

Molecular structure

10

The concepts developed in Chapter 9, particularly those of orbitals, can be extended to a description of the electronic structures of molecules. There are two principal quantum mechanical theories of molecular electronic structure. In valence-bond theory, the starting point is the concept of the shared electron pair. We see how to write the wavefunction for such a pair, and how it may be extended to account for the structures of a wide variety of molecules. The theory introduces the concepts of σ and π bonds, promotion, and hybridization that are used widely in chemistry. In molecular orbital theory (with which the bulk of the chapter is concerned), the concept of atomic orbital is extended to that of molecular orbital, which is a wavefunction that spreads over all the atoms in a molecule.

In this chapter we consider the origin of the strengths, numbers, and three-dimensional arrangement of chemical bonds between atoms. As we shall see, 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.

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 and denoted A–B. 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.

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 and its associated language. 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

Valence-bond theory

10.1 Homonuclear diatomic molecules

10.2 Polyatomic molecules

Molecular orbital theory

10.3 The hydrogen molecule-ion

10.4 Homonuclear diatomic molecules

10.5 Heteronuclear diatomic molecules

10.1 Impact on biochemistry:
The biochemical reactivity of O_2 , N_2 , and NO

Molecular orbitals for polyatomic systems

10.6 The Hückel approximation

10.7 Computational chemistry

10.8 The prediction of molecular properties

Checklist of key equations

Further information 10.1: Details of the Hartree–Fock method

Discussion questions

Exercises

Problems

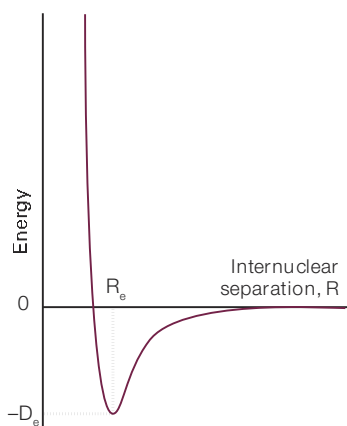


Fig. 10.1 A molecular potential energy curve. The equilibrium bond length R_e corresponds to the energy minimum.

A brief comment

The dissociation energy differs from the depth of the well by an energy equal to the zero-point vibrational energy of the bonded atoms: $D_0 = D_e - \frac{1}{2}h\nu$, where ν is the vibrational frequency of the bond (Section 12.8).

The Born–Oppenheimer approximation

Key point The nuclei of atoms in a molecule are regarded as fixed at selected locations, and the Schrödinger equation is then solved for the wavefunction of the electrons alone.

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 even 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. That is, we think of the nuclei as fixed at arbitrary locations, and then solve the Schrödinger equation for the wavefunction of the electrons alone.

The approximation is quite good for ground-state molecules, for calculations suggest that the nuclei in H_2 move through only about 1 pm while the electron speeds through 1000 pm, so even in this case 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 10.4) 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 and obtain a molecular potential energy curve (Fig. 10.1). 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 11 and 12), 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. When more than one molecular parameter is changed in a polyatomic molecule, such as its various bond lengths and angles, we obtain a potential energy surface; the overall equilibrium shape of the molecule corresponds to the global minimum of the surface.

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, σ and π bonds, and hybridization, is widely used throughout chemistry, especially in the description of the properties and reactions of organic compounds. Here we summarize essential topics of VB theory that should be familiar from introductory chemistry and set the stage for the development of MO theory.

10.1 Homonuclear diatomic molecules

Key point In VB theory, a bond forms 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.

We begin the account of VB theory by considering the simplest possible chemical bond, the one in molecular hydrogen, H_2 . The spatial wavefunction for an electron on each of two widely separated H atoms is

$$\psi = \chi_{H1s_A}(r_1)\chi_{H1s_B}(r_2) \quad (10.1)$$

if electron 1 is on atom A and electron 2 is on atom B; in this chapter we use χ (χ) 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 or electron 2 that is on A. An equally valid description is therefore $\psi = A(2)B(1)$, in which electron 2 is on A and electron 1 is on B. When two outcomes are equally probable, quantum mechanics instructs us to describe the true state of the system as a superposition of the wavefunctions for each possibility (Section 7.5e), so a better description of the molecule than either wavefunction alone is one of the (unnormalized) linear combinations $\psi = A(1)B(2) + A(2)B(1)$. The combination with lower energy is the one with a + sign, so the valence-bond wavefunction of the electrons in an H_2 molecule is

$$\psi = A(1)B(2) + A(2)B(1) \quad \text{Valence-bond wavefunction} \quad (10.2)$$

The reason why this linear combination has a lower energy than either the separate atoms or the linear combination with a negative sign can be traced to the constructive interference between the wave patterns represented by the terms $A(1)B(2)$ and $A(2)B(1)$, and the resulting enhancement of the probability density of the electrons in the internuclear region (Fig. 10.2).

The electron distribution described by the wavefunction in eqn 10.2 is called a σ bond. A σ bond has cylindrical symmetry around the internuclear axis, and is so called because, when viewed along the internuclear axis, it resembles a pair of electrons in an orbital (and σ is the Greek equivalent of s).

A chemist's picture of a covalent bond is one in which the spins of two electrons pair as the atomic orbitals overlap. The origin of the role of spin, as we show in the following justification, is that the wavefunction in eqn 10.2 can be formed only by a pair of spin-paired electrons. Spin pairing is not an end in itself: it is a means of achieving a wavefunction and the probability distribution implies that it corresponds to a low energy.

Justification 10.1 Electron pairing in VB theory

The Pauli principle requires the overall wavefunction of two electrons, the wavefunction including spin, to change sign when the labels of the electrons are interchanged (Section 9.4b). The overall VB wavefunction for two electrons is

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

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

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

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

$$\sigma(1,2) = \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

which corresponds to paired electron spins (Section 9.8). 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.

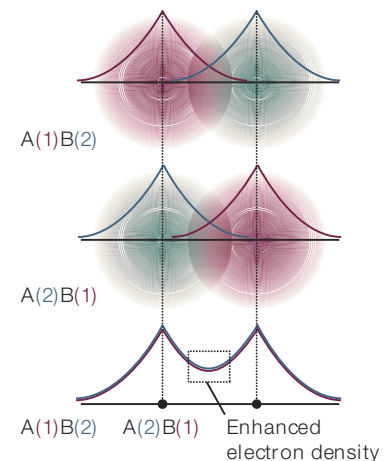


Fig. 10.2 It is very difficult to represent valence-bond wavefunctions because they refer to two electrons simultaneously. However, this illustration is an attempt. The top illustration represents $A(1)B(2)$, and the middle illustration represents the contribution $A(2)B(1)$. When the two contributions are superimposed, there is interference between the various contributions, resulting in an enhanced (two-electron) density in the internuclear region.

The VB description of H_2 can be applied to other homonuclear diatomic molecules. For N_2 , for instance, we consider the valence electron configuration of each atom,

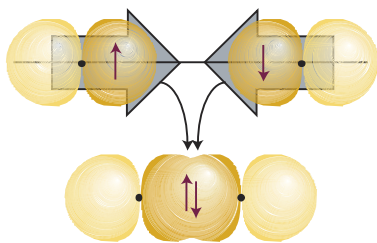


Fig. 10.3 The orbital overlap and spin pairing between electrons in two collinear p orbitals that results in the formation of a σ bond.

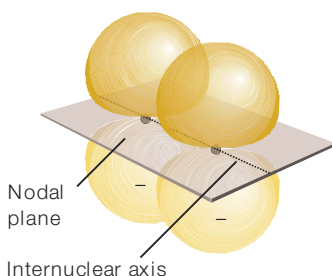


Fig. 10.4 A π bond results from orbital overlap and spin pairing between electrons in p orbitals with their axes perpendicular to the internuclear axis. The bond has two lobes of electron density separated by a nodal plane.

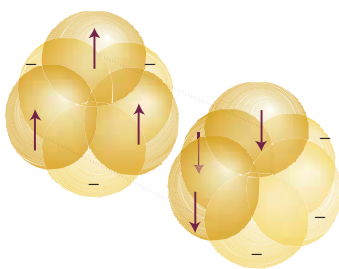


Fig. 10.5 The structure of bonds in a nitrogen molecule: there is one σ bond and two π bonds. As explained later, the overall electron density has cylindrical symmetry around the internuclear axis.

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. 10.3), with the $2p_x$ and $2p_y$ orbitals perpendicular to the axis. A σ bond is then formed by spin pairing between the two electrons in the two $2p_z$ orbitals. Its spatial wavefunction is given by eqn 10.2, but now A and B stand for the two $2p_z$ orbitals.

The remaining N 2p orbitals cannot merge to give σ bonds as they do not have cylindrical symmetry around the internuclear axis. Instead, they merge to form two π bonds. A π bond arises from the spin pairing of electrons in two p orbitals that approach side-by-side (Fig. 10.4). It is so called because, viewed along the internuclear axis, a π bond resembles a pair of electrons in a p orbital (and π is the Greek equivalent of p).

There are two π bonds in N_2 , one formed by spin pairing in two neighbouring $2p_x$ orbitals and the other by spin pairing in two neighbouring $2p_y$ orbitals. The overall bonding pattern in N_2 is therefore a σ bond plus two π bonds (Fig. 10.5), which is consistent with the Lewis structure: $:N \equiv N:$ for nitrogen.

10.2 Polyatomic molecules

To accommodate the shapes of polyatomic molecules, VB theory introduces the concepts of promotion and hybridization.

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

The VB description of H_2O will make this clear. The valence-electron configuration of an O atom is $2s^2 2p_x^2 2p_y^1 2p_z^1$. The two unpaired electrons in the O 2p orbitals can each pair with an electron in an H 1s orbital, and each combination results in the formation of a σ bond (each bond has cylindrical symmetry about the respective O–H internuclear axis). Because the $2p_x$ and $2p_z$ orbitals lie at 90° to each other, the two σ bonds also lie at 90° to each other (Fig. 10.6). We can predict, therefore, that H_2O should be an angular molecule, which it is. However, the theory predicts a bond angle of 90°, whereas the actual bond angle is 104.5°.

Self-test 10.1 Use VB theory to suggest a shape for the ammonia molecule, NH_3 .
Trigonal pyramidal with HNH bond angle 90°; experimental: 107°

Another deficiency of this initial formulation 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 H 1s orbitals if the molecule is CH_4), and hence form four σ bonds. Although energy was required to promote the electron, it is more than recovered by the promoted atom's ability to form four bonds in place of the two bonds of the unpromoted atom. Promotion, and the formation of four bonds, is a characteristic feature of carbon because the promotion energy is quite small: the promoted electron leaves

a doubly occupied 2s orbital and enters a vacant 2p orbital, hence significantly relieving the electron–electron repulsion it experiences in the former. However, we need to remember that promotion is not a ‘real’ process in which an atom somehow becomes excited and then forms bonds: it is a notional contribution to the overall energy change that occurs when bonds form.

The description of the bonding in CH₄ (and other alkanes) is still incomplete because it implies the presence of three σ bonds of one type (formed from H 1s and C 2p orbitals) and a fourth σ bond of a distinctly different character (formed from H 1s and C 2s). 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 C 2s and C 2p orbitals of the same atom. 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.

As we show in the following justification, the specific linear combinations that give rise to four equivalent hybrid orbitals are

$$\begin{matrix} h_1 & s & p_x & p_y & p_z & h_2 & s & p_x & p_y & p_z \\ h_3 & s & p_x & p_y & p_z & h_4 & s & p_x & p_y & p_z \end{matrix} \quad \boxed{\text{sp}^3 \text{ hybrid orbitals}} \quad (10.3)$$

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. 10.7). The angle between the axes of the hybrid orbitals is the tetrahedral angle, $\arccos(-1/3) = 109.47^\circ$. Because each hybrid is built from one s orbital and three p orbitals, it is called an sp³ hybrid orbital.

Justification 10.2 Determining the form of tetrahedral hybrids

We begin by supposing that each hybrid can be written in the form $h = b_x p_x + b_y p_y + b_z p_z$. The hybrid h_1 that points to the (1,1,1) corner of a cube (Fig. 10.8) must have equal contributions from all three p orbitals, so we can set the three b coefficients equal to each other and write h_1 as $b(p_x + p_y + p_z)$. The other three hybrids have the same composition (they are equivalent, apart from their direction in space), but are orthogonal to h_1 . This orthogonality is achieved by choosing different signs for the p orbitals but the same overall composition. For instance, we might choose h_2 as $b(p_x - p_y - p_z)$, in which case the orthogonality condition is

$$\int h_1 h_2 d\tau = \int (a s + b(p_x + p_y + p_z))(a s + b(p_x - p_y - p_z)) d\tau$$

$$= a^2 \int s^2 d\tau + b^2 \int p_x^2 d\tau + b^2 \int p_y^2 d\tau + b^2 \int p_z^2 d\tau + ab \int s p_x d\tau + b^2 \int p_x p_y d\tau$$

$$= a^2 + b^2 + b^2 + b^2 + 0 + 0 = 4a^2 + 4b^2 = 0$$

We conclude that a solution is $a = -b$ (the alternative solution, $a = b$, simply corresponds to choosing different absolute phases for the p-orbitals) and the two hybrid orbitals are the h_1 and h_2 in eqn 10.3. A similar argument but with h_3 as $b(p_x - p_y + p_z)$ or h_4 as $b(p_x + p_y - p_z)$ leads to the other two hybrids in eqn 10.3.

It is now easy to see how the valence-bond description of the CH₄ 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 H 1s electron can pair with each one, giving rise to a σ bond pointing in a tetrahedral direction. For example,

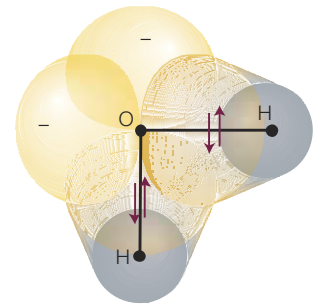


Fig. 10.6 A first approximation to the valence-bond description of bonding in an H₂O molecule. Each σ bond arises from the overlap of an H 1s orbital with one of the O 2p orbitals. This model suggests that the bond angle should be 90°, which is significantly different from the experimental value.

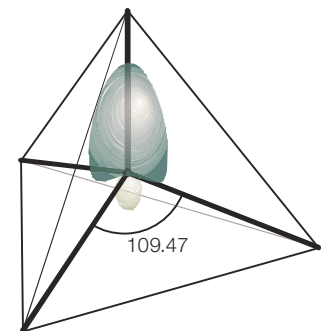


Fig. 10.7 An sp³ hybrid orbital formed from the superposition of s and p orbitals on the same atom. There are four such hybrids: each one points towards the corner of a regular tetrahedron. The overall electron density remains spherically symmetrical.

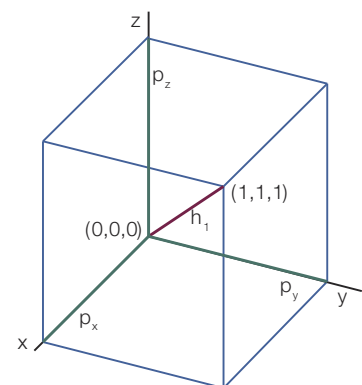


Fig. 10.8 One sp³ hybrid is constructed by supposing that it points to the (1,1,1) corner of a cube: it has equal contributions from all three p orbitals.

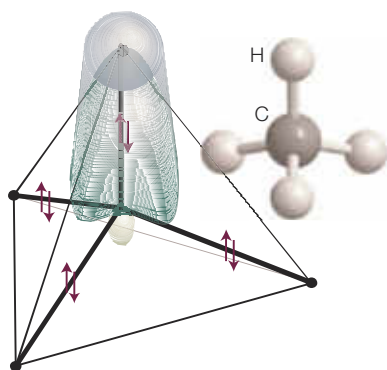


Fig. 10.9 Each sp^3 hybrid orbital forms a σ bond by overlap with an H $1s$ orbital located at the corner of the tetrahedron. This model accounts for the equivalence of the four bonds in CH_4 .

the (unnormalized) wavefunction for the bond formed by the hybrid orbital h_1 and the $1s_A$ orbital (with wavefunction that we shall denote A) is

$$\psi = h_1(1)A(2) + h_1(2)A(1) \quad (10.4)$$

As for H_2 , to achieve this wavefunction, the two electrons it describes must be paired. Because each sp^3 hybrid orbital has the same composition, all four σ bonds are identical apart from their orientation in space (Fig. 10.9).

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. 10.10). As a result, the bond strength is greater than for a bond formed from an s or p orbital alone. This increased bond strength is another factor that helps to repay the promotion energy.

Hybridization is used to describe the structure of an ethene molecule, $H_2C=CH_2$, and the torsional rigidity of double bonds. An ethene molecule is planar, with HCH and HCC bond angles close to 120° . To reproduce the σ bonding structure, we promote each C atom to a $2s^1 2p^3$ configuration. However, instead of using all four orbitals to form hybrids, we form sp^2 hybrid orbitals:

$$\begin{aligned} h_1 &= s + 2^{1/2} p_y \\ h_2 &= s + \left(\frac{3}{2}\right)^{1/2} p_x + \left(\frac{1}{2}\right)^{1/2} p_y \\ h_3 &= s + \left(\frac{3}{2}\right)^{1/2} p_x + \left(\frac{1}{2}\right)^{1/2} p_y \end{aligned} \quad \boxed{sp^2 \text{ hybrid orbitals}} \quad (10.5)$$

These hybrids lie in a plane and point towards the corners of an equilateral triangle at 120° to each other (Fig. 10.11 and Problem 10.17). The third $2p$ orbital ($2p_z$) is not included in the hybridization; its axis is perpendicular to the plane in which the hybrids lie. The different signs of the coefficients ensure that constructive interference takes place in different regions of space, so giving the patterns in the illustration. The sp^2 -hybridized C atoms each form three σ bonds by spin pairing with either the h_1

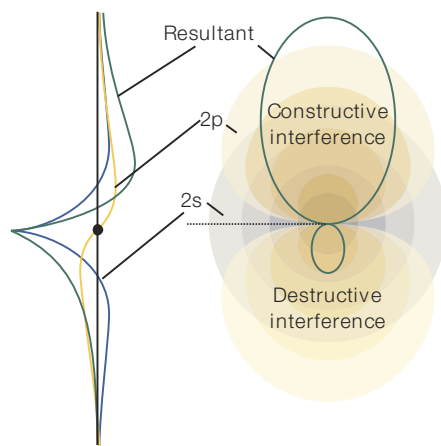


Fig. 10.10 A more detailed representation of the formation of an sp^3 hybrid by interference between wavefunctions centred on the same atomic nucleus. (To simplify the representation, we have ignored the radial node of the $2s$ orbital.)

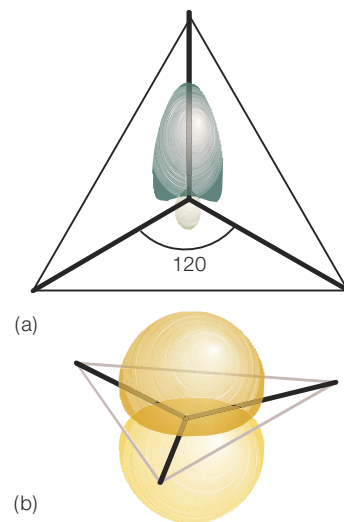


Fig. 10.11 (a) An s orbital and two p orbitals can be hybridized to form three equivalent orbitals that point towards the corners of an equilateral triangle. (b) The remaining unhybridized p orbital is perpendicular to the plane.

hybrid of the other C atom or with H 1s orbitals. The σ framework therefore consists of C–H and C–C σ bonds at 120° to each other. When the two CH_2 groups lie in the same plane, the two electrons in the unhybridized p orbitals can pair and form a π bond (Fig. 10.12). The formation of this π bond locks the framework into the planar arrangement, for any rotation of one CH_2 group relative to the other leads to a weakening of the π bond (and consequently an increase in energy of the molecule).

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

$$h_1 = s + p_z \quad h_2 = s - p_z \quad (10.6)$$

These two hybrids 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 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 π bonds (Fig. 10.13).

Self-test 10.2 Hybrid orbitals do not always form bonds: they may also contain lone pairs of electrons. Use VB theory to suggest possible shapes for the hydrogen peroxide molecule, H_2O_2 .

Each H–O–O bond angle is predicted to be approximately 109° (experimental: 94.8°); rotation around the O–O bond is possible, so the molecule is conformationally mobile.

Other hybridization schemes, particularly those involving d orbitals, are often invoked in elementary descriptions of molecular structure to be consistent with other molecular geometries (Table 10.1). 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 toward the corners of a regular octahedron; it is sometimes invoked to account for the structure of octahedral molecules, such as SF_6 .

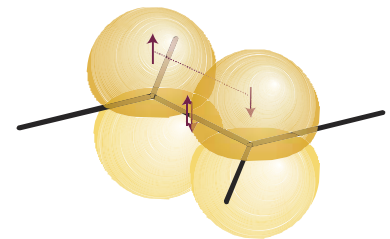


Fig. 10.12 A representation of the structure of a double bond in ethene; only the π bond is shown explicitly.

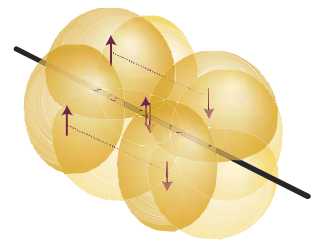


Fig. 10.13 A representation of the structure of a triple bond in ethyne; only the π bonds are shown explicitly. The overall electron density has cylindrical symmetry around the axis of the molecule.

Table 10.1* Some hybridization schemes

Coordination number	Arrangement	Composition
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp^2, p^2d
	Trigonal bipyramidal	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^3
	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^3

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

Molecular orbital theory

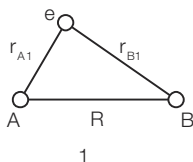
In MO theory, electrons do not belong to particular bonds but spread throughout the entire molecule. This theory has been more fully developed than VB theory and provides the language that is widely used in modern discussions of bonding. To introduce it, we follow the same strategy as in Chapter 9, where 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 to describe the structures of more complex systems.

10.3 The hydrogen molecule-ion

Key points (a) A molecular orbital is constructed as a linear combination of atomic orbitals. (b) A bonding orbital arises from the constructive overlap of neighbouring atomic orbitals. (c) An antibonding orbital arises from the destructive overlap of neighbouring atomic orbitals.

The hamiltonian for the single electron in H_2^+ is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} \right) + \frac{e^2}{4\pi\epsilon_0 R} \quad (10.7)$$



where r_{A1} and r_{B1} are the distances of the electron from the two nuclei A and B (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 collection of fundamental constants $e^2/4\pi\epsilon_0$ occurs widely throughout this chapter, and we shall denote it j_0 .

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

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

(a) Linear combinations of atomic orbitals

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

$$\psi = N(A + B) \quad \text{Linear combination of atomic orbitals} \quad (10.8)$$

where, for H_2^+ , A denotes χ_{H1s} , B denotes χ_{H1s} , and N is a normalization factor. The technical term for the superposition in eqn 10.8 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 an s 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 10.1 Normalizing a molecular orbital

Normalize the molecular orbital ψ in eqn 10.8.

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 Substitution of the wavefunction gives

$$\int \psi^* \psi d\tau = N^2 \left[\frac{1}{3} \int A^2 d\tau + \frac{5}{7} \int B^2 d\tau + 2 \int AB d\tau \right] = N^2 (1 + 1 + 2S)$$

where $S = \int AB d\tau$ and has a value that depends on the nuclear separation (this 'overlap integral' will play a significant role later). For the integral to be equal to 1, we require

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

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

Self-test 10.3 Normalize the orbital ψ in eqn 10.8.

$$N = \frac{1}{2(1 + S)^{1/2}}, \text{ so } N \approx 1.10$$

Figure 10.14 shows the contours of constant amplitude for the molecular orbital ψ in eqn 10.8, and Fig. 10.15 shows its boundary surface. 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

$$A = \frac{e^{-r_A/a_0}}{(\pi a_0^3)^{1/2}} \quad B = \frac{e^{-r_B/a_0}}{(\pi a_0^3)^{1/2}} \quad (10.9)$$

and note that r_A and r_B are not independent (2), but related by

$$r_B^2 = r_A^2 + R^2 - 2r_A R \cos \theta \quad (10.10)$$

(b) Bonding orbitals

According to the Born interpretation, the probability density of the electron at each point in H_2 is proportional to the square modulus of its wavefunction at that point. The probability density corresponding to the (real) wavefunction ψ in eqn 10.8 is

$$\psi^2 = N^2 (A^2 + B^2 + 2AB) \quad (10.11)$$

This probability density is plotted in Fig. 10.16 and an important feature becomes apparent when we examine the internuclear region, where both atomic orbitals have similar amplitudes. According to eqn 10.11, the total probability density is proportional to the sum of:

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

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

$2AB$, an extra contribution to the density from both atomic orbitals.

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

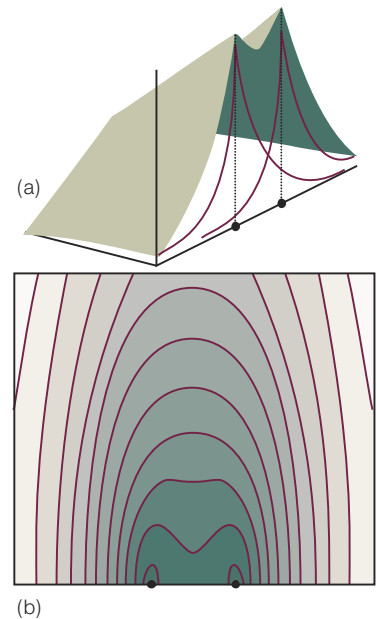


Fig. 10.14 (a) The amplitude of the bonding molecular orbital in a hydrogen molecule ion in a plane containing the two nuclei and (b) a contour representation of the amplitude. To make this plot, we have taken $N^2 = 0.31$ (Example 10.1).

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

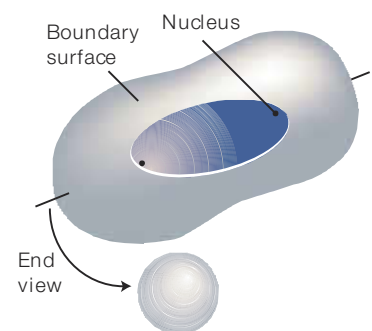
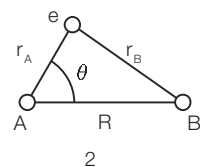


Fig. 10.15 A general indication of the shape of the boundary surface of a σ orbital.



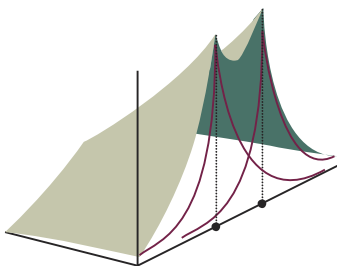


Fig. 10.16 The electron density calculated by forming the square of the wavefunction used to construct Fig. 10.14. Note the accumulation of electron density in the internuclear region.

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

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

The energy $E_{1\sigma}$ of the 1σ orbital is (see Problem 10.18):

$$E_{1\sigma} = E_{H1s} + \frac{j_0}{R} - \frac{j}{1} + \frac{k}{S} \quad (10.12)$$

where E_{H1s} is the energy of a $H1s$ orbital, j_0/R is the potential energy of repulsion between the two nuclei, and

$$S = \int AB d\tau = \frac{1}{3} \frac{R}{a_0} \frac{A R D^2}{C a_0 F} \frac{5}{7} e^{-R/a_0} \quad (10.13a)$$

$$j = j_0 \int \frac{A^2}{r_B} d\tau = \frac{j_0}{R} \frac{1}{3} \frac{A}{C} \frac{R D}{a_0 F} e^{-2R/a_0} \frac{5}{7} \quad (10.13b)$$

$$k = j_0 \int \frac{AB}{r_B} d\tau = \frac{j_0}{a_0} \frac{A}{C} \frac{R D}{a_0 F} e^{-R/a_0} \quad (10.13c)$$

We can interpret these three integrals as follows:

All three integrals are positive and tend towards zero at large internuclear separations (S and k on account of the exponential term; j on account of the factor $1/R$). The integral S is discussed in more detail in Section 10.4c.

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

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

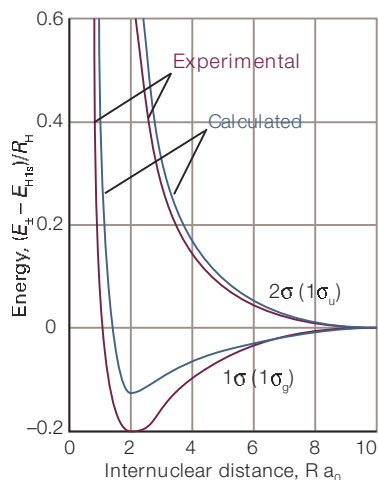


Fig. 10.17 The calculated and experimental molecular potential energy curves for a hydrogen molecule-ion showing the variation of the energy of the molecule as the bond length is changed. The alternative g,u notation is introduced in Section 10.3c.

Figure 10.17 is a plot of E_{σ} against R relative to the energy of the separated atoms. The energy of the 1σ orbital decreases as the internuclear separation decreases from large values because electron density accumulates in the internuclear region as the constructive interference between the atomic orbitals increases (Fig. 10.18). However, at small separations there is too little space between the nuclei for significant accumulation of electron density there. In addition, the nucleus-nucleus repulsion (which is proportional to $1/R$) becomes large. As a result, the energy of the molecule rises at short distances, and there is a minimum in the potential energy curve. Calculations on H_2 give $R_e = 130$ pm and $D_e = 1.77$ eV (171 k mol $^{-1}$); the experimental values are 106 pm and 2.6 eV, so this simple LCAO-MO description of the molecule, while inaccurate, is not absurdly wrong.

(c) Antibonding orbitals

The linear combination ψ in eqn 10.8 corresponds to a higher energy than that of ψ . Because it is also a σ orbital we label it 2σ . This orbital has an internuclear nodal plane where A and B cancel exactly (Figs. 10.19 and 10.20). The probability density is

$$\psi^2 = N^2(A^2 - B^2 - 2AB) \tag{10.14}$$

There is a reduction in probability density between the nuclei due to the $-2AB$ term (Fig. 10.21); in physical terms, there is destructive interference where the two atomic orbitals overlap. The 2σ orbital is an example of an antibonding orbital, an orbital that, if occupied, contributes to a reduction in the cohesion between two atoms and helps to raise the energy of the molecule relative to the separated atoms.

The energy $E_{2\sigma}$ of the 2σ antibonding orbital is given by (see Problem 10.18)

$$E_{2\sigma} = E_{H1s} \frac{j_0}{R} - \frac{j_1}{1} \frac{k}{S} \tag{10.15}$$

where the integrals S , j , and k are the same as before (eqn 10.13). The variation of $E_{2\sigma}$ with R is shown in Fig. 10.17, where we see the destabilizing effect of an antibonding

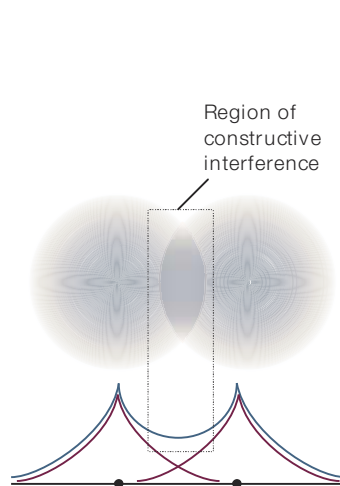


Fig. 10.18 A representation of the constructive interference that occurs when two $H1s$ orbitals overlap and form a bonding σ orbital.

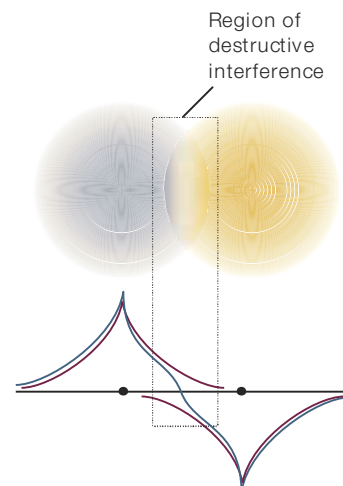


Fig. 10.19 A representation of the destructive interference that occurs when two $H1s$ orbitals overlap and form an antibonding 2σ orbital.

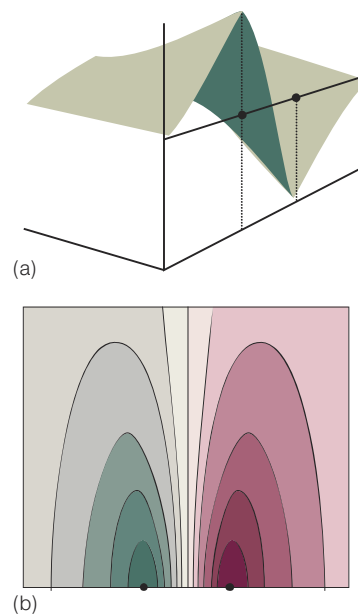



Fig. 10.20 (a) The amplitude of the antibonding molecular orbital in a hydrogen molecule-ion in a plane containing the two nuclei and (b) a contour representation of the amplitude. Note the internuclear node.

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

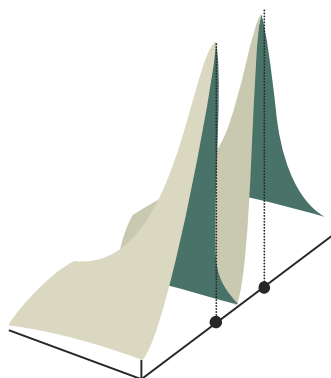


Fig. 10.21 The electron density calculated by forming the square of the wavefunction used to construct Fig. 10.20. Note the elimination of electron density from the internuclear region.

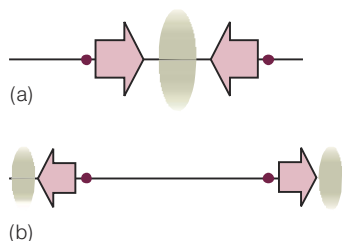


Fig. 10.22 A partial explanation of the origin of bonding and antibonding effects. (a) In a bonding orbital, the nuclei are attracted to the accumulation of electron density in the internuclear region. (b) In an antibonding orbital, the nuclei are attracted to an accumulation of electron density outside the internuclear region.

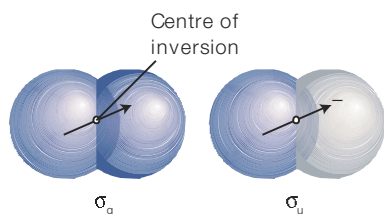


Fig. 10.23 The parity of an orbital is even (g) if its wavefunction is unchanged under inversion through the centre of symmetry of the molecule, but odd (u) if the wavefunction changes sign. Heteronuclear diatomic molecules do not have a centre of inversion, so for them the g, u classification is irrelevant.

electron. 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. 10.22). Figure 10.17 also shows another feature that we draw on later: $E_{2\sigma} > E_{H1s} > E_{1\sigma} < E_{H1s}$, 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 (J_{0R}): this contribution raises the energy of both molecular orbitals. Antibonding orbitals are often labelled with an asterisk (*), so the 2σ orbital could also be denoted $2\sigma^*$ (and read ‘two sigma star’).

For homonuclear diatomic molecules (molecules consisting of two atoms of the same element, such as N_2), it proves helpful to label a molecular orbital according to 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. 10.23). This so-called *gerade* symmetry (from the German word for ‘even’) is denoted by a subscript g, as in σ_g . The same procedure applied to the antibonding 2σ orbital results in the same amplitude but opposite sign of the wavefunction. This is *ungerade* symmetry (‘odd symmetry’) is denoted by a subscript u, as in σ_u . This inversion symmetry classification is not applicable to heteronuclear diatomic molecules (diatomic molecules formed by atoms from two different elements, such as CO) because these molecules do not have a centre of inversion. When using the g, u notation, each set of orbitals of the same inversion symmetry are labelled separately so, whereas 1σ becomes $1\sigma_g$, its antibonding partner, which so far we have called 2σ , is the first orbital of a different symmetry, and is denoted $1\sigma_u$. The general rule is that each set of orbitals of the same symmetry designation is labelled separately.

10.4 Homonuclear diatomic molecules

Key points Electrons are added to available molecular orbitals in a manner that achieves the lowest overall energy. (a) As a first approximation, σ orbitals are constructed separately from valence s and p orbitals. (b) π Orbitals are constructed from the side-by-side overlap of p orbitals of the appropriate symmetry. (c) The overlap integral is a measure of the extent of orbital overlap. (d) The ground-state electron configurations of diatomic molecules are predicted by using the building up principle, and the bond order is a measure of the resulting net bonding character. (e) Photoelectron spectroscopy is a technique for determining the energies of electrons in molecular orbitals.

In Chapter 9 we used the hydrogenic atomic orbitals and the building-up principle to deduce the ground electronic configurations of many-electron atoms. We now do the same for many-electron diatomic molecules by using the H_2 molecular orbitals as a basis for their discussion. The general procedure is to construct molecular orbitals by combining the available atomic orbitals:

1. The electrons supplied by the atoms are 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).
2. If several degenerate molecular orbitals are available, electrons are added singly to each individual orbital before doubly occupying any one orbital (because that minimizes electron–electron repulsions).

Building-up
principle for
molecules

3. According to Hund's maximum multiplicity rule (Section 9.4d), if two electrons do occupy different degenerate orbitals, then a lower energy is obtained if they do so with parallel spins.

(a) σ Orbitals

Consider H_2 , the simplest many-electron diatomic molecule. Each H atom contributes a 1s orbital (as in H_2), so we can form the $1\sigma_g$ and $1\sigma_u$ orbitals from them, as we have seen already. At the experimental internuclear separation these orbitals will have the energies shown in Fig. 10.24, 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 (just as for atoms, Section 9.4b). The ground-state configuration is therefore $1\sigma_g^2$ and the atoms are joined by a bond consisting of an electron pair in a bonding σ orbital. This approach shows that an electron pair, which was the focus of Lewis's account of chemical bonding, represents the maximum number of electrons that can enter a bonding molecular orbital.

The same argument explains 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 H_2 , their general shapes are 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. 10.25). The ground electronic configuration of He_2 is therefore $1\sigma_g^2 1\sigma_u^2$. We see that there is one bond and one antibond. Because $1\sigma_u$ is raised in energy relative to the separate atoms more than $1\sigma_g$ is lowered, an He_2 molecule has a higher energy than the separated atoms, so it is unstable relative to them.

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. We shall make that approximation here too.

A general principle of molecular orbital theory is that all orbitals of the appropriate symmetry contribute to a molecular orbital. Thus, to build σ orbitals, we form linear combinations of all atomic orbitals that have cylindrical symmetry about the internuclear axis. These orbitals include the 2s orbitals on each atom and the $2p_z$ orbitals on the two atoms (Fig. 10.26). The general form of the σ orbitals that may be formed is therefore

$$\Psi = c_{A2s}\chi_{A2s} + c_{B2s}\chi_{B2s} + c_{A2p_z}\chi_{A2p_z} + c_{B2p_z}\chi_{B2p_z} \quad (10.16)$$

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

The procedure for calculating the coefficients will be described in Section 10.6. At this stage we adopt a simpler route, and suppose that, because the 2s and $2p_z$ orbitals have distinctly different energies, they may be treated separately. That is, the four σ orbitals fall approximately into two sets, one consisting of two molecular orbitals of the form

$$\Psi = c_{A2s}\chi_{A2s} + c_{B2s}\chi_{B2s} \quad (10.17a)$$

and another consisting of two orbitals of the form

$$\Psi = c_{A2p_z}\chi_{A2p_z} + c_{B2p_z}\chi_{B2p_z} \quad (10.17b)$$

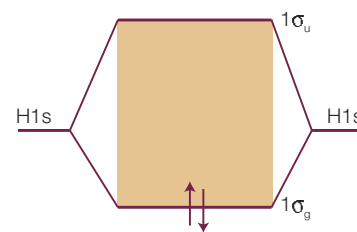


Fig. 10.24 A molecular orbital energy level diagram for orbitals constructed from the overlap of H 1s orbitals; the separation of the levels corresponds to that found at the equilibrium bond length. The ground electronic configuration of H_2 is obtained by accommodating the two electrons in the lowest available orbital (the bonding orbital).

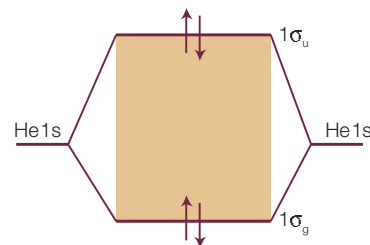


Fig. 10.25 The ground electronic configuration of the hypothetical four-electron molecule He_2 has two bonding electrons and two antibonding electrons. It has a higher energy than the separated atoms, and so is unstable.

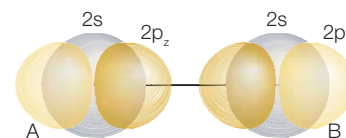


Fig. 10.26 According to molecular orbital theory, σ orbitals are built from all orbitals that have the appropriate symmetry. In homonuclear diatomic molecules of Period 2, that means that two 2s and two $2p_z$ orbitals should be used. From these four orbitals, four molecular orbitals can be built.

A brief comment

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.

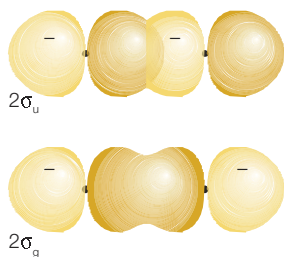


Fig. 10.27 A representation of the composition of bonding and antibonding σ orbitals built from the overlap of p orbitals. These illustrations are schematic.

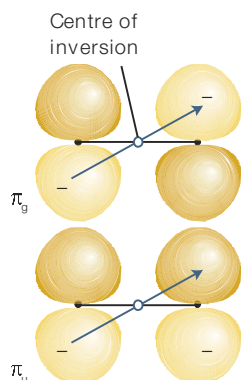


Fig. 10.28 A schematic representation of the structure of π bonding and antibonding molecular orbitals. The figure also shows that the bonding π orbital has odd parity, whereas the antibonding π orbital has even parity.

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 $2p_z$ orbitals. Therefore, the two sets of orbitals have the form χ_{A2s} , χ_{B2s} and χ_{A2p_z} , χ_{B2p_z} .

The $2s$ orbitals on the two atoms overlap to give a bonding and an antibonding σ orbital ($1\sigma_g$ and $1\sigma_u$, respectively) in exactly the same way as we have already seen for $1s$ orbitals. The two $2p_z$ orbitals directed along the internuclear axis overlap strongly. They may interfere either constructively or destructively, and give a bonding or antibonding σ orbital (Fig. 10.27). These two σ orbitals are labelled $2\sigma_g$ and $2\sigma_u$, respectively. In general, note how the numbering follows the order of increasing energy.

(b) π Orbitals

Now consider the $2p_x$ and $2p_y$ orbitals of each atom. These orbitals are perpendicular to the internuclear axis and may overlap broadside-on. This overlap may be constructive or destructive and results in a bonding or an antibonding p orbital (Fig. 10.28). The notation π is the analogue of p in atoms; for when viewed along the axis of the molecule, a π orbital looks like a p orbital and has one unit of orbital angular momentum around the internuclear axis. The two neighbouring $2p_x$ orbitals overlap to give a bonding and antibonding π_x orbital, and the two $2p_y$ orbitals overlap to give two π_y orbitals. The π_x and π_y bonding orbitals are degenerate; so too are their antibonding partners. We also see from Fig. 10.28 that a bonding π orbital has odd parity and is denoted π_u and an antibonding π orbital has even parity, denoted π_g .

(c) The overlap integral

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

$$S = \int \chi_A^* \chi_B d\tau \quad \text{Definition of overlap integral} \quad 10.18$$

We have already met this integral (in Example 10.1 and eqn 10.13). If the atomic orbital χ_A on A is small wherever the orbital χ_B on B is large, or vice versa, then the product of their amplitudes is everywhere small and the integral—the sum of these products—is small (Fig. 10.29). If χ_A and χ_B are both 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. For instance, the variation of S with internuclear separation for hydrogenic $1s$ orbitals on atoms of atomic number Z is given by

$$S(1s, 1s) = \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \frac{5}{6} e^{-R/a_0} \quad (10.19)$$

and is plotted in Fig. 10.30 (eqn 10.19 is a generalization of eqn 10.13a, which was for H $1s$ orbitals). It follows that $S = 0.59$ (an unusually large value) for two H $1s$ orbitals at the equilibrium bond length in H_2 . Typical values of S 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. 10.31). The integral over the region where the product of orbitals is positive exactly cancels the integral over the region where the product of orbitals is negative, so overall $S = 0$ exactly. Therefore, there is no net overlap between the s and p orbitals in this arrangement.

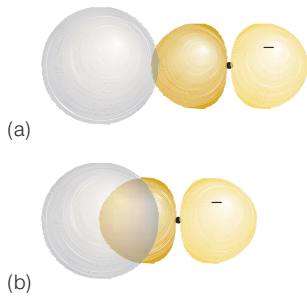


Fig. 10.29 (a) When two orbitals are on atoms that are far apart, the wavefunctions are small where they overlap, so S is small. (b) When the atoms are closer, both orbitals have significant amplitudes where they overlap, and S may approach 1. Note that S will decrease again as the two atoms approach 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, $S = 0$.

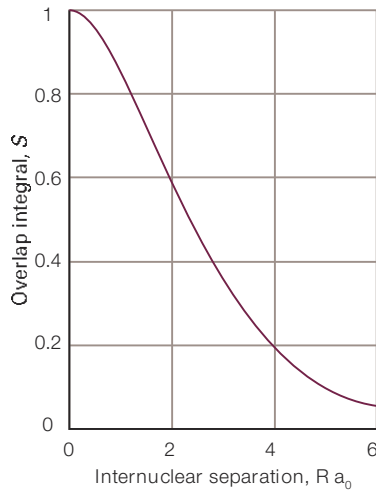


Fig. 10.30 The overlap integral, S , between two $1s$ orbitals as a function of their separation, R .

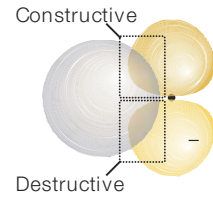


Fig. 10.31 A p orbital in the orientation shown here has zero net overlap ($S = 0$) with the s orbital at all internuclear separations.

(d) The electronic structures of homonuclear diatomic molecules

To construct the molecular orbital energy level diagram for Period 2 homonuclear diatomic molecules, we form eight molecular orbitals from the eight valence shell orbitals (four from each atom). In some cases, π orbitals are less strongly bonding than σ orbitals because their maximum overlap occurs off-axis. This relative weakness suggests that the molecular orbital energy level diagram ought to be as shown in Fig. 10.32. However, we must remember that we have assumed that $2s$ and $2p_z$ orbitals contribute to different sets of molecular orbitals, whereas in fact all four atomic orbitals have the same symmetry around the internuclear axis and contribute jointly to the four σ orbitals. Hence, there is no guarantee that this order of energies should prevail, and it is found experimentally (by spectroscopy) and by detailed calculation that the order varies along Period 2 (Fig. 10.33). The order shown in Fig. 10.34 is

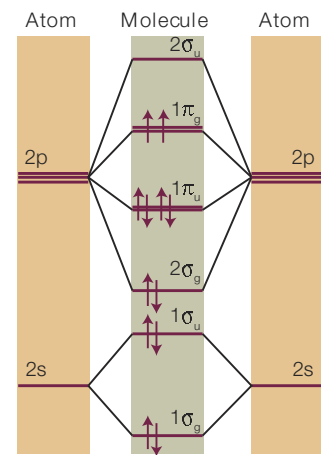


Fig. 10.32 The molecular orbital energy level diagram for homonuclear diatomic molecules. The lines in the middle are an indication of the energies of the molecular orbitals that can be formed by overlap of atomic orbitals. As remarked in the text, this diagram should be used for O_2 (the configuration shown) and F_2 .

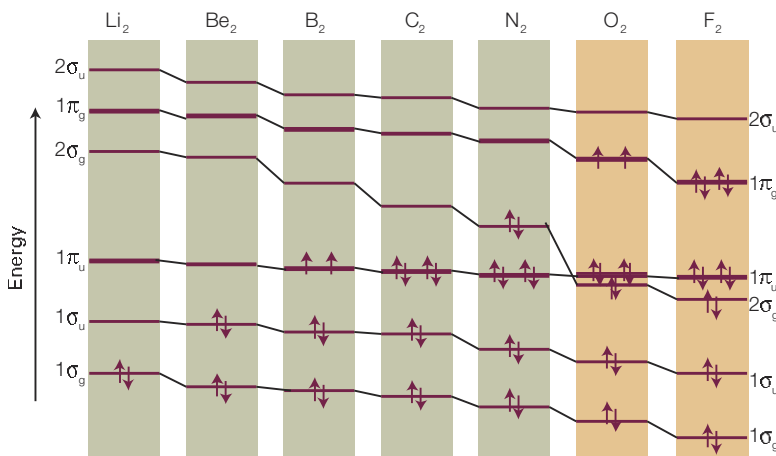


Fig. 10.33 The variation of the orbital energies as calculated for Period 2 homonuclear diatomics.

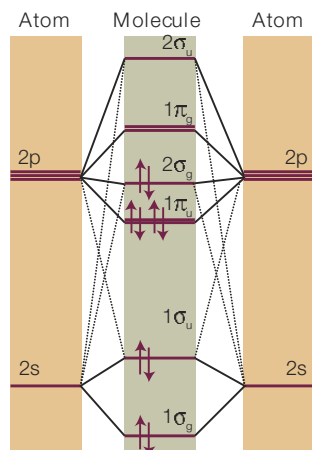


Fig. 10.34 An alternative molecular orbital energy level diagram for homonuclear diatomic molecules. As remarked in the text, this diagram should be used for diatomics up to and including N_2 (the configuration shown).

Brief comment

Bond dissociation energies are commonly used in thermodynamic cycles, where bond enthalpies, $\Delta_{\text{bond}}H^\ominus$, should be used instead. It follows from the same kind of argument used in *Justification 9.7* concerning ionization enthalpies that



To derive this relation, we have supposed that the molar constant-pressure heat capacity of X_2 is $\frac{7}{2}R$ (Section 2.4 and eqn 2.26), for there is a contribution from two rotational modes as well as three translational modes.

appropriate as far as N_2 , and Fig. 10.32 is appropriate for O_2 and F_2 . 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_2 .

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

Consider N_2 , which has 10 valence electrons. Two electrons pair, occupy, and fill the $1\sigma_g$ orbital; the next two occupy and fill the $1\sigma_u$ orbital. Six electrons remain. There are two $1\pi_u$ orbitals, so four electrons can be accommodated in them. The last two enter the $2\sigma_g$ orbital. Therefore, the ground-state configuration of N_2 is $1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2$. It is sometimes helpful to include an asterisk to denote an antibonding orbital, in which case this configuration would be denoted $1\sigma_g^2 1\sigma_u^{*2} 1\pi_u^4 2\sigma_g^2$.

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

$$b = \frac{1}{2}(N - N^*)$$

Definition of
bond order

10.20

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

The ground-state electron configuration of O_2 , with 12 valence electrons, is based on Fig. 10.32, and is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$ (or $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*2}$). Its bond order is 2. According to the building-up principle, however, the two $1\pi_g$ electrons occupy different orbitals: one will enter $1\pi_{gx}$ and the other will enter $1\pi_{gy}$. Because the electrons are in different orbitals, they will have parallel spins. Therefore, we can predict that an O_2 molecule will have a net spin angular momentum $S = 1$ and, in the language introduced in Section 9.8, be in a triplet state. As electron spin is the source of a magnetic moment, we can go on to predict that oxygen should be paramagnetic, a substance that tends to move into a magnetic field (see Chapter 19). This prediction, which VB theory does not make, is confirmed by experiment.

An F_2 molecule has two more electrons than an O_2 molecule. Its configuration is therefore $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*4}$ and $b = 1$. We conclude that F_2 is a singly bonded molecule, in agreement with its Lewis structure. The hypothetical molecule dineon, Ne_2 , has two additional electrons: its configuration is $1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 1\pi_u^4 1\pi_g^{*4} 2\sigma_u^{*2}$ 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:

The greater the bond order, the shorter the bond.

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

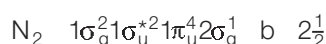
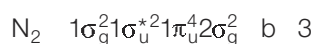
Table 10.2 lists some typical bond lengths in diatomic and polyatomic molecules. The strength of a bond is measured by its bond dissociation energy, D_0 , the energy required to separate the atoms to infinity or by the well depth D_e , with $D_0 = D_e - \frac{1}{2}\omega$ (see the brief comment in this chapter; $\omega = 2\pi\nu$). Table 10.3 lists some experimental values of D_0 .

Example 10.2 Judging the relative bond strengths of molecules and ions

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

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

Answer From Fig. 10.34, 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 k mol^{-1} for N_2 and 842 k mol^{-1} for N_2^+ .

Self-test 10.4 Which can be expected to have the higher dissociation energy, F_2 or F_2^+ ?

(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 known energy, and uses the information to infer the energies of molecular orbitals. The technique is also used to study solids, and in Chapter 22 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 sum of the ionization energy, I , of the sample and the kinetic energy of the photoelectron, the ejected electron, must be equal to the energy of the incident photon $h\nu$ (Fig. 10.35):

$$h\nu = \frac{1}{2}m_e v^2 + I \quad (10.21a)$$

This equation (which is like the one used for the photoelectric effect, eqn 7.15) 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

$$h\nu = \frac{1}{2}m_e v^2 + I_i \quad (10.21b)$$

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

Table 10.2* Bond lengths

Bond	Order	R_b , 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.

Table 10.3* Bond dissociation energies

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

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

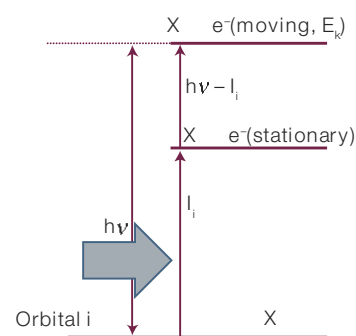


Fig. 10.35 An incoming photon carries an energy $h\nu$; an energy I_i is needed to remove an electron from an orbital i , and the difference appears as the kinetic energy of the electron.

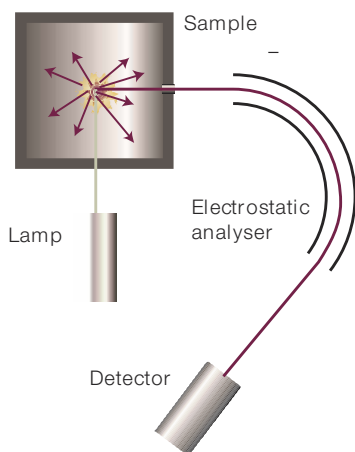


Fig. 10.36 A photoelectron spectrometer consists of a source of ionizing radiation (such as a helium discharge lamp for PES and an X-ray source for XPS), an electrostatic analyser, and an electron detector. The deflection of the electron path caused by the analyser depends on their speed.

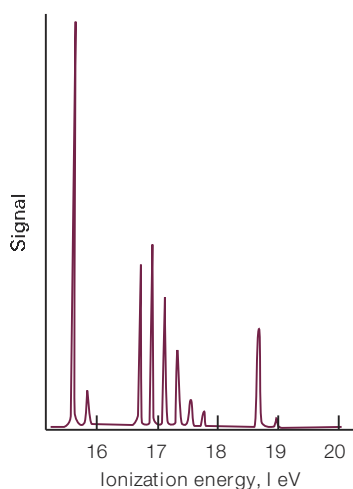


Fig. 10.37 The ν photoelectron spectrum of N_2 .

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. 10.36). 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.

A brief illustration

Photoelectrons ejected from N_2 with He(I) radiation have kinetic energies of 5.63 eV ($1 \text{ eV} = 8065.5 \text{ cm}^{-1}$, Fig. 10.37). 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 10.21, $21.22 \text{ eV} - 5.63 \text{ eV} = I_i$, 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.

Self-test 10.5 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, 1π

It is often observed that photoejection results in cations that are excited vibrationally. Because different energies are needed to excite different vibrational states of the ion, the photoelectrons appear with different kinetic energies. The result is vibrational fine structure, a progression of lines with a frequency spacing that corresponds to the vibrational frequency of the molecule. Figure 10.38 shows an example of vibrational fine structure in the photoelectron spectrum of Br_2 .

10.5 Heteronuclear diatomic molecules

Key points (a) A polar bond can be regarded as arising from a molecular orbital that is concentrated more on one atom than its partner. (b) The electronegativity of an element is a measure of the power of an atom to attract electrons to itself when it is part of a compound. (c) The variation principle provides a criterion of acceptability of an approximate wavefunction.

The electron distribution in a covalent bond in a heteronuclear diatomic molecule is not shared equally by the atoms 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 δ^- . There is a matching partial positive charge, δ^+ , on the H atom.

(a) Polar bonds

A polar bond consists of two electrons in a bonding molecular orbital of the form

$$\psi = c_A A + c_B B \quad \text{Form of wavefunction of a polar bond} \quad (10.22)$$

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