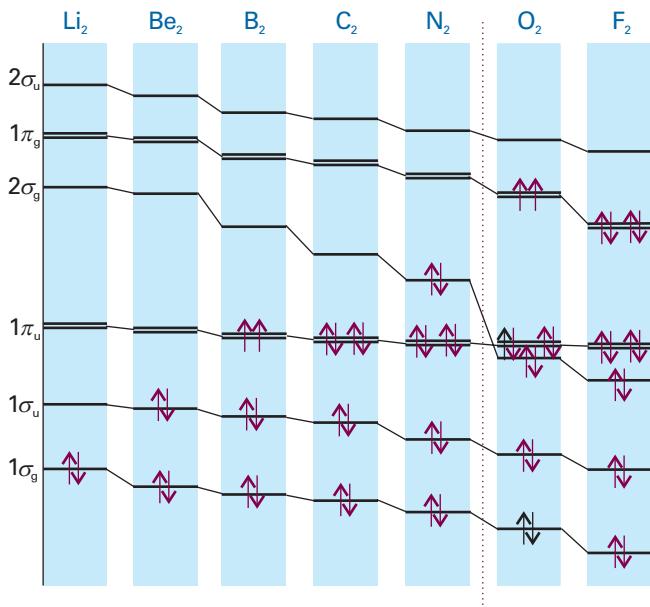
Now consider the arrangement in which an  $s$  orbital is superimposed on a  $p_x$  orbital of a different atom (Fig. 11.30). The integral over the region where the product of orbitals is positive exactly cancels the integral over the region where the product of orbitals is negative, so overall  $S =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

### (d) The electronic structures of homonuclear diatomic molecules

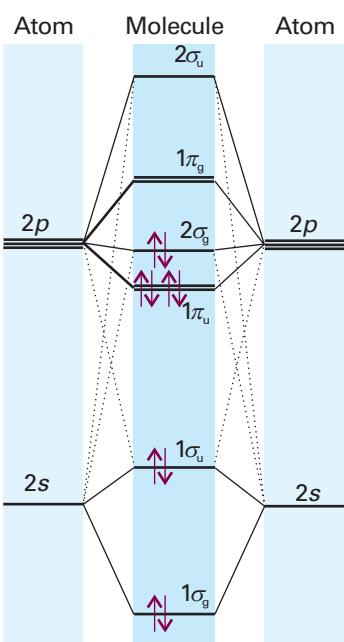
To construct the molecular orbital energy level diagram for Period 2 homonuclear diatomic molecules, we form eight molecular orbitals from the eight valence shell orbitals (four from each atom). In some cases,  $\pi$  orbitals are less strongly bonding than  $\sigma$  orbitals because their maximum overlap 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. 11.31** 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  $F_2$ .



**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<sub>2</sub> (the configuration shown).

contribute to different sets of molecular orbitals whereas in fact all four atomic orbitals contribute jointly to the four  $\sigma$  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<sub>2</sub>, and Fig. 11.31 applies for O<sub>2</sub> and F<sub>2</sub>. The relative order is controlled by the separation of the 2s and 2p orbitals in the atoms, which increases across the group. The consequent switch in order occurs at about N<sub>2</sub>.

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<sub>2</sub><sup>2-</sup>) need more electrons than the parent neutral molecules; cationic species (such as O<sub>2</sub><sup>+</sup>) need fewer.

Consider N<sub>2</sub>, which has 10 valence electrons. Two electrons pair, occupy, and fill the 1 $\sigma$ <sub>g</sub> orbital; the next two occupy and fill the 1 $\sigma$ <sub>u</sub> orbital. Six electrons remain. There are two 1 $\pi$ <sub>u</sub> orbitals, so four electrons can be accommodated in them. The last two enter the 2 $\sigma$ <sub>g</sub> orbital. Therefore, the ground-state configuration of N<sub>2</sub> is 1 $\sigma$ <sub>g</sub><sup>2</sup>1 $\sigma$ <sub>u</sub><sup>2</sup>1 $\pi$ <sub>u</sub><sup>4</sup>2 $\sigma$ <sub>g</sub><sup>2</sup>.

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

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

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<sub>2</sub>, *b* = 1, corresponding to a single bond, H—H, between the two atoms. In He<sub>2</sub>, *b* = 0, and there is no bond. In N<sub>2</sub>, *b* =  $\frac{1}{2}(8 - 2) = 3$ . This bond order accords with the Lewis structure of the molecule (:N≡N:).

The ground-state electron configuration of O<sub>2</sub>, with 12 valence electrons, is based on Fig. 11.31, and is 1 $\sigma$ <sub>g</sub><sup>2</sup>1 $\sigma$ <sub>u</sub><sup>2</sup>2 $\sigma$ <sub>g</sub><sup>2</sup>1 $\pi$ <sub>g</sub><sup>4</sup>1 $\pi$ <sub>u</sub><sup>2</sup>. Its bond order is 2. According to the building-up principle, however, the two 1 $\pi$ <sub>g</sub> electrons occupy different orbitals: one will enter 1 $\pi$ <sub>u,x</sub> and the other will enter 1 $\pi$ <sub>u,y</sub>. Because the electrons are in different orbitals, they will have parallel spins. Therefore, we can predict that an O<sub>2</sub> 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	$R_e/\text{pm}$
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	$D_0/(\text{kJ mol}^{-1})$
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.

An F<sub>2</sub> molecule has two more electrons than an O<sub>2</sub> 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<sub>2</sub> is a singly-bonded molecule, in agreement with its Lewis structure. The hypothetical molecule dineon, Ne<sub>2</sub>, 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.

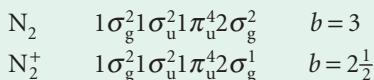
Table 11.2 lists some typical bond lengths in diatomic and polyatomic molecules. The strength of a bond is measured by its bond dissociation energy,  $D_e$ , the energy required to separate the atoms to infinity. Table 11.3 lists some experimental values of dissociation energies.

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

Judge whether N<sub>2</sub><sup>+</sup> is likely to have a larger or smaller dissociation energy than N<sub>2</sub>.

**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



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<sup>-1</sup> for N<sub>2</sub> and 842 kJ mol<sup>-1</sup> for N<sub>2</sub><sup>+</sup>.

**Self-test 11.4** Which can be expected to have the higher dissociation energy, F<sub>2</sub> or F<sub>2</sub><sup>+</sup>?

### Comment 11.7

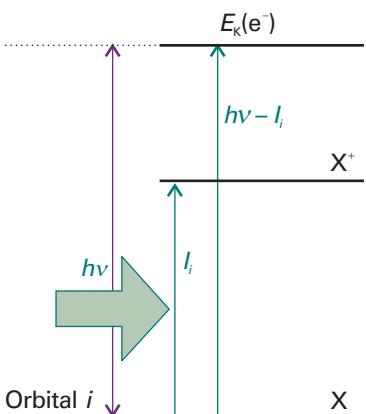
A paramagnetic substance tends to move into a magnetic field; a diamagnetic substance tends to move out of one. Paramagnetism, the rarer property, arises when the molecules have unpaired electron spins. Both properties are discussed in more detail in Chapter 20.

### Comment 11.8

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



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



**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):

$$h\nu = \frac{1}{2}m_e v^2 + I \quad (11.19)$$

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

$$h\nu = \frac{1}{2}m_e v^2 + I_i \quad (11.20)$$

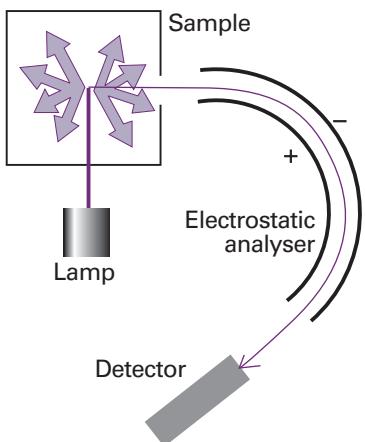
where  $I_i$  is the ionization energy for ejection of an electron from an orbital  $i$ . Therefore, by measuring the kinetic energies of the photoelectrons, and knowing  $v$ , these ionization energies can be determined. Photoelectron spectra are interpreted in terms of an approximation called **Koopmans' theorem**, which states that the ionization energy  $I_i$  is equal to the orbital energy of the ejected electron (formally:  $I_i = -\epsilon_i$ ). 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 ( $1s^1 2p^1 \rightarrow 1s^2$ ) 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.

#### 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 =  $8065.5 \text{ cm}^{-1}$ ). Helium(I) radiation of wavelength 58.43 nm has wavenumber  $1.711 \times 10^5 \text{ cm}^{-1}$  and therefore corresponds to an energy of 21.22 eV. Then, from eqn 11.20,  $21.22 \text{ eV} = 5.63 \text{ eV} + I_i$ , so  $I_i = 15.59 \text{ eV}$ . 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).



**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.

**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

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

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

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

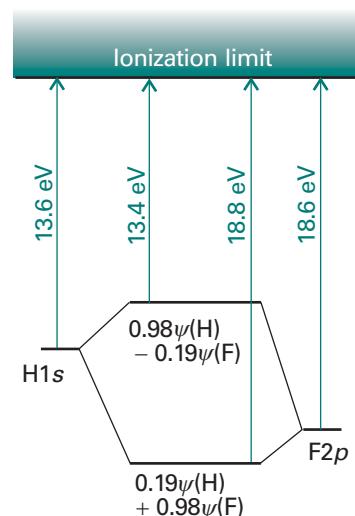
where  $\chi_H$  is an  $H1s$  orbital and  $\chi_F$  is an  $F2p$  orbital. The  $H1s$  orbital lies 13.6 eV below the zero of energy (the separated proton and electron) and the  $F2p$  orbital lies at 18.6 eV (Fig. 11.36). Hence, the bonding  $\sigma$  orbital in HF is mainly  $F2p$  and the antibonding  $\sigma$  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.

### (b) Electronegativity

The charge distribution in bonds is commonly discussed in terms of the **electronegativity**,  $\chi$ , of the elements involved (there should be little danger of confusing this use of  $\chi$  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

$$|\chi_A - \chi_B| = 0.102 \{D(A-B) - \frac{1}{2}[D(A-A) + D(B-B)]\}^{1/2} \quad [11.23]$$

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



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

**Synoptic table 11.4\*** Pauling electronegativities

Element	$\chi_P$
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

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

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.

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**

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

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

The parameter  $\alpha$  is called a **Coulomb integral**. It is negative and can be interpreted as the energy of the electron when it occupies A (for  $\alpha_A$ ) or B (for  $\alpha_B$ ). In a homonuclear diatomic molecule,  $\alpha_A = \alpha_B$ . The parameter  $\beta$  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.

### 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.

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### 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):

$$E = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} \quad (11.26)$$

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

$$\frac{\partial E}{\partial c_A} = 0 \quad \frac{\partial E}{\partial c_B} = 0$$

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

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

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

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

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

$$\begin{aligned} \alpha_A &= \int A \hat{H} A d\tau \quad \alpha_B = \int B \hat{H} B d\tau \\ \beta &= \int A \hat{H} B d\tau = \int B \hat{H} A d\tau \text{ (by the hermiticity of } \hat{H}) \end{aligned} \quad [11.27]$$

Then

$$\int \psi \hat{H} \psi d\tau = c_A^2 \alpha_A + c_B^2 \alpha_B + 2c_A c_B \beta$$

The complete expression for  $E$  is

$$E = \frac{c_A^2 \alpha_A + c_B^2 \alpha_B + 2c_A c_B \beta}{c_A^2 + c_B^2 + 2c_A c_B S} \quad (11.28)$$

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

$$\frac{\partial E}{\partial c_A} = \frac{2 \times (c_A \alpha_A - c_A E + c_B \beta - c_B S E)}{c_A^2 + c_B^2 + 2c_A c_B S} = 0$$

$$\frac{\partial E}{\partial c_B} = \frac{2 \times (c_B \alpha_B - c_B E + c_A \beta - c_A S E)}{c_A^2 + c_B^2 + 2c_A c_B S} = 0$$

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

$$\begin{aligned} c_A\alpha_A - c_A E + c_B\beta - c_B SE &= (\alpha_A - E)c_A + (\beta - ES)c_B = 0 \\ c_A\beta - c_A SE + c_B\alpha_B - c_B E &= (\beta - ES)c_A + (\alpha_B - E)c_B = 0 \end{aligned}$$

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

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

#### Comment 11.10

We need to know that a  $2 \times 2$  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

$$\int \psi^2 d\tau = c_A^2 + c_B^2 + 2c_A c_B S = 1 \quad (11.30)$$

#### 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

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

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

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

This expression implies that

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

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

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

which implies that

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

#### (d) Two simple cases

The complete solutions of the secular equations are very cumbersome, even for  $2 \times 2$  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

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

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

In this case, the bonding orbital has the form

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

and the corresponding antibonding orbital is

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

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  $\zeta$  (zeta), with

$$\zeta = \frac{1}{2} \arctan \frac{2|\beta|}{\alpha_B - \alpha_A} \quad (11.33)$$

and are

$$E_- = \alpha_B - \beta \tan \zeta \quad \psi_- = -A \sin \zeta + B \cos \zeta \quad (11.34a)$$

$$E_+ = \alpha_A + \beta \tan \zeta \quad \psi_+ = A \cos \zeta + B \sin \zeta \quad (11.34b)$$

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  $\zeta$  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  $\beta$ ) is so small.

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**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  $\beta$  is normally a negative number, so that  $\beta/|\beta| = -1$ , we can use eqn 11.34 to write

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

(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  $\sigma$  orbitals in the HF molecule, taking  $\beta = -1.0$  eV and the following ionization energies: H1s: 13.6 eV, F2s: 40.2 eV, F2p: 17.4 eV.

**Method** Because the F2p and H1s orbitals are much closer in energy than the F2s and H1s orbitals, to a first approximation neglect the contribution of the F2s orbital. To use eqn 11.34, we need to know the values of the Coulomb integrals  $\alpha_H$  and  $\alpha_F$ . Because these integrals represent the energies of the H1s and F2p electrons, respectively, they are approximately equal to (the negative of) the ionization energies of the atoms. Calculate  $\zeta$  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  $\zeta = 13.9^\circ$ . Then

$$\begin{aligned}E_- &= -13.4 \text{ eV} & \psi_- &= 0.97\chi_H - 0.24\chi_F \\E_+ &= -17.6 \text{ eV} & \psi_+ &= 0.24\chi_H + 0.97\chi_F\end{aligned}$$

Notice how the lower energy orbital (the one with energy  $-17.6 \text{ eV}$ ) has a composition that is more F $2p$  orbital than H $1s$ , 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  $\sigma$  orbitals in the HCl molecule using  $\beta = -1.0 \text{ eV}$ .

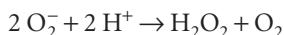
$$[E_- = -12.8 \text{ eV}, \psi_- = -0.62\chi_H + 0.79\chi_{\text{Cl}}; E_+ = -13.9 \text{ eV}, \psi_+ = 0.79\chi_H + 0.62\chi_{\text{Cl}}]$$

## IMPACT ON BIOCHEMISTRY

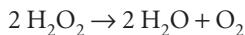
### 11.1 The biochemical reactivity of O<sub>2</sub>, N<sub>2</sub>, and NO

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<sub>2</sub> and 75.5 per cent N<sub>2</sub> by mass. Molecular orbital theory predicts—correctly—that O<sub>2</sub> 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<sub>2</sub>, 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<sub>2</sub> to NH<sub>3</sub>, 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 micro-organisms 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.

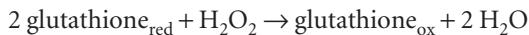
The reactivity of O<sub>2</sub>, while important for biological energy conversion, also poses serious physiological problems. During the course of metabolism, some electrons escape from complexes I, II, and III of the respiratory chain and reduce O<sub>2</sub> to superoxide ion, O<sub>2</sub><sup>−</sup>. The ground-state electronic configuration of O<sub>2</sub><sup>−</sup> is 1σ<sub>g</sub><sup>2</sup>1σ<sub>u</sub><sup>2</sup>2σ<sub>g</sub><sup>2</sup>1π<sub>u</sub><sup>4</sup>1π<sub>g</sub><sup>3</sup>, 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<sub>2</sub><sup>−</sup> into O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>:



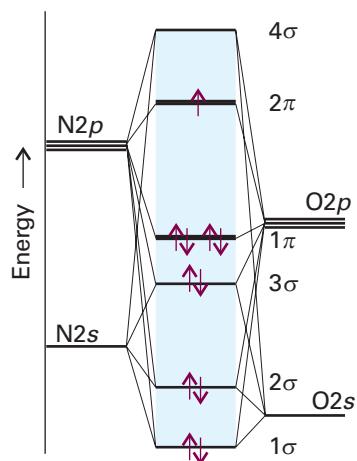
However, H<sub>2</sub>O<sub>2</sub> (hydrogen peroxide), formed by the reaction above and by leakage of electrons out of the respiratory chain, is a powerful oxidizing agent and also harmful to cells. It is metabolized further by catalases and peroxidases. A catalase catalyses the reaction



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



There is growing evidence for the involvement of the damage caused by reactive oxygen species (ROS), such as O<sub>2</sub><sup>−</sup>, H<sub>2</sub>O<sub>2</sub>, and ·OH (the hydroxyl radical), in the mechanism of ageing and in the development of cardiovascular disease, cancer,



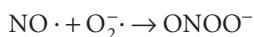
**Fig. 11.37** The molecular orbital energy level diagram for NO.

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 ( $\alpha$ -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  $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^4 2\pi^1$ . The  $3\sigma$  and  $1\pi$  orbitals are predominantly of O character as that is the more electronegative element. The highest-energy occupied orbital is  $2\pi$ , 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  $4\sigma$ , 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 peroxy nitrite ion:



where we have shown the unpaired electrons explicitly. The peroxy nitrite 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

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

where  $\chi_i$  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  $\sigma$  or  $\pi$  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  $\pi$  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  $\pi$  orbitals are treated separately from the  $\sigma$  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  $\alpha$  for the atomic orbitals that contribute to the  $\pi$  orbitals are set equal. For example, in ethene, we take the  $\sigma$  bonds as fixed, and concentrate on finding the energies of the single  $\pi$  bond and its companion antibond.

### (a) Ethene and frontier orbitals

We express the  $\pi$  orbitals as LCAOs of the  $C_2p$  orbitals that lie perpendicular to the molecular plane. In ethene, for instance, we would write

$$\psi = c_A A + c_B B \quad (11.36)$$

where the  $A$  is a  $C_2p$  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  $\alpha_A = \alpha_B = \alpha$ :

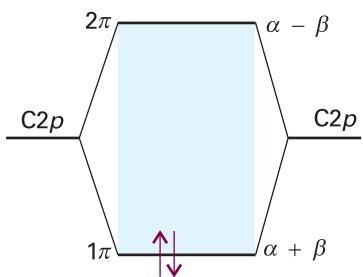
$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \quad (11.37)$$

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  $\beta$ ).

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:  $\beta$ .
- 3 All other elements: 0.



**Fig. 11.38** The Hückel molecular orbital energy levels of ethene. Two electrons occupy the lower  $\pi$  orbital.

These approximations lead to

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

The roots of the equation are

$$E_{\pm} = \alpha \pm \beta \quad (11.39)$$

The + sign corresponds to the bonding combination ( $\beta$  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  $\pi$  system. The **highest occupied molecular orbital** in ethene, its HOMO, is the  $1\pi$  orbital; the **lowest unfilled molecular orbital**, its LUMO, is the  $2\pi$  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  $1\pi$  to the  $2\pi$  orbital. The constant  $\beta$  is often left as an adjustable parameter; an approximate value for  $\pi$ 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

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

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

where the eigenvalue  $E_i$  corresponds to a wavefunction of the form  $\psi_i = c_{i,A}A + c_{i,B}B$ . (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  $\psi_1$ :

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

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

and another corresponding to  $E_2$  and  $\psi_2$ :

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

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

If we introduce the following matrices and column vectors

$$\mathbf{H} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \quad \mathbf{S} = \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \quad \mathbf{c}_i = \begin{pmatrix} c_{i,A} \\ c_{i,B} \end{pmatrix} \quad (11.42)$$

then each pair of equations may be written more succinctly as

$$(\mathbf{H} - E_i \mathbf{S})\mathbf{c}_i = 0 \quad \text{or} \quad \mathbf{H}\mathbf{c}_i = \mathbf{S}\mathbf{c}_i E_i \quad (11.43)$$

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

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

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

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{E} \quad (11.45)$$

**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  $\mathbf{S} = \mathbf{1}$ , the unit matrix (with 1 on the diagonal and 0 elsewhere). Then

$$\mathbf{H}\mathbf{C} = \mathbf{C}\mathbf{E}$$

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

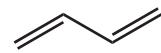
$$\mathbf{C}^{-1}\mathbf{H}\mathbf{C} = \mathbf{E} \quad (11.46)$$

where we have used  $\mathbf{C}^{-1}\mathbf{C} = \mathbf{1}$ . In other words, to find the eigenvalues  $E_i$ , we have to find a transformation of  $\mathbf{H}$  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  $\mathbf{C}$  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  $\mathbf{c}_i$ . As a result, we have to solve  $N$  equations of the form  $\mathbf{H}\mathbf{c}_i = \mathbf{S}\mathbf{c}_i E_i$  by diagonalization of the  $N \times N$  matrix  $\mathbf{H}$ , 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  $\pi$ -orbitals of butadiene (3).

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



3

#### Solution

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

Mathematical software then diagonalizes this matrix to

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

and the matrix that achieves the diagonalization is

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

We can conclude that the energies and molecular orbitals are

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

where the  $C_{2p}$  atomic orbitals are denoted by  $\chi_A, \dots, \chi_D$ . Note that the orbitals are mutually orthogonal and, with overlap neglected, normalized.

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

$$\begin{aligned} E &= \alpha + 2^{1/2}\beta, \alpha, \alpha - 2^{1/2}\beta; \psi_1 = \frac{1}{2}\chi_A + (\frac{1}{2})^{1/2}\chi_B + \frac{1}{2}\chi_C, \\ \psi_2 &= (\frac{1}{2})^{1/2}\chi_A - (\frac{1}{2})^{1/2}\chi_C, \psi_3 = \frac{1}{2}\chi_A - (\frac{1}{2})^{1/2}\chi_B + \frac{1}{2}\chi_C \end{aligned}$$

### (c) Butadiene and $\pi$ -electron binding energy

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

$$E = \alpha \pm 1.62\beta, \quad \alpha \pm 0.62\beta \quad (11.47)$$

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  $2\pi$  orbital (the HOMO, which is largely bonding) and the  $3\pi$  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  **$\pi$ -electron binding energy**,  $E_\pi$ , the sum of the energies of each  $\pi$  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

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

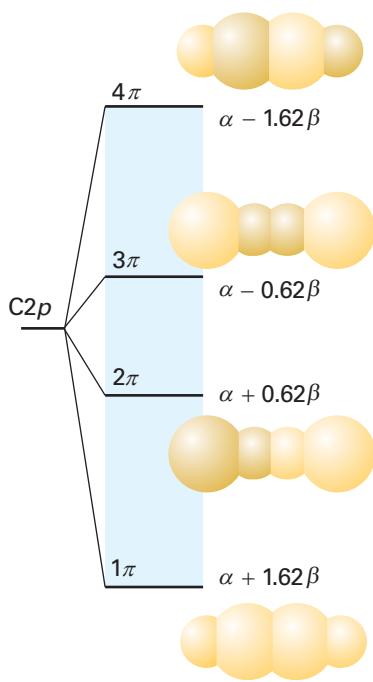
Therefore, the energy of the butadiene molecule lies lower by  $0.48\beta$  (about 110 kJ mol<sup>-1</sup>) than the sum of two individual  $\pi$  bonds. This extra stabilization of a conjugated system is called the **delocalization energy**. A closely related quantity is the  **$\pi$ -bond formation energy**, the energy released when a  $\pi$  bond is formed. Because the contribution of  $\alpha$  is the same in the molecule as in the atoms, we can find the  $\pi$ -bond formation energy from the  $\pi$ -electron binding energy by writing

$$E_{bf} = E_\pi - N\alpha \quad (11.48)$$

where  $N$  is the number of carbon atoms in the molecule. The  $\pi$ -bond formation energy in butadiene, for instance, is  $4.48\beta$ .

### Example 11.5 Estimating the delocalization energy

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



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

**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  $\pi$ -bond energy. For the delocalization energy, subtract from the total  $\pi$ -bond energy the energy of two  $\pi$ -bonds.

**Answer** The hamiltonian matrix is

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

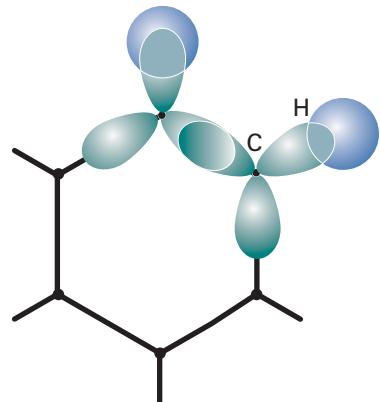
Diagonalization gives the energies of the orbitals as

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

Four electrons must be accommodated. Two occupy the lowest orbital (of energy  $\alpha + 2\beta$ ), and two occupy the doubly degenerate orbitals (of energy  $\alpha$ ). The total energy is therefore  $4\alpha + 4\beta$ . Two isolated  $\pi$  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  $\sigma$  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  $\sigma$  framework and molecular orbital language used to describe its  $\pi$  electrons.

First, the valence-bond component. The six C atoms are regarded as  $sp^2$  hybridized, with a single unhybridized 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  $120^\circ$ , so  $sp^2$  hybridization is ideally suited for forming  $\sigma$  bonds. We see that benzene's hexagonal shape permits strain-free  $\sigma$  bonding.

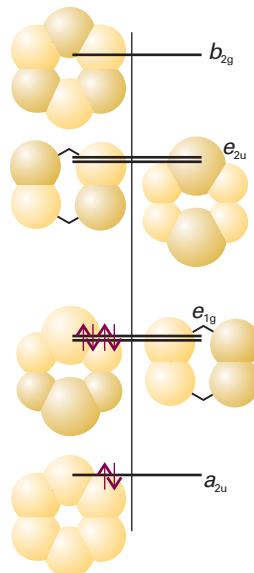
Now consider the molecular orbital component of the description. The six  $C2p$  orbitals overlap to give six  $\pi$  orbitals that spread all round the ring. Their energies are calculated within the Hückel approximation by diagonalizing the hamiltonian matrix

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

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

$$E = \alpha \pm 2\beta, \alpha \pm \beta, \alpha \pm \beta \quad (11.49)$$

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  $\pi$  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  $\pi$ -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  $\pi$  bonds, it would be ascribed a  $\pi$ -electron energy of only  $3(2\alpha + 2\beta) = 6\alpha + 6\beta$ . The delocalization energy is therefore  $2\beta \approx -460 \text{ kJ mol}^{-1}$ , which is considerably more than for butadiene. The  $\pi$ -bond formation energy in benzene is  $8\beta$ .

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  $\sigma$  bonds: the  $\sigma$  framework is relaxed and without strain. Second, the  $\pi$  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:

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

This is the wavefunction for an  $N$ -electron closed-shell molecule in which electron 1 occupies molecular orbital  $\psi_a$  with spin  $\alpha$ , electron 2 occupies molecular orbital  $\psi_a$  with spin  $\beta$ , 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:

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

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

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

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

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

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**:

$$f_1 \psi_{a,\sigma}(1) = \epsilon \psi_{a,\sigma}(1) \quad (11.51)$$

where  $\sigma$  is either  $\alpha$  or  $\beta$ . The **Fock operator**  $f_1$  is

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

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

$$h_1 = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \sum_n \frac{Z_n e^2}{4\pi\epsilon_0 r_{ni}} \quad [11.53a]$$

the **Coulomb operator**  $J$ , where

$$J_j(1) \psi_a(1) = \int \psi_j^*(2) \psi_j(2) \left( \frac{e^2}{4\pi\epsilon_0 r_{12}} \right) \psi_a(1) d\tau_2 \quad [11.53b]$$

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

$$K_j(1) \psi_a(1) = \int \psi_j^*(2) \psi_a(2) \left( \frac{e^2}{4\pi\epsilon_0 r_{12}} \right) \psi_j(1) d\tau_2 \quad [11.53c]$$

Although the Hartree–Fock equations look deceptively simple, with the Fock operator looking like a hamiltonian, we see from these definitions that *factually* 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  $\chi_i$ , 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**:

$$FC = SC\epsilon \quad (11.54)$$

where  $F$  is the matrix formed from the Fock operator:

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

and  $S$  is the matrix of overlap integrals

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

**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

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

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

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

That is,

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

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

$$(AB|CD) = \int A(1)B(1) \left( \frac{e^2}{4\pi\epsilon_0 r_{12}} \right) C(2)D(2) d\tau_1 d\tau_2 \quad (11.56)$$

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

$$(AB|CD) = \int X(1) \left( \frac{e^2}{4\pi\epsilon_0 r_{12}} \right) Y(2) d\tau_1 d\tau_2 \quad (11.57)$$

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.

### (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,  $\rho$ , rather than the wavefunction  $\psi$ . 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,  $\rho(\mathbf{r})$ , and in mathematics a function of a function is called a *functional*. The exact ground-state energy of an  $n$ -electron molecule is

$$E[\rho] = E_K + E_{P,e,N} + E_{P,e,e} + E_{XC}[\rho] \quad (11.58)$$

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

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

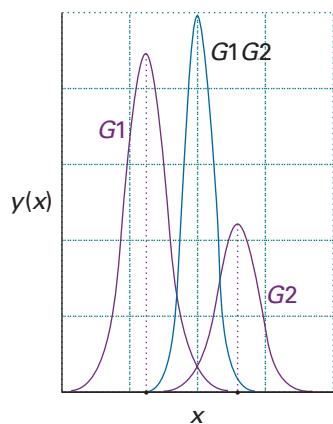
are calculated from the **Kohn–Sham equations**, which are found by applying the variation principle to the electron energy, and are like the Hartree–Fock equations except for a term  $V_{XC}$ , which is called the **exchange–correlation potential**:

$$\left\{ \begin{array}{l} \text{Kinetic energy} \\ \frac{\hbar^2}{2m_e} \nabla_1^2 - \sum_{j=1}^N \frac{Z_j e^2}{4\pi\epsilon_0 r_{1j}} \\ \text{Electron–nucleus attraction} \\ \text{Electron–electron repulsion} \\ \text{Exchange–correlation} \end{array} \right\} \psi_i(\mathbf{r}_1) = \epsilon_i \psi_i(\mathbf{r}_1) \quad (11.60)$$

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

$$V_{XC}[\rho] = \frac{\delta E_{XC}[\rho]}{\delta \rho} \quad (11.61)$$

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



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

### 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

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

where the manner in which  $\delta f$  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

$$E_{\text{XC}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{\text{XC}}[\rho(\mathbf{r})] d\mathbf{r} \quad (11.62)$$

where  $\varepsilon_{\text{XC}}$  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.

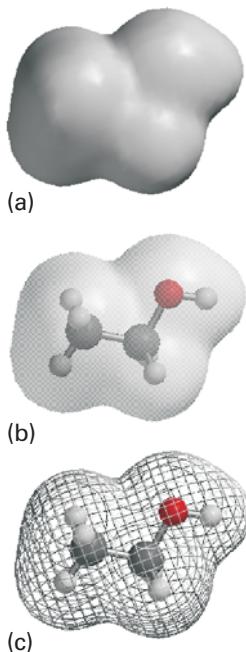
### (a) Electron density and the electrostatic potential surfaces

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.

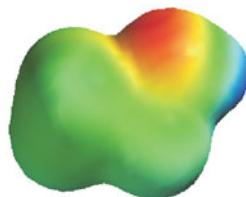
Once the coefficients are known, we can build up a representation of the electron density in the molecule by noting which orbitals are occupied and then forming the squares of those orbitals. The total electron density at any point is then the sum of the squares of the wavefunctions evaluated at that 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 from 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. 11.43** Various representations of an isodensity surface of ethanol (a) solid surface, (b) transparent surface, and (c) mesh surface.

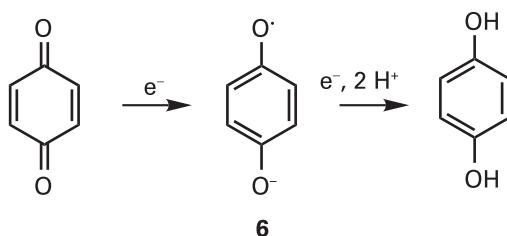


**Fig. 11.44** An elpot diagram of ethanol.

### (b) Thermodynamic and spectroscopic properties

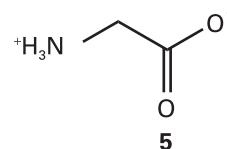
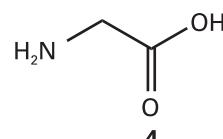
We already saw in Section 2.8 that computational chemistry is becoming the technique of choice for estimating standard enthalpies of formation of molecules with complex three-dimensional structures. The computational approach also makes it possible to gain insight into the effect of solvation on the 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.

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 ( $-\text{CH}_3$ ) 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**):



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*).

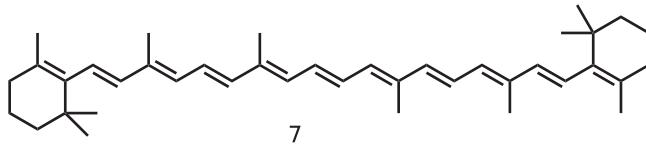
We remarked in Chapter 8 that a molecule can absorb or emit a photon of energy  $hc/\lambda$ , resulting in a transition between two quantized molecular energy levels. The transition of lowest energy (and longest wavelength) occurs between the HOMO and LUMO. We can use calculations based on semi-empirical, *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 ( $\text{C}_2\text{H}_4$ ), butadiene ( $\text{C}_4\text{H}_6$ ), hexatriene ( $\text{C}_6\text{H}_8$ ), and octatetraene ( $\text{C}_8\text{H}_{10}$ ), 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	$\{E(\text{HOMO}) - E(\text{LUMO})\}/\text{eV}$	$\lambda/\text{nm}$
$= = = (\text{C}_2\text{H}_4)$	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  $\beta$ -carotene (7), which absorbs light with  $\lambda \approx 450$  nm. The ability of  $\beta$ -carotene to absorb visible light is part of the strategy employed by plants to harvest solar energy for use in photosynthesis (Chapter 23).



## 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 atom 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  $\sigma$  bond. A  $\pi$  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 of 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  $\sigma$  molecular orbital has zero orbital angular momentum about the internuclear axis. A  $\pi$  molecular orbital has one unit of angular momentum around the internuclear axis; in a nonlinear molecule, it has a nodal plane that includes the internuclear 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,  $\chi$ , 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.

13. The hamiltonian matrix,  $\mathbf{H}$ , is formed of all integrals  $H_{ij} = \int \psi_i^* \hat{H} \psi_j d\tau$ . The overlap matrix,  $\mathbf{S}$ , is formed of all  $S_{ij} = \int \psi_i^* \psi_j d\tau$ .
14. The variation principle states that if an arbitrary wavefunction is used to calculate the energy, the value calculated is never less than the true energy.
15. In the Hückel method, all Coulomb integrals  $H_{ii}$  are set equal (to  $\alpha$ ), all overlap integrals are set equal to zero, all resonance integrals  $H_{ij}$  between non-neighbours are set equal to zero, and all remaining resonance integrals are set equal (to  $\beta$ ).
16. The  $\pi$ -electron binding energy is the sum of the energies of each  $\pi$  electron. The  $\pi$ -bond formation energy is the energy released when a  $\pi$  bond is formed. The delocalization energy is the extra stabilization of a conjugated system.
17. In the self-consistent field procedure, an initial guess about the composition of the molecular orbitals is successively refined until the solution remains unchanged in a cycle of calculations.
18. In semi-empirical methods for the determination of electronic structure, the Schrödinger equation is written in terms of parameters chosen to agree with selected experimental quantities. In *ab initio* and density functional methods, the Schrödinger equation is solved numerically, without the need of parameters that appeal to experimental data.

## Further reading

### Articles and texts

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- P.W. Atkins and R.S. Friedman, *Molecular quantum mechanics*. Oxford University Press (2005).
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- R.C. Mebane, S.A. Schanley, T.R. Rybolt, and C.D. Bruce, The correlation of physical properties of organic molecules with computed molecular surface areas. *J. Chem. Educ.* **76**, 688 (1999).

- L. Pauling, *The nature of the chemical bond*. Cornell University Press, Ithaca (1960).
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### Sources of data and information

- D.R. Lide (ed.), *CRC handbook of chemistry and physics*, Section 9, CRC Press, Boca Raton (2000).
- P.R. Scott and W.G. Richards, *Energy levels in atoms and molecules*. Oxford Chemistry Primers, Oxford University Press (1994).

## Discussion questions

- 11.1** Compare the approximations built into valence-bond theory and molecular-orbital theory.
- 11.2** Discuss the steps involved in the construction of  $sp^3$ ,  $sp^2$ , and  $sp$  hybrid orbitals.
- 11.3** Distinguish between the Pauling and Mulliken electronegativity scales.
- 11.4** Discuss the steps involved in the calculation of the energy of a system by using the variation principle.

- 11.5** Discuss the approximations built into the Hückel method.
- 11.6** Distinguish between delocalization energy,  $\pi$ -electron binding energy, and  $\pi$ -bond formation energy.
- 11.7** Use concepts of molecular orbital theory to describe the biochemical reactivity of  $O_2$ ,  $N_2$ , and  $NO$ .
- 11.8** Distinguish between semi-empirical, *ab initio*, and density functional theory methods of electronic structure determination.

## Exercises

- 11.1a** Give the ground-state electron configurations and bond orders of (a)  $Li_2$ , (b)  $Be_2$ , and (c)  $C_2$ .

- 11.1b** Give the ground-state electron configurations of (a)  $H_2^-$ , (b)  $N_2$ , and (c)  $O_2^-$ .

- 11.2a** Give the ground-state electron configurations of (a)  $CO$ , (b)  $NO$ , and (c)  $CN^-$ .

- 11.2b** Give the ground-state electron configurations of (a)  $ClF$ , (b)  $CS$ , and (c)  $O_2^-$ .

**11.3a** From the ground-state electron configurations of  $\text{B}_2$  and  $\text{C}_2$ , predict which molecule should have the greater bond dissociation energy.

**11.3b** Which of the molecules  $\text{N}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{C}_2$ ,  $\text{F}_2$ , and  $\text{CN}$  would you expect to be stabilized by (a) the addition of an electron to form  $\text{AB}^-$ , (b) the removal of an electron to form  $\text{AB}^+$ ?

**11.4a** Sketch the molecular orbital energy level diagram for  $\text{XeF}$  and deduce its ground-state electron configurations. Is  $\text{XeF}$  likely to have a shorter bond length than  $\text{XeF}^+$ ?

**11.4b** Sketch the molecular orbital energy level diagrams for  $\text{BrCl}$  and deduce its ground-state electron configurations. Is  $\text{BrCl}$  likely to have a shorter bond length than  $\text{BrCl}^-$ ?

**11.5a** Use the electron configurations of  $\text{NO}$  and  $\text{N}_2$  to predict which is likely to have the shorter bond length.

**11.5b** Arrange the species  $\text{O}_2^+$ ,  $\text{O}_2$ ,  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$  in order of increasing bond length.

**11.6a** Show that the  $sp^2$  hybrid orbital  $(s + 2^{1/2}p)/3^{1/2}$  is normalized to 1 if the  $s$  and  $p$  orbitals are normalized to 1.

**11.6b** Normalize the molecular orbital  $\psi_A + \lambda\psi_B$  in terms of the parameter  $\lambda$  and the overlap integral  $S$ .

**11.7a** Confirm that the bonding and antibonding combinations  $\psi_A \pm \psi_B$  are mutually orthogonal in the sense that their mutual overlap is zero.

**11.7b** Suppose that a molecular orbital has the form  $N(0.145A + 0.844B)$ . Find a linear combination of the orbitals  $A$  and  $B$  that is orthogonal to this combination.

**11.8a** Can the function  $\psi = x(L - x)$  be used as a trial wavefunction for the  $n = 1$  state of a particle with mass  $m$  in a one-dimensional box of length  $L$ ? If the answer is yes, then express the energy of this trial wavefunction in terms of  $h$ ,  $m$ , and  $L$  and compare it with the exact result (eqn 9.4). If the answer is no, explain why this is not a suitable trial wavefunction.

**11.8b** Can the function  $\psi = x^2(L - 2x)$  be used as a trial wavefunction for the  $n = 1$  state of a particle with mass  $m$  in a one-dimensional box of length  $L$ ? If the answer is yes, then express the energy of this trial wavefunction in terms of  $h$ ,  $m$ , and  $L$  and compare it with the exact result (eqn 9.4). If the answer is no, explain why this is not a suitable trial wavefunction.

**11.9a** Suppose that the function  $\psi = Ae^{-ar^2}$ , with  $A$  being the normalization constant and  $a$  being an adjustable parameter, is used as a trial wavefunction for the  $1s$  orbital of the hydrogen atom. Express the energy of this trial

wavefunction as a function of the  $h$ ,  $a$ ,  $e$ , the electron charge, and  $\mu$ , the effective mass of the H atom.

**11.9b** Suppose that the function  $\psi = Ae^{-ar^2}$ , with  $A$  being the normalization constant and  $a$  being an adjustable parameter, is used as a trial wavefunction for the  $1s$  orbital of the hydrogen atom. The energy of this trial wavefunction is

$$E = \frac{3ah^2}{2\mu} - \frac{e^2}{\epsilon_0} \left( \frac{a}{2\pi^3} \right)^{1/2}$$

where  $e$  is the electron charge, and  $\mu$  is the effective mass of the H atom. What is the minimum energy associated with this trial wavefunction?

**11.10a** What is the energy of an electron that has been ejected from an orbital of ionization energy 11.0 eV by a photon of radiation of wavelength 100 nm?

**11.10b** What is the energy of an electron that has been ejected from an orbital of ionization energy 4.69 eV by a photon of radiation of wavelength 584 pm?

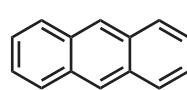
**11.11a** Construct the molecular orbital energy level diagrams of ethene on the basis that the molecule is formed from the appropriately hybridized  $\text{CH}_2$  or  $\text{CH}$  fragments.

**11.11b** Construct the molecular orbital energy level diagrams of ethyne (acetylene) on the basis that the molecule is formed from the appropriately hybridized  $\text{CH}_2$  or  $\text{CH}$  fragments.

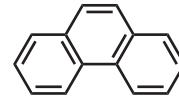
**11.12a** Write down the secular determinants for (a) linear  $\text{H}_3$ , (b) cyclic  $\text{H}_3$  within the Hückel approximation.

**11.12b** Predict the electronic configurations of (a) the benzene anion, (b) the benzene cation. Estimate the  $\pi$ -electron binding energy in each case.

**11.13a** Write down the secular determinants (a) anthracene (**8**), (b) phenanthrene (**9**) within the Hückel approximation and using the  $\text{C}2p$  orbitals as the basis set.



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**11.13b** Use mathematical software to estimate the  $\pi$ -electron binding energy of (a) anthracene (**7**), (b) phenanthrene (**8**) within the Hückel approximation.

## Problems\*

### Numerical problems

**11.1** Show that, if a wave  $\cos kx$  centred on A (so that  $x$  is measured from A) interferes with a similar wave  $\cos k'x$  centred on B (with  $x$  measured from B) a distance  $R$  away, then constructive interference occurs in the intermediate region when  $k = k' = \pi/2R$  and destructive interference if  $kR = \frac{1}{2}\pi$  and  $k'R = \frac{3}{2}\pi$ .

**11.2** The overlap integral between two  $\text{H}1s$  orbitals on nuclei separated by a distance  $R$  is  $S = \{1 + (R/a_0) + \frac{1}{3}(R/a_0)^2\}e^{-R/a_0}$ . Plot this function for  $0 \leq R < \infty$ .

**11.3** Before doing the calculation below, sketch how the overlap between a  $1s$  orbital and a  $2p$  orbital can be expected to depend on their separation. The overlap integral between an  $\text{H}1s$  orbital and an  $\text{H}2p$  orbital on nuclei

separated by a distance  $R$  and forming a  $\sigma$  orbital is  $S = (R/a_0)\{1 + (R/a_0) + \frac{1}{3}(R/a_0)^2\}e^{-R/a_0}$ . Plot this function, and find the separation for which the overlap is a maximum.

**11.4** Calculate the total amplitude of the normalized bonding and antibonding LCAO-MOs that may be formed from two  $\text{H}1s$  orbitals at a separation of 106 pm. Plot the two amplitudes for positions along the molecular axis both inside and outside the internuclear region.

**11.5** Repeat the calculation in Problem 11.4 but plot the probability densities of the two orbitals. Then form the difference density, the difference between  $\psi^2$  and  $\frac{1}{2}\{\psi_A^2 + \psi_B^2\}$ .

\* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

**11.6‡** Use the  $2p_x$  and  $2p_z$  hydrogenic atomic orbitals to construct simple LCAO descriptions of  $2p\sigma$  and  $2p\pi$  molecular orbitals. (a) Make a probability density plot, and both surface and contour plots of the  $xz$ -plane amplitudes of the  $2p_z\sigma$  and  $2p_z\sigma^*$  molecular orbitals. (b) Make surface and contour plots of the  $xz$ -plane amplitudes of the  $2p_x\pi$  and  $2p_x\pi^*$  molecular orbitals. Include plots for both internuclear distances,  $R$ , of  $10a_0$  and  $3a_0$ , where  $a_0 = 52.9$  pm. Interpret the graphs, and describe why this graphical information is useful.

**11.7** Imagine a small electron-sensitive probe of volume  $1.00 \text{ pm}^3$  inserted into an  $\text{H}_2^+$  molecule-ion in its ground state. Calculate the probability that it will register the presence of an electron at the following positions: (a) at nucleus A, (b) at nucleus B, (c) half-way between A and B, (c) at a point 20 pm along the bond from A and 10 pm perpendicularly. Do the same for the molecule-ion the instant after the electron has been excited into the antibonding LCAO-MO.

**11.8** The energy of  $\text{H}_2^+$  with internuclear separation  $R$  is given by the expression

$$E = E_{\text{H}} + \frac{e^2}{4\pi\epsilon_0 R} - \frac{V_1 + V_2}{1 + S}$$

where  $E_{\text{H}}$  is the energy of an isolated H atom,  $V_1$  is the attractive potential energy between the electron centred on one nucleus and the charge of the other nucleus,  $V_2$  is the attraction between the overlap density and one of the nuclei,  $S$  is the overlap integral. The values are given below. Plot the molecular potential energy curve and find the bond dissociation energy (in electronvolts) and the equilibrium bond length.

$R/a_0$	0	1	2	3	4
$V_1/E_{\text{h}}$	11.000	10.729	10.473	10.330	10.250
$V_2/E_{\text{h}}$	11.000	10.736	10.406	10.199	10.092
$S$	1.000	0.858	0.587	0.349	0.189

where  $E_{\text{h}} = 27.3$  eV and  $a_0 = 52.9$  pm and  $E_{\text{H}} = -\frac{1}{2}E_{\text{h}}$ .

**11.9** The same data as in Problem 11.8 may be used to calculate the molecular potential energy curve for the antibonding orbital, which is given by

$$E = E_{\text{H}} + \frac{e^2}{4\pi\epsilon_0 R} - \frac{V_1 - V_2}{1 - S}$$

Plot the curve.

**11.10‡** J.G. Dojahn, E.C.M. Chen, and W.E. Wentworth (*J. Phys. Chem.* **100**, 9649 (1996)) characterized the potential energy curves of homonuclear diatomic halogen molecules and molecular anions. Among the properties they report are the equilibrium internuclear distance  $R_e$ , the vibrational wavenumber,  $\bar{v}$ , and the dissociation energy,  $D_e$ :

Species	$R_e$	$\bar{v}/\text{cm}^{-1}$	$D_e/\text{eV}$
$\text{F}_2$	1.411	916.6	1.60
$\text{F}_2^-$	1.900	450.0	1.31

Rationalize these data in terms of molecular orbital configurations.

**11.11‡** Rydberg molecules are molecules with an electron in an atomic orbital with principal quantum number  $n$  one higher than the valence shells of the constituent atoms. Speculate about the existence of ‘hyper Rydberg’  $\text{H}_2$  formed from two H atoms with 100s electrons. Make reasonable guesses about the binding energy, the equilibrium internuclear separation, the vibrational force constant, and the rotational constant. Is such a molecule likely to exist under any circumstances?

**11.12** In a particular photoelectron spectrum using 21.21 eV photons, electrons were ejected with kinetic energies of 11.01 eV, 8.23 eV, and 5.22 eV. Sketch the molecular orbital energy level diagram for the species, showing the ionization energies of the three identifiable orbitals.

**11.13‡** Set up and solve the Hückel secular equations for the  $\pi$  electrons of  $\text{NO}_3^-$ . Express the energies in terms of the Coulomb integrals  $\alpha_O$  and  $\alpha_N$  and the resonance integral  $\beta$ . Determine the delocalization energy of the ion.

**11.14** In the ‘free electron molecular orbital’ (FEMO) theory, the electrons in a conjugated molecule are treated as independent particles in a box of length  $L$ . Sketch the form of the two occupied orbitals in butadiene predicted by this model and predict the minimum excitation energy of the molecule. The tetraene  $\text{CH}_2=\text{CHCH}=\text{CHCH}=\text{CHCH}=\text{CH}_2$  can be treated as a box of length  $8R$ , where  $R \approx 140$  pm (as in this case, an extra half bond-length is often added at each end of the box). Calculate the minimum excitation energy of the molecule and sketch the HOMO and LUMO. Estimate the colour a sample of the compound is likely to appear in white light.

**11.15** The FEMO theory (Problem 11.14) of conjugated molecules is rather crude and better results are obtained with simple Hückel theory. (a) For a linear conjugated polyene with each of  $N$  carbon atoms contributing an electron in a  $2p$  orbital, the energies  $E_k$  of the resulting  $\pi$  molecular orbitals are given by (see also Section 20.9):

$$E_k = \alpha + 2\beta \cos \frac{k\pi}{N+1} \quad k = 1, 2, 3, \dots, N$$

Use this expression to determine a reasonable empirical estimate of the resonance integral  $\beta$  for the homologous series consisting of ethene, butadiene, hexatriene, and octatetraene given that  $\pi^* \leftarrow \pi$  ultraviolet absorptions from the HOMO to the LUMO occur at 61 500, 46 080, 39 750, and  $32\ 900 \text{ cm}^{-1}$ , respectively. (b) Calculate the  $\pi$ -electron delocalization energy,  $E_{\text{deloc}} = E_\pi - n(\alpha + \beta)$ , of octatetraene, where  $E_\pi$  is the total  $\pi$ -electron binding energy and  $n$  is the total number of  $\pi$ -electrons. (c) In the context of this Hückel model, the  $\pi$  molecular orbitals are written as linear combinations of the carbon  $2p$  orbitals. The coefficient of the  $j$ th atomic orbital in the  $k$ th molecular orbital is given by:

$$c_{kj} = \left( \frac{2}{N+1} \right)^{1/2} \sin \frac{jk\pi}{N+1} \quad j = 1, 2, 3, \dots, N$$

Determine the values of the coefficients of each of the six  $2p$  orbitals in each of the six  $\pi$  molecular orbitals of hexatriene. Match each set of coefficients (that is, each molecular orbital) with a value of the energy calculated with the expression given in part (a) of the molecular orbital. Comment on trends that relate the energy of a molecular orbital with its ‘shape’, which can be inferred from the magnitudes and signs of the coefficients in the linear combination that describes the molecular orbital.

**11.16** For monocyclic conjugated polyenes (such as cyclobutadiene and benzene) with each of  $N$  carbon atoms contributing an electron in a  $2p$  orbital, simple Hückel theory gives the following expression for the energies  $E_k$  of the resulting  $\pi$  molecular orbitals:

$$E_k = \alpha + 2\beta \cos \frac{2k\pi}{N} \quad k = 0, \pm 1, \pm 2, \dots, \pm N/2 \text{ (even } N) \\ k = 0, \pm 1, \pm 2, \dots, \pm (N-1)/2 \text{ (odd } N)$$

(a) Calculate the energies of the  $\pi$  molecular orbitals of benzene and cyclooctatetraene. Comment on the presence or absence of degenerate energy levels. (b) Calculate and compare the delocalization energies of benzene (using the expression above) and hexatriene (see Problem 11.15a). What do you conclude from your results? (c) Calculate and compare the delocalization energies of cyclooctaene and octatetraene. Are your conclusions for this pair of molecules the same as for the pair of molecules investigated in part (b)?

**11.17** If you have access to mathematical software that can perform matrix diagonalization, use it to solve Problems 11.15 and 11.16, disregarding the expressions for the energies and coefficients given there.

**11.18** Molecular orbital calculations based on semi-empirical, *ab initio*, and DFT methods describe the spectroscopic properties of conjugated molecules a

bit better than simple Hückel theory. (a) Using molecular modelling software<sup>2</sup> and the computational method of your choice (semi-empirical, *ab initio*, or density functional methods), calculate the energy separation between the HOMO and LUMO of ethene, butadiene, hexatriene, and octatetraene. (b) Plot the HOMO–LUMO energy separations against the experimental frequencies for  $\pi^* \leftarrow \pi$ -ultraviolet absorptions for these molecules (Problem 11.15). Use mathematical software to find the polynomial equation that best fits the data. (c) Use your polynomial fit from part (b) to estimate the frequency of the  $\pi^* \leftarrow \pi$ -ultraviolet absorption of decapentaene from the calculated HOMO–LUMO energy separation. (d) Discuss why the calibration procedure of part (b) is necessary.

**11.19** Electronic excitation of a molecule may weaken or strengthen some bonds because bonding and antibonding characteristics differ between the HOMO and the LUMO. For example, a carbon–carbon bond in a linear polyene may have bonding character in the HOMO and antibonding character in the LUMO. Therefore, promotion of an electron from the HOMO to the LUMO weakens this carbon–carbon bond in the excited electronic state, relative to the ground electronic state. Display the HOMO and LUMO of each molecule in Problem 11.15 and discuss in detail any changes in bond order that accompany the  $\pi^* \leftarrow \pi$ -ultraviolet absorptions in these molecules.

**11.20** As mentioned in Section 2.8, molecular electronic structure methods may be used to estimate the standard enthalpy of formation of molecules in the gas phase. (a) Using molecular modelling software and a semi-empirical method of your choice, calculate the standard enthalpy of formation of ethene, butadiene, hexatriene, and octatetraene in the gas phase. (b) Consult a database of thermochemical data, such as the online sources listed in this textbook's web site, and, for each molecule in part (a), calculate the relative error between the calculated and experimental values of the standard enthalpy of formation. (c) A good thermochemical database will also report the uncertainty in the experimental value of the standard enthalpy of formation. Compare experimental uncertainties with the relative errors calculated in part (b) and discuss the reliability of your chosen semi-empirical method for the estimation of thermochemical properties of linear polyenes.

### Theoretical problems

**11.21** An  $sp^2$  hybrid orbital that lies in the  $xy$ -plane and makes an angle of  $120^\circ$  to the  $x$ -axis has the form

$$\psi = \frac{1}{3^{1/2}} \left( s - \frac{1}{2^{1/2}} p_x + \frac{3^{1/2}}{2^{1/2}} p_y \right)$$

Use hydrogenic atomic orbitals to write the explicit form of the hybrid orbital. Show that it has its maximum amplitude in the direction specified.

**11.22** Use the expressions in Problems 11.8 and 11.9 to show that the antibonding orbital is more antibonding than the bonding orbital is bonding at most internuclear separations.

**11.23** Derive eqns 11.11 and 11.14 by working with the normalized LCAO-MOs for the  $H_2^+$  molecule-ion (Section 11.3a). Proceed by evaluating the expectation value of the hamiltonian for the ion. Make use of the fact that  $A$  and  $B$  each individually satisfy the Schrödinger equation for an isolated H atom.

**11.24** Take as a trial function for the ground state of the hydrogen atom (a)  $e^{-kr}$ , (b)  $e^{-k^2r}$  and use the variation principle to find the optimum value of  $k$  in each case. Identify the better wavefunction. The only part of the laplacian that need be considered is the part that involves radial derivatives (eqn 9.5).

**11.25** We saw in Section 11.5 that, to find the energies of the bonding and antibonding orbitals of a heteronuclear diatomic molecule, we need to solve the secular determinant

$$\begin{vmatrix} \alpha_A - E & B \\ \beta & \alpha_B - E \end{vmatrix} = 0$$

where  $\alpha_A \neq \alpha_B$  and we have taken  $S = 0$ . Equations 11.34a and 11.34b give the general solution to this problem. Here, we shall develop the result for the case  $(\alpha_B - \alpha_A)^2 \gg \beta^2$ . (a) Begin by showing that

$$E_{\pm} = \frac{\alpha_A + \alpha_B}{2} \pm \frac{\alpha_A - \alpha_B}{2} \left[ 1 + \frac{4\beta^2}{(\alpha_A - \alpha_B)^2} \right]^{1/2}$$

where  $E_+$  and  $E_-$  are the energies of the bonding and antibonding molecular orbitals, respectively. (b) Now use the expansion

$$(1+x)^{1/2} = 1 + \frac{x}{2} - \frac{x^3}{8} + \dots$$

to show that

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

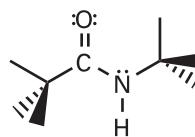
which is the limiting result used in *Justification 11.4*.

### Applications: to astrophysics and biology

**11.26†** In Exercise 11.12a you were invited to set up the Hückel secular determinant for linear and cyclic  $H_3$ . The same secular determinant applies to the molecular ions  $H_3^+$  and  $D_3^+$ . The molecular ion  $H_3^+$  was discovered as long ago as 1912 by J.J. Thomson, but only more recently has the equivalent equilateral triangular structure been confirmed by M.J. Gaillard *et al.* (*Phys. Rev.* **A17**, 1797 (1978)). The molecular ion  $H_3^+$  is the simplest polyatomic species with a confirmed existence and plays an important role in chemical reactions occurring in interstellar clouds that may lead to the formation of water, carbon monoxide, and ethyl alcohol. The  $H_3^+$  ion has also been found in the atmospheres of Jupiter, Saturn, and Uranus. (a) Solve the Hückel secular equations for the energies of the  $H_3$  system in terms of the parameters  $\alpha$  and  $\beta$ , draw an energy level diagram for the orbitals, and determine the binding energies of  $H_3^+$ ,  $H_3$ , and  $H_3^-$ . (b) Accurate quantum mechanical calculations by G.D. Carney and R.N. Porter (*J. Chem. Phys.* **65**, 3547 (1976)) give the dissociation energy for the process  $H_3^+ \rightarrow H + H + H^+$  as  $849 \text{ kJ mol}^{-1}$ . From this information and data in Table 11.3, calculate the enthalpy of the reaction  $H^+(g) + H_2(g) \rightarrow H_3^+(g)$ . (c) From your equations and the information given, calculate a value for the resonance integral  $\beta$  in  $H_3^+$ . Then go on to calculate the bind energies of the other  $H_3$  species in (a).

**11.27†** There is some indication that other hydrogen ring compounds and ions in addition to  $H_3$  and  $D_3$  species may play a role in interstellar chemistry. According to J.S. Wright and G.A. DiLabio (*J. Phys. Chem.* **96**, 10793 (1992)),  $H_5^-$ ,  $H_6$ , and  $H_7^+$  are particularly stable whereas  $H_4$  and  $H_5^+$  are not. Confirm these statements by Hückel calculations.

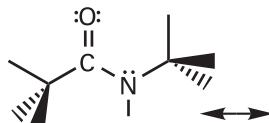
**11.28** Here we develop a molecular orbital theory treatment of the peptide group (**10**), which links amino acids in proteins. Specifically, we shall describe the factors that stabilize the planar conformation of the peptide group.



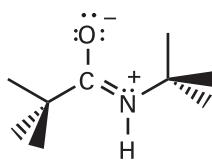
10

<sup>2</sup> The web site contains links to molecular modelling freeware and to other sites where you may perform molecular orbital calculations directly from your web browser.

(a) It will be familiar from introductory chemistry that valence bond theory explains the planar conformation of the peptide group by invoking delocalization of the  $\pi$  bond between the oxygen, carbon, and nitrogen atoms (11, 11):



11



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It follows that we can model the peptide group with molecular orbital theory by making LCAO-MOs from  $2p$  orbitals perpendicular to the plane defined by the O, C, and N atoms. The three combinations have the form:

$$\psi_1 = a\psi_O + b\psi_C + c\psi_N \quad \psi_2 = d\psi_O - e\psi_N \quad \psi_3 = f\psi_O - g\psi_C + h\psi_N$$

where the coefficients  $a$  through  $h$  are all positive. Sketch the orbitals  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$  and characterize them as bonding, non-bonding, or antibonding molecular orbitals. In a non-bonding molecular orbital, a pair of electrons resides in an orbital confined largely to one atom and not appreciably involved in bond formation. (b) Show that this treatment is consistent only with a planar conformation of the peptide link. (c) Draw a diagram showing the relative energies of these molecular orbitals and determine the occupancy of the orbitals. Hint. Convince yourself that there are four electrons to be distributed among the molecular orbitals. (d) Now consider a non-planar conformation of the peptide link, in which the O $2p$  and C $2p$  orbitals are perpendicular to the plane defined by the O, C, and N atoms, but the N $2p$  orbital lies on that plane. The LCAO-MOs are given by

$$\psi_4 = a\psi_O + b\psi_C \quad \psi_5 = e\psi_N \quad \psi_6 = f\psi_O - g\psi_C$$

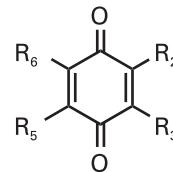
Just as before, sketch these molecular orbitals and characterize them as bonding, non-bonding, or antibonding. Also, draw an energy level diagram and determine the occupancy of the orbitals. (e) Why is this arrangement of atomic orbitals consistent with a non-planar conformation for the peptide link? (f) Does the bonding MO associated with the planar conformation have the same energy as the bonding MO associated with the non-planar conformation? If not, which bonding MO is lower in energy? Repeat the analysis for the non-bonding and anti-bonding molecular orbitals. (g) Use your results from parts (a)–(f) to construct arguments that support the planar model for the peptide link.

**11.29** Molecular orbital calculations may be used to predict trends in the standard potentials of conjugated molecules, such as the quinones and flavins, that are involved in biological electron transfer reactions (*Impact I17.2*). It is

commonly assumed 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. Furthermore, a number of studies indicate that there is a linear correlation between the LUMO energy and the reduction potential of aromatic hydrocarbons (see, for example, J.P. Lowe, *Quantum chemistry*, Chapter 8, Academic Press (1993)).

(a) The standard potentials at pH = 7 for the one-electron reduction of methyl-substituted 1,4-benzoquinones (13) to their respective semiquinone radical anions are:

$R_2$	$R_3$	$R_5$	$R_6$	$E^\circ/V$
H	H	H	H	0.078
CH <sub>3</sub>	H	H	H	0.023
CH <sub>3</sub>	H	CH <sub>3</sub>	H	-0.067
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	-0.165
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	-0.260



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Using molecular modelling software and the computational method of your choice (semi-empirical, *ab initio*, or density functional theory methods), calculate  $E_{\text{LUMO}}$ , the energy of the LUMO of each substituted 1,4-benzoquinone, and plot  $E_{\text{LUMO}}$  against  $E^\circ$ . Do your calculations support a linear relation between  $E_{\text{LUMO}}$  and  $E^\circ$ ? (b) The 1,4-benzoquinone for which  $R_2 = R_3 = \text{CH}_3$  and  $R_5 = R_6 = \text{OCH}_3$  is a suitable model of ubiquinone, a component of the respiratory electron transport chain (*Impact I7.2*). Determine  $E_{\text{LUMO}}$  of this quinone and then use your results from part (a) to estimate its standard potential. (c) The 1,4-benzoquinone for which  $R_2 = R_3 = R_5 = \text{CH}_3$  and  $R_6 = \text{H}$  is a suitable model of plastoquinone, a component of the photosynthetic electron transport chain (*Impact I7.2*). Determine  $E_{\text{LUMO}}$  of this quinone and then use your results from part (a) to estimate its standard potential. Is plastoquinone expected to be a better or worse oxidizing agent than ubiquinone? (d) Based on your predictions and on basic concepts of biological electron transport (*Impact I7.2 and I23.2*), suggest a reason why ubiquinone is used in respiration and plastoquinone is used in photosynthesis.