# 8

An introduction to molecular structure

Now we come to the heart of chemistry. If we can understand the forces that hold atoms together in molecules, we may also be able to understand why, under certain conditions, initial arrangements of atoms change into new ones in the course of the events we call 'chemical reactions'. The aim of this chapter is to introduce some of the features of **valence theory**, the theory of the formation of chemical bonds. The description of bonding has been greatly enriched by numerical techniques, and the following chapter describes these more quantitative aspects of the subject.

There are two principal models of molecular structure: *molecular orbital theory* and *valence bond theory*. Both models contribute concepts to the everyday language of chemistry and so it is worthwhile to examine them both. However, molecular orbital theory has undergone much more development than valence bond theory, and we shall concentrate on it.
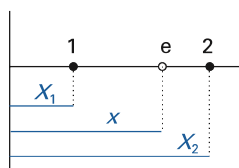
The Born–Oppenheimer approximation

It is an unfortunate fact that, having arrived in sight of the promised land, we are forced to make an approximation at the outset. Even the simplest molecule, H_2^+, consists of three particles, and its Schrödinger equation cannot be solved analytically. To overcome this difficulty, we adopt the **Born–Oppenheimer approximation**, which takes note of the great difference in masses of electrons and nuclei. Because of this difference, the electrons can respond almost instantaneously to displacement of the nuclei. Therefore, instead of trying to solve the Schrödinger equation for all the particles simultaneously, we regard the nuclei as fixed in position and solve the Schrödinger equation for the electrons in the static electric potential arising from the nuclei in that particular arrangement. Different arrangements of nuclei may then be adopted and the calculation repeated. The set of solutions so obtained allows us to construct the **molecular potential energy curve** of a diatomic molecule (Fig. 8.1), and in general a potential energy *surface* of a polyatomic species, and to identify the equilibrium conformation of the molecule with the lowest point on this curve (or surface). The Born–Oppenheimer approximation is very reliable for ground electronic states, but it is less reliable for excited states.

Equilibrium
bond length

Internuclear
distance
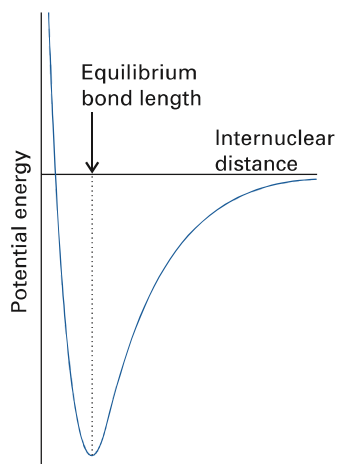
Fig. 8.1 A typical molecular potential energy curve for a diatomic species.

Fig. 8.2 The coordinates used in the discussion of the Born–Oppenheimer approximation.

8.1 The formulation of the approximation

The simplest approach to the formulation of the Born–Oppenheimer approximation is to consider a one-dimensional analogue of the hydrogen molecule–ion, in which all motion is confined to the z-axis (Fig. 8.2). The full hamiltonian, H, for the problem is

$$H = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial z^2} - \sum_{j=1,2}\frac{\hbar^2}{2m_j}\frac{\partial^2}{\partial Z_j^2} + V(z, Z_1, Z_2) \tag{8.1}$$

where z is the location of the electron and Z_j, with $j = 1, 2$, the locations of the two nuclei. More simply:

$$H = T_e + T_N + V$$

for the electron kinetic energy, the nuclear kinetic energy, and the potential energy of the system, respectively. The Schrödinger equation is

$$H\Psi(z, Z_1, Z_2) = E\Psi(z, Z_1, Z_2) \tag{8.2}$$

We attempt a solution of the form

$$\Psi(z, Z_1, Z_2) = \psi(z; Z_1, Z_2)\chi(Z_1, Z_2) \tag{8.3}$$

where ψ is the electronic wavefunction and χ (chi) is the nuclear wavefunction. The notation $\psi(z; Z_1, Z_2)$ means that the wavefunction for the electron is a function of its position z and depends parametrically on the coordinates of the two nuclei in the sense that we get a different wavefunction $\psi(z)$ for each arrangement of the nuclei. When this trial solution is substituted into eqn 8.2 we obtain

$$H\psi\chi = \chi T_e\psi + \psi T_N\chi + V\psi\chi + W = E\psi\chi \tag{8.4}$$

where

$$W = -\sum_{j=1,2}\frac{\hbar^2}{2m_j}\left(2\frac{\partial\psi}{\partial Z_j}\frac{\partial\chi}{\partial Z_j} + \frac{\partial^2\psi}{\partial Z_j^2}\chi\right)$$

This latter quantity is non-zero because ψ depends on the nuclear coordinates, so $\partial\psi/\partial Z_j$ is non-zero. However, because the nuclear masses occur in the denominator, we suppose that W is small and can be neglected and instead of eqn 8.4 try to solve[1]

$$\chi T_e\psi + \psi T_N\chi + V\psi\chi = E\psi\chi$$

or, collecting terms and rearranging slightly,

$$\psi T_N\chi + (T_e\psi + V\psi)\chi = E\psi\chi \tag{8.5}$$

As a first step at solving eqn 8.5 we write

$$T_e\psi + V\psi = E_e(Z_1, Z_2)\psi \tag{8.6}$$

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1. W is responsible for so-called 'non-adiabatic effects', which can be very important when interactions between electronic states are significant. For further details, see the *Further reading* section.

for fixed values of the nuclear coordinates. This equation is the Schrödinger equation for the electron in a potential V that depends on the fixed locations of the two nuclei. The solution is the electronic wavefunction ψ, and the eigenvalue $E_e(Z_1,Z_2)$ is the electronic contribution to the total energy of the molecule plus the potential energy of internuclear repulsion at the preselected nuclear locations. It is this function that when plotted against the nuclear position gives the molecular potential energy curve.

Finally, on substituting eqn 8.6 into eqn 8.5, we find

$$\psi T_N \chi + E_e \psi \chi = E \psi \chi$$
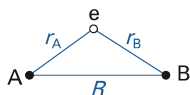
and on cancelling ψ obtain

$$T_N \chi + E_e \chi = E \chi \qquad (8.7)$$

This equation is the Schrödinger equation for the wavefunction χ of the nuclei when the nuclear potential energy, now represented by E_e, has the form of the molecular potential energy curve. Its eigenvalue E is the total energy of the molecule within the Born–Oppenheimer approximation.
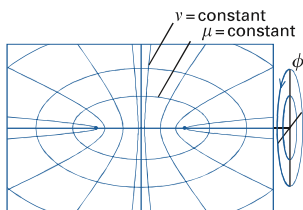
From now on (in this chapter) we shall concentrate on eqn 8.6, but write it more simply and generally, and with the normal symbols for the potential energy and total energy, as

$$H\psi = E\psi \qquad H = -\frac{\hbar^2}{2m_e}\nabla^2 + V \qquad (8.8)$$

where V is the potential energy of the electron in the field of the stationary nuclei plus the nuclear interaction contribution and E is the total electronic and nucleus–nucleus repulsion energy for a stationary nuclear conformation.

8.2 An application: the hydrogen molecule–ion

Even within the Born–Oppenheimer approximation there is only one molecular species for which the Schrödinger equation can be solved exactly: the hydrogen molecule–ion, H_2^+. The hamiltonian for this species is
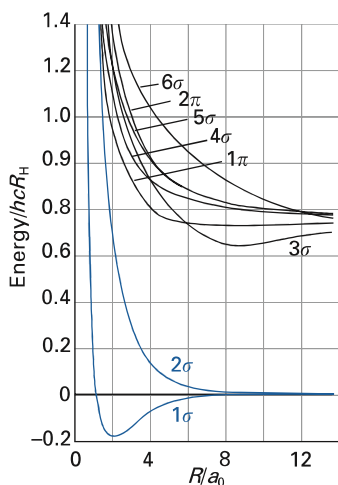
$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R} \qquad (8.9)$$

with the distances defined in Fig. 8.3. The final term represents the repulsive interaction between the two nuclei, and within the Born–Oppenheimer approximation is a constant for a given relative location of the nuclei.
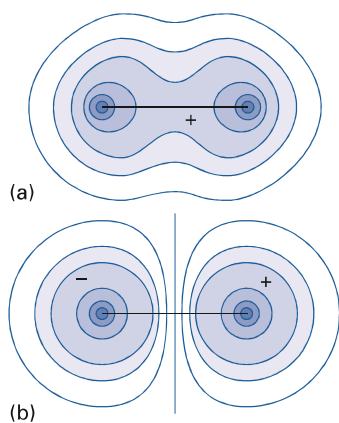
As H_2^+ has only one electron, it has a status in valence theory analogous to the hydrogen atom in the theory of atomic structure. Just as the Schrödinger equation for the hydrogen atom is separable and solvable when expressed in spherical polar coordinates, so the equation for H_2^+ is separable and solvable when expressed in 'ellipsoidal coordinates' (μ, v, ϕ), where

$$\mu = \frac{r_A + r_B}{R} \qquad v = \frac{r_A - r_B}{R} \qquad (8.10)$$

and ϕ is the azimuthal angle around the internuclear axis (Fig. 8.4). In these coordinates, the two nuclei lie at the foci of ellipses of constant μ. The

Fig. 8.3 The coordinates used to specify the hamiltonian for the hydrogen molecule–ion.

Fig. 8.4 The elliptical coordinates μ, v, and ϕ used for the separation of variables in the exact treatment (within the Born–Oppenheimer approximation) of the hydrogen molecule–ion.

Fig. 8.5 The molecular potential energy curves for the hydrogen molecule–ion.

Fig. 8.6 Contour diagrams of the (a) bonding and (b) antibonding orbitals (1σ and 2σ, respectively) of the hydrogen molecule–ion in the LCAO approximation.

resulting solutions are called **molecular orbitals** and resemble atomic orbitals but spread over both nuclei.

The 'exact' molecular orbitals of H_2^+ are mathematically much more complicated than the atomic orbitals of hydrogen, and as we shall shortly make yet another approximation, there is little point in giving their detailed form.[2] However, some of their features are very important and will occur in other contexts.

The molecular potential energy curves vary with internuclear distance, R, as shown in Fig. 8.5. The two lowest curves are of the greatest interest, and we concentrate on them. The steep rise in energy as $R \rightarrow 0$ is largely due to the increase in the nucleus–nucleus potential energy as the two nuclei are brought close together. At large distances, as $R \rightarrow \infty$, the curves tend towards the values typical of a hydrogen atom with the second proton a long way away. The lowest curve passes through a minimum close to $R = 2a_0$, and its energy then lies about $0.20 hcR_H$ (2.7 eV) below the energy of a separated hydrogen atom and proton. This result suggests that H_2^+ is a stable species (in the sense of having a lower energy than its dissociation products, but not in a chemical sense of being non-reactive), and that its bond length will be close to $2a_0$ (106 pm). The species is known spectroscopically: its minimum lies at 2.648 eV and its bond length is 106 pm, in very good agreement.

The origin of the lowering of energy can be discovered by examining the form of the wavefunctions, but we have to be circumspect. Figure 8.6 shows the two molecular orbitals of lowest energy as contour diagrams for various values of R. The striking difference between them is that the higher energy orbital (denoted 2σ) has an internuclear node whereas the lower energy orbital (1σ) does not. There is therefore a much greater probability of finding the electron in the internuclear region if it is described by the wavefunction 1σ than if it is described by 2σ.[3] The conventional argument then runs that because the electron can interact with both nuclei if its wavefunction is 1σ, then it is in a favourable electrostatic environment and will have a lower energy than that of a separated hydrogen atom and proton. It is on the basis of such a simplistic argument that chemical bond formation is commonly associated with the accumulation of electron density in an internuclear region.

The actual interpretation of the wavefunctions is, however, a much more delicate problem. The total energy of a molecule has contributions from several sources, including the kinetic energy of the electron. What appears to happen on bond formation (in H_2^+ at least) is that, as R is reduced from a large value, the lowest energy wavefunction shrinks on to the nuclei slightly as well as accumulating in the internuclear region. The transfer of electron density into the internuclear region is disadvantageous, because it is removed from close to the nuclei. However, the shrinkage of the orbitals overcomes this disadvantage, for although a slight increase in kinetic energy accompanies the shrinking (because the wavefunction becomes more sharply

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2. A reference to their form is provided in the *Further reading* section.

3. The label σ signifies the cylindrical symmetry of the orbital about the internuclear axis. A σ orbital has zero units of electronic orbital angular momentum about that axis, a fact used in Section 8.4.

curved), a significant reduction in potential energy overcomes all these unwanted effects, and the net outcome is a lowering of energy. The formation of 2σ, on the other hand, results in a small expansion of the electron distribution around the nuclei, and that has a net energy-raising effect. In other words, it is not the shift of electron density into the internuclear region that lowers the energy of the molecule but the freedom that this redistribution gives for the wavefunction to shrink in the vicinity of the two nuclei.

   In what follows, we shall anticipate the formation of a bond—as signalled by a lowering of the energy of the molecule—whenever there is an enhanced probability density in the internuclear region, but accept that this might be no more than a correlation rather than a direct effect on the energy of the molecule. A detailed analysis has been performed only for H_2^+, and the argument might be quite different in other molecules.[4]

Molecular orbital theory

A difficulty will already have become apparent: the solution of the Schrödinger equation for H_2^+ is so complicated (even after making the Born–Oppenheimer approximation) that there can be little hope that exact solutions will be found for more complicated molecules. Therefore, we must resort to another approximation, but use the exact solutions for H_2^+ as a guide. Another reason why making a further approximation is quite sensible is that we already have available quite good atomic orbitals for many-electron atoms, and it seems appropriate to try to use them as a starting point for the description of many-electron molecules built from those atoms.

8.3 Linear combinations of atomic orbitals

Inspection of the form of the wavefunctions for H_2^+ shown in Fig. 8.6 suggests that they can be simulated by forming linear combinations of hydrogen atomic orbitals:

$$\psi_+ \approx \phi_a + \phi_b \qquad \psi_- \approx \phi_a - \phi_b \tag{8.11}$$

where ϕ_a is a H1s-orbital on nucleus A and ϕ_b its analogue on nucleus B.[5] In the first case, the accumulation of electron density in the internuclear region is simulated by the constructive interference that takes place between the two waves centred on neighbouring atoms. The nodal plane in the true wavefunction is recreated by the destructive interference between waves superimposed with opposite signs.

   The partial justification for simulating molecular orbitals as an LCAO, a **linear combination of atomic orbitals**, can be appreciated by examining

4.   See M.J. Feinberg, K. Ruedenberg, and E.L. Mehler, The origin of binding and antibinding in the hydrogen molecule–ion. *Adv. Quantum Chem.*, 27, 5 (1970).

   5.   In this chapter, we use ϕ to denote an atomic orbital and ψ to denote a molecular orbital.