

The Chemical Bond in the Simplest Molecules: H_2^+ and H_2

In this chapter we begin to address the problem of the chemical bond. What makes atoms stick together to form a molecule? Why are some bonds strong and others weak? Can we predict the properties of a molecule—the energy levels, the spectra resulting from transitions among them, the spatial distribution of nuclei and electrons? And how are these properties related to those of the separated atoms? These are typical of the questions we must try to answer.

The simplest molecules, of course, are those with only two atoms. Studying these allows us to examine a single chemical bond in isolation. We begin with a general discussion of the forces between two atoms and how they are responsible for bonding. It will become clear that the key to bonding is how the electron distribution changes when the atoms are brought together. In the rest of the chapter we deal with ways to find this electron distribution, in terms of various computational approaches to obtain the wave function.

The present chapter is concerned explicitly with only the two simplest molecules. Despite their simplicity, they are rich enough to illustrate most of the main principles of bonding and some fundamental ideas that underly our description of molecules. The H_2^+ ion, with only one electron, is the simplest possible molecule; we use it to introduce the most widely employed approximation of bonding theory, the concept of the molecular orbital. From H_2^+ we go on to H_2 , in which the presence of two electrons gives us the first complete picture of a “normal” bond. We consider these molecules in both ground and excited states, and in terms of several approximate descriptions. In Chapter 7 we shall extend our theory to diatomic molecules in general.

6.1 Bonding Forces between Atoms

What forces hold a molecule together as an entity? Within any molecule there are attractive forces between electrons and nuclei, and repulsive forces between pairs of nuclei and between pairs of electrons. We must examine how these forces reach a delicate balance that enables molecules to

have stable and well-defined structures, structures that neither fall apart at the slightest touch nor collapse into a united atom. We must ask how the attractive forces can just balance the repulsive forces for some particular molecular geometry and make that geometry a stable one. If the molecule is stretched, squeezed, or twisted from its most stable shape, then the forces within the molecule will tend to restore it to that shape. Each molecular structure is thus in true stable equilibrium, corresponding to the bottom of a reasonably deep potential energy well.¹

But in speaking of molecular structures we are already making an important assumption. The term “structure” implies a rather rigid arrangement of the atomic nuclei, close to the equilibrium positions for which the molecule’s energy is minimized. The molecule cannot be totally rigid; it would violate the uncertainty principle for any particle to be at rest at a fixed point. However, the assumption of near-rigid structure is very good indeed. Since nuclei have thousands of times the mass of electrons, Δp for a nucleus can be a quite small fraction of its total momentum and still large enough to give a negligible Δq . To put it another way, the light electrons move so much faster than the heavy nuclei that they have a smooth average distribution over a time during which the nuclei hardly move at all. We can thus obtain a good description of the molecule’s electronic structure even if we assume the nuclei to be at rest.

This assumption is part of what is known as the *Born–Oppenheimer approximation* (after Max Born and J. Robert Oppenheimer). What is this approximation? Let us approach it by stages. Consider a diatomic molecule composed of nuclei A and B , with charges of $+Z_Ae$ and $+Z_Be$,

¹ One could imagine a different kind of molecule, in which the energy of the molecule would be quite insensitive to the location of the constituent atoms. Such a molecule would be more like a liquid drop than the conventional ball-and-stick structure. Although this is not a good description of most molecules, many properties of atomic nuclei, especially heavy nuclei, are nicely described by a liquid drop model.

respectively, and some electrons. We define the distance between the two nuclei as R (if there were more atoms we would have to specify R_{AB}), and the distances of the i th electron from the two nuclei as r_{Ai} and r_{Bi} . These coordinates are illustrated in Fig. 6.1. The Hamiltonian operator (neglecting all magnetic interactions) is then

$$\begin{aligned} H = & \left[\frac{\mathbf{p}_A^2}{2m_A} + \frac{\mathbf{p}_B^2}{2m_B} \right] \\ & + \left[\sum_i \frac{\mathbf{p}_i^2}{2m_e} + \frac{e^2}{4\pi\epsilon_0} \right. \\ & \times \left. \left(\frac{Z_A Z_B}{R} - \sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}} \right) \right] \\ = & H_{\text{nuc}} + H_{\text{elec}}, \end{aligned} \quad (6.1)$$

where H_{nuc} and H_{elec} are defined by the two sets of square brackets, r_{ij} is as usual the distance between electrons i and j , and the sums are taken over all the electrons; H_{nuc} is the kinetic energy operator for the nuclei, and H_{elec} corresponds to the energy with the nuclei fixed. The molecular wave function ψ is the solution of the equation $H\psi = E\psi$. Now we make the Born–Oppenheimer approximation, which is simply that the nuclear and electronic motions are separable (cf. Section 3.9), meaning that we can write two Schrödinger equations, one for the electronic energy and wave function, and one for the nuclei. Thus, having collected the kinetic energy of the heavy—and presumably slowly moving—nuclei in the first set of brackets in Eq. 6.1, and all the terms governing the motion of the light, fast electrons in the second set of brackets, we can write

$$\psi(r, R) = \psi_{\text{nuc}}(R) \psi_{\text{elec}}(r, R). \quad (6.2)$$

Here r stands for all the r_i and r_{ij} . Eq. 6.2 implicitly reveals a key point of the Born–Oppenheimer approximation: The electronic wave function, and therefore the electronic energy, depend on the distance R between the nuclei so that $\psi_{\text{elec}}(r, R)$ must contain R . However $\psi_{\text{elec}}(r, R)$ satisfies the equation

$$H_{\text{elec}} \psi_{\text{elec}}(r, R) = E(R) \psi_{\text{elec}}(r, R). \quad (6.3)$$

The Hamiltonian H_{elec} contains R explicitly only in the potential energy of repulsion between the nuclei, but R is implicit in the electron–nuclear attraction terms, $-\sum_i \frac{Z_A}{r_{Ai}} - \sum_i \frac{Z_B}{r_{Bi}}$.

The central element of the Born–Oppenheimer approximation is the way R is treated in Eq. 6.3: The internuclear distance is handled as a parameter with a fixed value for each electronic wavefunction $\psi_{\text{elec}}(r, R)$ and each electronic energy we determine. That is, $\psi_{\text{elec}}(r, R)$ is defined as the eigenfunction of the operator H_{elec} , whose eigenvalue $E(R)$ gives the energy of the molecule for a given value of the parameter R . Although ψ_{nuc} must be a function of *all* the nuclear coordinates, only R

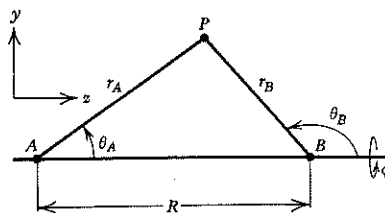


Figure 6.1 Coordinates in a diatomic molecule. The nuclei A and B (charges $+Z_A e$ and $+Z_B e$) are a distance R apart. Any point P can be described in terms of r_A and r_B , the distances from the two nuclei; θ_A and θ_B , the angles relative to the A – B axis; and an angle ϕ describing rotation about that axis.

affects the electronic energy and appears in ψ_{elec} . In other words, $|\psi_{\text{elec}}(r, R)|^2$ and $E(R)$ describe the electron distribution (as a function of r) and energy that the molecule would have if the nuclei were fixed a distance, R , apart. These are the quantities we want to know at this point.

In this chapter we shall address only the solution of the electronic problem expressed in Eq. 6.3, but let us briefly survey the remainder of the problem. To the extent that the Born–Oppenheimer approximation is valid, one can solve Eq. 6.3 to obtain $E(R)$ for any value of R . Combining these values gives a function $E(R)$ from $R = 0$ to $R = \infty$, which for the ground state of a stable diatomic molecule has a form like that in Fig. 6.2. From such a function $E(R)$, we obtain the part of the wave function describing nuclear motion by solving²

$$H_{\text{nuc}} \psi_{\text{nuc}}(R) = [E - E(R)] \psi_{\text{nuc}}(R); \quad (6.4)$$

in this equation, R is now a quantum-mechanical variable, E is the total energy, $E(R)$ is the effective potential energy in which the nuclei move, and their difference $E - E(R)$ is the kinetic energy of the nuclei associated with changes of R , that is, with their vibration. Since a system in a potential well always has a zero-point energy, the lowest eigenvalue of E must be some distance above the bottom of the well. We shall come back to this problem in Section 7.1.

² Substituting Eqs. 6.1 and 6.2 into $H\psi = E\psi$, we have

$$(H_{\text{nuc}} + H_{\text{elec}}) \psi_{\text{nuc}}(R) \psi_{\text{elec}}(r, R) = E \psi_{\text{nuc}}(R) \psi_{\text{elec}}(r, R)$$

and

$$\begin{aligned} \psi_{\text{elec}}(r, R) H_{\text{nuc}} \psi_{\text{nuc}}(R) + \psi_{\text{nuc}}(R) H_{\text{nuc}} \psi_{\text{elec}}(r, R) \\ + \psi_{\text{nuc}}(R) H_{\text{elec}} \psi_{\text{elec}}(r, R) = E \psi_{\text{nuc}}(R) \psi_{\text{elec}}(r, R), \end{aligned}$$

since H_{nuc} and H_{elec} act only on the nuclear and electronic coordinates, respectively. Substituting Eq. 6.3 in the third term and rearranging gives us

$$\begin{aligned} \psi_{\text{elec}}(r, R) H_{\text{nuc}} \psi_{\text{nuc}}(R) + \psi_{\text{nuc}}(R) H_{\text{nuc}} \psi_{\text{elec}}(r, R) \\ = \psi_{\text{elec}}(r, R) [E - E(R)] \psi_{\text{nuc}}(R). \end{aligned}$$

In the second term we find $H_{\text{nuc}} \psi_{\text{elec}}(r, R)$, which contains the usually small interactions between electronic and nuclear motions; the Born–Oppenheimer approximation says that this term can be neglected. If we do this, dividing through by $\psi_{\text{elec}}(r, R)$ yields Eq. 6.4.

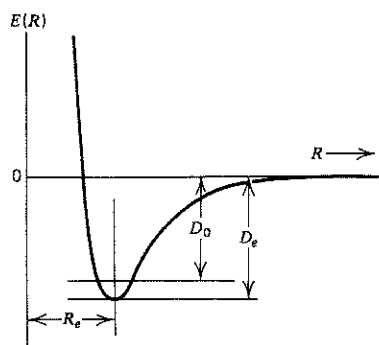


Figure 6.2 Internal energy $E(R)$ of a stable diatomic molecule as a function of the internuclear distance R . The zero of energy is the two separated atoms at rest in the limit $R \rightarrow \infty$. The dissociation energy can be defined as D_e , relative to the bottom of the well, at the equilibrium distance R_e , or as D_0 , relative to the ground state; $D_e - D_0$ is the zero-point energy of the molecule. In a typical molecule D_e is of the order of 5 eV, and R_e is about 1–2 Å.

When atoms A and B are very far apart, there is essentially no interaction between them; we define the energy of infinitely separated $A + B$ without kinetic energy to be our zero. At the other extreme, when the nuclei are close to each other, the repulsive energy $Z_A Z_B e^2 / 4\pi\epsilon_0 R$ becomes much larger than all the other terms in Eq. 6.1, and $E(R)$ appears to become infinite as R goes to zero.³ This repulsion is what keeps molecules from collapsing into single atoms. We are interested in what happens in the region between these limits. A stable molecule can exist only if $E(R)$ has a minimum at some value of R , as in Fig. 6.2. Otherwise the nuclear repulsion would make the atoms fly apart without limit. The depth of this minimum, relative to the energy at infinite separation, is called the *dissociation energy* (D_e) of the molecule, and the value of R at which it occurs is the *equilibrium distance* (R_e). To see how such a minimum can occur, let us examine the balance of forces in a molecule.

In our diatomic molecule with nuclei A and B a distance R apart, the repulsive force between the nuclei is, of course, of magnitude

$$F_{AB} = \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R^2}, \quad (6.5)$$

³ As earlier discussion indicated, this inference of infinite repulsion is predicated on the assumption that the molecule is not rotating; if it is, then the effective force of centrifugal motion keeps the nuclei apart. However there is another kind of force, largely beyond the scope of this volume, that becomes important when nuclei come close to one another. At very small distances—about 10^{-15} m—the strong nuclear forces become dominant. Since these forces are attractive, $E(R)$ goes not to infinity, but to a very high peak bounding a potential well. If we were to push the two nuclei together hard enough, they would cross this barrier and combine into a single nucleus of charge $(Z_A + Z_B)e$; this would be a nuclear *fusion* process, such as occurs in stars and thermonuclear bombs. But since the barrier height is in the MeV range, there is little danger of producing fusion with ordinary chemical energies. As we mentioned in Section 4.1, the emission of α particles by radioactive nuclei corresponds to the reverse process, tunneling through the barrier from inside.

acting directly along the A – B axis. Suppose now that there is a bit of electronic charge, say an amount $-q$, at the arbitrary point P (Fig. 6.1). This charge exerts an attractive force F_{AP} on nucleus A , in the direction AP , and an attractive force F_{BP} on nucleus B , in the direction BP . The magnitudes of these forces are

$$F_{AP} = \frac{Z_A e q}{4\pi\epsilon_0 r_A^2} \quad \text{and} \quad F_{BP} = \frac{Z_B e q}{4\pi\epsilon_0 r_B^2}. \quad (6.6)$$

We can define a *bonding* force as one that tends to draw the nuclei together, and an *antibonding* force as one that tends to push them apart. The repulsive force F_{AB} is clearly antibonding; what about the forces exerted by the charge at point P ?

Only the force exerted along the A – B axis has any effect on the bonding. We thus break the forces F_{AP} and F_{BP} into their components parallel to the A – B axis (our z axis) and perpendicular to it—that is, into the interesting z components and the irrelevant y components. In terms of the coordinates shown in Fig. 6.1, the z components are

$$\begin{aligned} (F_{AP})_z &= \frac{Z_A e q}{4\pi\epsilon_0 r_A^2} \cos \theta_A \quad \text{and} \\ (F_{BP})_z &= \frac{Z_B e q}{4\pi\epsilon_0 r_B^2} \cos \theta_B. \end{aligned} \quad (6.7)$$

The bonding force on nucleus A is the force that tends to push it toward B , that is, the component of force in the positive z direction. The bonding force on nucleus B , however, is the force in the *negative* z direction. The net classical bonding force on the nuclei due to the charge $-q$ at point P is therefore the single component of a force vector,

$$\begin{aligned} F_{\text{bonding},P} &= (F_{AP})_z - (F_{BP})_z \\ &= \frac{eq}{4\pi\epsilon_0} \left(\frac{Z_A \cos \theta_A}{r_A^2} - \frac{Z_B \cos \theta_B}{r_B^2} \right). \end{aligned} \quad (6.8)$$

The quantum mechanical bonding force operator $F_{\text{bonding},P}$ looks exactly the same.

To obtain the total bonding force exerted by the electrons, we would have to sum Eq. 6.8 over the entire electron distribution, which we can obtain only by solving the Schrödinger equation. Assume that we have solved Eq. 6.3 to obtain the wave function $\psi_{\text{elec}}(r, R)$ for a given R . The expectation value of the total bonding force is then

$$\begin{aligned} \langle F_{\text{bonding}}(R) \rangle &= \langle F_{\text{bonding},P} \rangle - F_{AB} \\ &= \int \psi_{\text{elec}}^* F_{\text{bonding},P} \psi_{\text{elec}} d\tau - \frac{Z_A Z_B}{4\pi\epsilon_0 R} \end{aligned} \quad (6.9)$$

with the integral taken over all possible positions of all the electrons. (The symbol “ $d\tau$ ” is shorthand for what we earlier called “ $dq_1 \cdots dq_N$,” and is meant to indicate three coordinates for each electron.)

One does not have to evaluate the integral in Eq. 6.9 explicitly to obtain the total bonding force. The operator corresponding to $F_{\text{bonding}}(R)$ is $\partial V(R, r)/\partial R$, where $V(R, r)$ is the potential energy of H_{elec} . We thus have

$$\begin{aligned}\langle F_{\text{bonding}}(R) \rangle &= \left\langle \frac{\partial V(R, r)}{\partial R} \right\rangle \\ &= \int \psi_{\text{elec}}^* \frac{\partial V(R, r)}{\partial R} \psi_{\text{elec}} d\tau \\ &\quad + \int \frac{\partial \psi_{\text{elec}}^*}{\partial R} E(R) \psi_{\text{elec}} d\tau \\ &\quad + \int \psi_{\text{elec}}^* E(R) \frac{\partial \psi_{\text{elec}}}{\partial R} d\tau.\end{aligned}\quad (6.10)$$

We shall now see that

$$\begin{aligned}\int \psi_{\text{elec}}^* \frac{\partial H_{\text{elec}}}{\partial R} \psi_{\text{elec}} d\tau &= \frac{\partial}{\partial R} \int \psi_{\text{elec}}^* H_{\text{elec}} \psi_{\text{elec}} d\tau \\ &= \frac{dE(R)}{dR},\end{aligned}\quad (6.11)$$

which leads to the result that the effective bonding force is the slope of the electronic energy $E(R)$:

$$\langle F_{\text{bonding}}(R) \rangle = \frac{dE(R)}{dR}, \quad (6.12)$$

as follows. (Note that because the bonding force is defined as a force that *reduces* R , Eq. 6.12 lacks the usual negative sign connecting force with the slope of the potential energy.) We have

$$\begin{aligned}\frac{\partial}{\partial R} \int \psi_{\text{elec}}^* H_{\text{elec}} \psi_{\text{elec}} d\tau &= \int \frac{\partial \psi_{\text{elec}}^*}{\partial R} H_{\text{elec}} \psi_{\text{elec}} d\tau \\ &\quad + \int \psi_{\text{elec}}^* H_{\text{elec}} \frac{\partial \psi_{\text{elec}}}{\partial R} d\tau \\ &\quad + \int \psi_{\text{elec}}^* \frac{\partial H_{\text{elec}}}{\partial R} \psi_{\text{elec}} d\tau.\end{aligned}$$

Since H_{elec} is a real Hermitian operator (cf. Appendix 6B), we can write

$$\int \psi_{\text{elec}}^* H_{\text{elec}} \frac{\partial \psi_{\text{elec}}}{\partial R} d\tau = \int \frac{\partial \psi_{\text{elec}}}{\partial R} H_{\text{elec}} \psi_{\text{elec}}^* d\tau.$$

Substitution of Eq. 6.3 then removes the first two terms on the right-hand side above, yielding

$$\begin{aligned}\int \frac{\partial \psi_{\text{elec}}^*}{\partial R} E(R) \psi_{\text{elec}} d\tau + \int \frac{\partial \psi_{\text{elec}}}{\partial R} E(R) \psi_{\text{elec}}^* d\tau \\ = E(R) \frac{\partial}{\partial R} \int \psi_{\text{elec}}^* \psi_{\text{elec}} d\tau = 0,\end{aligned}$$

since $\int \psi_{\text{elec}}^* \psi_{\text{elec}} d\tau$ has the constant value unity. The same substitution gives the last term of Eq. 6.11.

Equation 6.12 is known as the *Hellmann–Feynman theorem*. This confirms our earlier statement that $E(R)$ is the effective potential energy for nuclear motion.

Without solving the Schrödinger equation for $\langle F_{\text{bonding}}(R) \rangle$, we can get a good deal of insight into the nature of the bonding forces simply by looking at the form of Eq. 6.8. Following a method introduced by T. Berlin and K. Fajans, let us see how $F_{\text{bonding},P}$ varies with the location of the point P . First, whenever P lies between A and B ($z_A < z_P < z_B$), we have $\theta_A < \pi/2$ and $\theta_B > \pi/2$; thus $\cos \theta_A$ is positive, $\cos \theta_B$ is negative, and $F_{\text{bonding},P}$ must be positive. This is a very fundamental (if obvious) point, which we must recognize from the outset: Any electronic charge lying between two nuclei is necessarily bonding because it pulls the two nuclei toward each other. In order for charge to be antibonding, it must lie “beyond” the nuclei.

Now suppose we place our test point P to the right of nucleus B ($z_P > z_B$), so that $\cos \theta_A$ and $\cos \theta_B$ are both positive. A negative charge at P then pulls both nuclei to the right, pulling A toward B but B away from A . Which force wins? For simplicity, let us suppose that point P lies on the A – B axis ($\cos \theta_A = \cos \theta_B = 0$). Suppose that the charges Z_A and Z_B are equal. A charge to the right of B must be closer to B than to A ($r_B < r_A$), so the right-hand term in Eq. 6.8 is larger than the left-hand term, and the net force is antibonding. For equal nuclear charges, then, any electronic charge on the axis to the right of B or the left of A is antibonding. This is not true in every case, however. Suppose, for example, that $Z_A > Z_B$, with point P still on the A – B axis to the right of B . For P close to B , the small value of r_B will outweigh the charge difference ($Z_B/r_B^2 > Z_A/r_A^2$) and $F_{\text{bonding},P}$ will be negative. As we move P to the right, the ratio (r_A/r_B) comes closer and closer to unity. Eventually a point is reached at which the larger charge on nucleus A makes the first (bonding) term in Eq. 6.8 exceed the second (antibonding) term, even though the second term has a smaller denominator; for all points on the axis beyond this the charge is bonding. Similar calculations can be made for points not on the A – B axis.

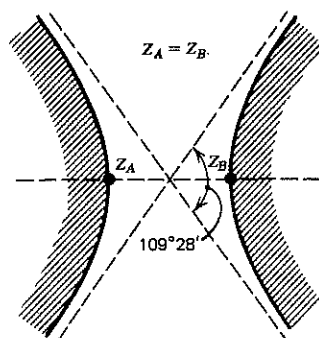
We thus recognize that regions of space in the vicinity of nuclei are inherently bonding or antibonding; whether or not a bond is formed depends on how the electrons are distributed among these regions. To find the positions and shapes of the bonding and antibonding regions, one need merely locate the surfaces that divide them. These boundary surfaces are obtained by solving Eq. 6.8 for those values of r_A , r_B , θ_A , θ_B at which $F_{\text{bonding},P} = 0$. Although we shall not go through the algebra, it is not difficult to simplify this equation to

$$\alpha(1 + \rho^2 - 2\rho\alpha)^{3/2} = \frac{Z_B}{Z_A}(\rho - \alpha), \quad (6.13)$$

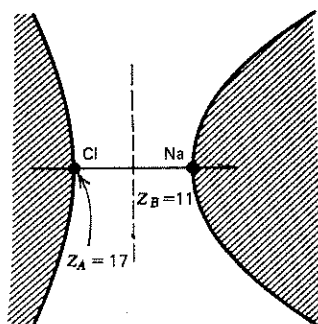
where $\rho \equiv R/r_A$ and $\alpha \equiv \cos \theta_A$; Eq. 6.13 contains only one physical parameter (Z_B/Z_A) and two independent variables

(ρ and α). Illustrations of the boundary surfaces for several values of Z_A/Z_B are given in Fig. 6.3. Note that the larger the ratio Z_A/Z_B , the smaller is the antibonding region near the low- Z nucleus B . In a molecule such as HCl, this region includes only that charge very close behind the H nucleus; because of the large ratio $Z_{\text{Cl}}/Z_{\text{H}}$, a charge almost anywhere except beyond the Cl nucleus is in the bonding region.

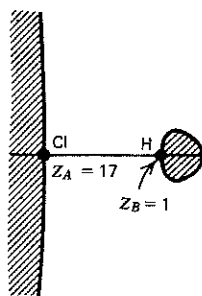
How much charge is needed to balance the repulsive force between the two nuclei? Suppose that a negative charge $-q$ is at the midpoint of the bond between A and B ,



(a)



(b)



(c)

Figure 6.3 Bonding (unshaded) and antibonding (shaded) regions of space for diatomic molecules with various values of Z_A/Z_B . (a) Homonuclear molecule (for example, H_2 , Cl_2), $Z_A = Z_B$. (b) NaCl molecule, $Z_A/Z_B = 17/11 = 1.545$. (c) HCl molecule, $Z_A/Z_B = 17$. From Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 936.

so that $r_A = r_B = R/2$, $\cos \theta_A = 1$, $\cos \theta_B = -1$. How large must this bit of charge be for the binding force it exerts to equal the repulsive force F_{AB} ? Combining Eqs. 6.5 and 6.8, we require that

$$\frac{Z_A e q}{(R/2)^2} + \frac{Z_B e q}{(R/2)^2} = \frac{Z_A Z_B e^2}{R^2}, \quad (6.14)$$

or with a bit of rearrangement,

$$q = \frac{(Z_A + Z_B)e}{4Z_A Z_B}. \quad (6.15)$$

If the two charges are equal, $Z_A = Z_B = Z$, then q need be only $-Ze/8$ to balance the nuclear repulsion. If Z_A is larger than Z_B , then q must be somewhat larger, but even in the limit $Z_A/Z_B \rightarrow \infty$ it need not exceed $Z_B e/4$. From this rough model we see that the amount of negative charge in the bonding region required to stabilize a molecule is very small, at least when the charge lies on the bond axis. The bonding effectiveness of a given charge of course decreases as it moves away from the axis.

Thus, we have a rationalization of how electrons draw nuclei together and counter the mutual repulsion of the nuclei of a diatomic molecule. But closer examination shows that we only have part of the picture. Thus far, the discussion has neglected the electronic kinetic energy, and surely, when an electron with a well-defined total energy passes into a region of low potential energy, its kinetic energy must increase. This implies that if the potential energy of the electron in the region between the nuclei is lowered by the approach of the two nuclei, then the electron must spend less time there. And if that happens, how can we expect charge to accumulate between the nuclei?

This question was examined in detail by Ruedenberg and coworkers, and the results have been discussed by Mulliken and Ermler.⁴ The picture that emerges is this: Because the potential between the nuclei shows a maximum, and is relatively flat in that region, the force on an electron there is low and the computed local electronic kinetic energy T_e is low near the midpoint of the internuclear axis. Near the nuclei, however, the electronic kinetic energy is increased above that of the free atom, and this increase is greater than its decrease between the nuclei, so the average, $\langle T_e \rangle$, is greater for electrons in the diatomic molecule than in the separated atoms. The total energy of a bound system with only Coulombic forces is related to the average kinetic energy and to the average potential energy: $E = -\langle T \rangle = \frac{1}{2} \langle V \rangle$ (the virial theorem as applied to a Coulombic system), and if the

⁴ K. Ruedenberg, in O. Chalvet, ed., *Localization and Relocalization in Quantum Chemistry*, Vol. 1, (Reidel, Dordrecht, 1975), pp. 223–245; K. Ruedenberg, *Rev. Mod. Phys.* **34**, 326 (1962); M. J. Feinberg, K. Ruedenberg, and E. L. Mehler, *Adv. Quantum Chem.* **5**, 27 (1970); R. S. Mulliken and W. C. Ermler, *Diatomic Molecules, Results of ab initio Calculations* (Academic, New York, 1977), p. 38–43.

diatomic molecule is at its equilibrium internuclear distance, $\langle T \rangle = \langle T_e \rangle$. Therefore, because $\langle T_e \rangle_{\text{molecule}} > \langle T_e \rangle_{\text{free atoms}}$, $E(R_e) < E(\infty)$. In short, the simple model based on the statics of electrostatic forces hides the delicate balance between potential and kinetic energy. Without the electrostatic forces of attraction between the nuclei and the electronic charge there would be no chemical bond, but the *effective* potential, the internal energy $E_{\text{elec}}(R)$, takes its form—slow drop with decreasing R to a minimum at R_e and a sharp rise for $R < R_e$ —from the increasing kinetic energy of the electrons, as much as from their decreased potential.

Anticipating our discussion of vibrations in Chapter 7, we recognize that if q exceeds the value given in Eq. 6.15, then the net force between the nuclei is attractive, and if q is less than that value, the net force is repulsive. In effect, this is just how the electron distribution generates the chemical bond: when the distance R between two atoms that bond is moderately large, then the electron distribution has a small excess, above the value in Eq. 6.15, between those nuclei, generating an effective attractive force. When R is small, the electron distribution between the nuclei depletes (as a consequence of the exclusion principle), the nuclei become somewhat unshielded and repel each other more than the electrons attract them toward each other, giving a net repulsion.

We are now in a position to ask the following questions: First, under what conditions does negative charge distribute itself so as to create a stable bond? Second, is there a meaningful way to subdivide the electron density so that we can speak of bonding and antibonding electrons (or orbitals), rather than bonding and antibonding regions of space? And third, can one calculate the bonding forces with sufficient detail and accuracy to make reliable predictions of bond energies and molecular geometries?

The first of these three questions is really a rather large one. To know how the charge density in a molecule is distributed, we must presumably know the electronic wave function of the molecule. This means that we must solve the Schrödinger equation for the molecule at many internuclear distances, a task appreciably more formidable than that for an atom. Nevertheless, in strongly bound molecules the problem can be solved with reasonable accuracy by an approach similar to the one used for atoms, the method of one-electron orbitals. This method, in so far as it is valid, suffices to answer our second question in the affirmative. If each electron has its own wave function, we can indeed classify electrons and speak meaningfully of individual electrons as being responsible for particular bonds. The orbital method has its limitations, even with regard to electronic energies and charge distributions. In particular, it is not sufficiently accurate to describe weakly bound molecules in which the bonding forces are due in large part to correlation between the electrons. To the third question, on the possibility of predicting molecular properties, we can only answer, "Sometimes." Given a wave function, one can make such calculations; their accuracy depends on how good the wave function is. For very simple molecules, those with no more

than three or four atoms, the theoretical calculations reach or exceed the accuracy of experimental measurements. For slightly larger molecules, calculations can be accurate enough to give useful assistance in the interpretation of complex experimental results. For quite large molecules, the prediction from theory of such things as bond angles and lengths still lies at the limits of our technical ability. However we rarely need to know these with the same accuracy that we demand for small molecules. Moreover we can rely on the very powerful generalization that bond lengths and bond angles among a given kind of atoms remain about the same in extremely large classes of compounds. This principle of *transferability* underlies a vast range of generalizations used throughout chemistry and molecular biology.

We have seen how small a charge is needed to produce a net bonding force; it should not be surprising that the delicately balanced attractive and repulsive forces must be known with considerable accuracy before one can say how the balance actually works out in any particular case. With this overview of the problem, we are now prepared to examine its solution in the simplest possible molecule.

6.2 The Simplest Molecule: The Hydrogen Molecule-Ion, H_2^+

Naturally, the simplest molecule is the one that contains the smallest number of particles. There must be two nuclei if we are to have a molecule at all, the simplest nuclei are protons, and there must be at least one electron to provide a bonding force. The species made from these constituents is called the *hydrogen molecule-ion*, H_2^+ . It is a real species, known to exist in electric discharges; it is readily detected in a mass spectrometer. The spectrum of H_2^+ has been observed, and something is known of its chemistry. It is a fragile species, reacting almost any time it collides with a molecule of H_2 to produce the molecule-ion H_3^+ and a neutral H atom. Nevertheless, a great deal is known about H_2^+ because it is simple enough to be analyzed by reliable theoretical methods. We shall examine the H_2^+ molecule-ion in several ways, successively more precise and quantitative, each giving a slightly different viewpoint on how such a molecule can exist. In the present section we make a preliminary survey, before getting down to the business of finding the wave function.

In studying a molecule, a good starting point is to consider its properties when the atoms are very far apart, the limit at which we define the zero of energy. In the case of H_2^+ , then, we begin with a hydrogen atom in its $1s$ ground state and a bare proton far away from it. Let us consider what happens when the distance R between the two protons is decreased.⁵

⁵ This may sound as if we are talking about a dynamic (time-dependent) process. Actually, although we are considering a sequence of values of R , in each case we use the Born-Oppenheimer approximation and treat the nuclei as motionless. What we want is the solution to the time-independent Eq. 6.3 for each value of R .

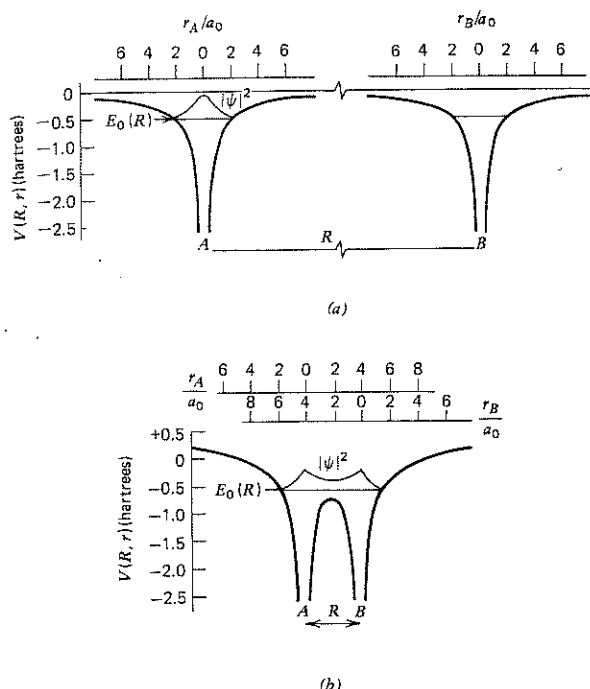


Figure 6.4 Potential energy of H_2^+ ,

$$V(R, r) = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{R} - \frac{1}{r_A} - \frac{1}{r_B} \right),$$

along the internuclear axis. (a) $\text{H} + \text{H}^+$, nuclei far apart, electron localized around one nucleus. (b) H_2^+ , $R = 4a_0$, electron equally likely to be around either nucleus. In each case the ground-state energy $E_0(R)$ and corresponding $|\psi|^2$ (arbitrary units) are shown; in part (a) these differ only slightly from those of a $1s$ H atom. Note that $V(R, r)$ and $E(R)$ include the internuclear repulsion, which in 6.4(b) equals $+0.25$ hartree; this is the limit of $V(R, r)$ as $r_A, r_B \rightarrow \infty$.

When the two are very far apart, the energy $E(R)$ must be essentially independent of R . As the free proton approaches the atom, however, the repulsive force between the two protons and the attractive force between the electron and the free proton must begin to make themselves apparent. The electron will be more likely to be found on the side of the atom toward the free proton—in quantum mechanical terms, its wave function will be distorted from the symmetric $1s$ function to one with a greater amplitude in this direction. The centers of positive and negative charge no longer coincide, and we say that the atom is *polarized* by the free proton. The attractive force is greater than the repulsive force (since the electron is on the average closer to the free proton), and a net bonding force appears. According to Eq. 6.12, $dE(R)/dR$ is then positive, and $E(R)$ must be negative, since we have defined $E(\infty) = 0$. One can show (see Section 10.1) that $E(R) \propto -1/R^4$ in this fairly long-range region.

In the long-range limit of very large R , it is still legitimate to speak of the H atom and the H^+ ion as two distinct entities. Consider Fig. 6.4a, which shows the potential energy

along a line through the two nuclei: There are two potential energy wells, separated by a high, very wide barrier. Although the probability of tunneling from one well to the other is not quite zero, at large R (say, over 20 \AA) it is low enough to be neglected for practical purposes. We can thus treat a state with the electron localized near one nucleus as a stationary (time-independent) state of the system. The electron's potential energy and wave function differ only slightly from those in an isolated hydrogen atom.

Now suppose that the nuclei are fairly close together. As shown in Fig. 6.4b, there is no longer an effective barrier between the two potential wells. The electron is thus free to travel anywhere in the combined well, and is as likely to be found near one nucleus as the other in any given observation. In such a situation the two protons are completely equivalent with regard to their interaction with the electron. More than that, they are *indistinguishable*. This is a very important concept. Two macroscopic charged spheres might also exert identical forces, but we could distinguish them from one another in various ways—say, by painting them different colors. But there is no way to do this with protons. Two protons—or two electrons, or two of any fundamental particle—are absolutely indistinguishable by any kind of measurement. In our H_2^+ system, then, neither we nor the electron can distinguish proton A from proton B. Even if we prepare the H_2^+ molecule by bringing together atom A and free proton B, there is no experiment that can distinguish A from B once they are together. If we then draw the two apart again, there is no way to tell if the electron has ended up around the same nucleus as at the start.⁶ Like the simultaneous position and momentum of a particle, these things are simply unknowable.

What does this indistinguishability imply about the wave function of H_2^+ ? We may “label” the nuclei A and B for convenience, but any physically measurable quantity must not be affected when the labels are interchanged. Since $|\psi|^2$, the probability density of finding an electron at a given point, is a measurable quantity, the value of $|\psi|^2$ at $r_A = a, r_B = b$ must be the same as at the corresponding point $r_A = b, r_B = a$. This can be summarized by writing

$$|\psi(A, B)|^2 = |\psi(B, A)|^2. \quad (6.16)$$

For Eq. 6.16 to be valid, $|\psi|^2$ must be symmetric with respect to a plane equidistant from the nuclei, the plane normal to the bond at its midpoint.

⁶ Unless the atoms passed each other so fast that their de Broglie wavelengths were much less than the shortest distance between them (though even then there is a small chance of what is called *exchange scattering*). Here we see the fundamental difference between classical and quantum mechanics. If classical mechanics were valid, one could distinguish the protons by following the trajectory of each particle with as much precision as required. But the uncertainty principle makes this impossible.

We can say a bit more about the form of ψ . Given the Born–Oppenheimer approximation, the electronic wave function must satisfy Eq. 6.3, which for H_2^+ becomes

$$\mathbf{H}\psi = \left[\frac{\mathbf{p}^2}{2m} + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{R} - \frac{1}{r_A} - \frac{1}{r_B} \right) \right] \psi = E(R)\psi. \quad (6.17)$$

(From here on, \mathbf{H} and ψ will stand for \mathbf{H}_{elec} and ψ_{elec} , unless we indicate otherwise.) The potential energy goes to $-\infty$ at two points, the two nuclei. Near each nucleus it diverges in exactly the same way as does $V(r)$ in the hydrogen atom. We can thus carry over the reasoning of Section 4.3 to find the behavior of ψ in the vicinity of the nuclei. In particular, the ground-state wave function at each nucleus must decay exponentially from a cusp, like the corresponding hydrogen $1s$ function. The ground state $|\psi|^2$ thus has two equal peaks, one centered on each nucleus, as shown in Fig. 6.4*b*. However, since $\int |\psi|^2 d\tau$ over the molecule must equal unity, each of these peaks must be only about half the size of the peak in a hydrogen atom. Note that most of the electron density in Fig. 6.4*b* appears to lie in the bonding region between the nuclei. We shall see that this is indeed the case, and that the net bonding force is sufficient for H_2^+ to be a stable molecule in its ground state.

Now let us look again at the long-range case. Since the arguments of the previous paragraph still apply, should we not expect to find two equal peaks even at large R ? The answer is yes, as long as the two nuclei are still indistinguishable. If all we know about the system is that an electron is somewhere in the field of two protons, the probability density $|\psi|^2$ must be symmetric. But ordinarily we do know more than this. In Fig. 6.4*a* the presumption is that we have prepared the system in such a way that the electron is known to be around nucleus A —so that the system is $\text{H}(A) + \text{H}^+(B)$, rather than just H_2^+ . This amounts to our imposing an additional condition that $r_A \ll r_B$. One can obtain an approximate solution of Eq. 6.17 with such a condition, giving a wave function ψ' like that in Fig. 6.4*a*. This solution is only as good as the approximation on which it is based, and obviously cannot be valid over the whole of space. Still, for large R it is at least as good as many of our other assumptions. One cannot expect the approximate ψ' to be valid at small R , however; it becomes a poor description when the potential barrier is so low that the electron is not likely to stay around one nucleus for the duration of a measurement.

Another way to look at the problem, then, is in time-dependent terms. Suppose that we have the Hamiltonian of Eq. 6.17, with fixed nuclei, but that we no longer try to assume a stationary state. We must solve the time-dependent Schrödinger equation, $\mathbf{H}\psi = -i\hbar(\partial\psi/\partial t)$. One possible solution is a wave function $\psi(r, t)$ that at $t = 0$ is almost entirely located around nucleus A . The function ψ' of the previous paragraph will be a good approximation to $\psi(r, t)$ in the region where its magnitude is significant. Both functions must have cusps at nucleus B , but the amplitudes of these cusps at B are far too small to be observed. Now suppose that we leave the system alone for a long time. Since tun-

neling from A to B has a nonzero (if very low) probability, the likelihood of the electron's being found at B will steadily increase. Eventually the system will approach a stationary state in which the electron is equally likely to be found on A or B , and the wave function will have two equal peaks. For large R , however, “eventually” may easily mean many times the age of the universe. On the other hand, when R is a few angstroms, it may take only 10^{-16} s (about a Bohr period) for the wave function to equalize itself, and the time-dependent process can be ignored. The distinction between our two cases is thus simply one of time scale: A stationary state is one that does not change measurably over the time in which we are interested.

All this raises another interesting question. Our three particles continue to interact, even if they are a meter or a mile apart. But what about *other* particles? Must the wave function of each electron somehow contain information on the positions of all the other particles in the universe? Stated in these grandiose terms, the question may be considered a philosophical one, but it symbolizes a real problem. As far as we know, all particles do interact with one another, no matter how far apart they are. If the principles of quantum mechanics are universally valid—and there is no reason to think otherwise—then strictly speaking the wave function of the universe (or as much of it as we care to consider) is not separable. It is only an approximation to speak of a wave function for any particular piece of matter; how good an approximation this is depends on how weak the interactions are. For a molecule in a gas the approximation is excellent; for an atom in a molecule it is rather poor, unless the atoms are very far apart; for an individual electron in an atom it is moderately good (the orbital approach, which we shall see is also useful in molecules). In general, one makes successive approximations of this sort until the interactions left out are too small to worry about.

6.3 H_2^+ : Molecular Orbitals and the LCAO Approximation

We can now proceed to find the electronic wave function of the H_2^+ molecule. This wave function is what we call a *molecular orbital* (abbreviated MO): Just as an atomic orbital describes a single electron in an atom, a molecular orbital describes a single electron in a molecule. In H_2^+ the molecular orbital is identical with the true molecular wave function, but in many-electron molecules the orbital approach is again only an approximation.

As we have already seen, in describing molecules we have an important added complication that we did not face in atoms, the dependence of the wave function on the inter-nuclear distance. We again start with the long-range case, where the problem is relatively simple; however, we wish to obtain a wave function that will join smoothly with the short-range solution. This means that we want the stationary-state solution to the time-independent Eq. 6.17 with indistinguishable nuclei. Even our long-range solution, then, must

satisfy Eq. 6.16 and have equal amplitudes around the two nuclei: It must describe a stationary state of H₂⁺, not of H + H⁺. This is not a state that one would ordinarily observe, but its properties can be easily described.

Suppose, then, that we look at the system in the limit of infinitely large R . In the vicinity of nucleus A , the Schrödinger equation 6.17 then reduces to

$$H\psi = H_A\psi = \left(\frac{\mathbf{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r_A} \right) \psi = E(\infty)\psi. \quad (6.18)$$

Since this is of the same form as the hydrogen atom wave equation, it will be satisfied by any function of the form $c_A\phi_A$, where c_A is a constant and ϕ_A is a normalized hydrogen wave function centered at A . In other words, as $R \rightarrow \infty$, the wave function near A becomes identical to that in a hydrogen atom, except for a constant multiplier. By the same reasoning, the wave function near nucleus B must have the form $c_B\phi_B$, with ϕ_B a normalized hydrogen wave function centered at B . If A and B are infinitely far apart, the regions "near A " and "near B " are the only places where ψ will differ significantly from zero; anywhere that ϕ_A has a reasonable amplitude, ϕ_B will be negligibly small, and vice versa, since each decreases exponentially with distance from its nucleus. We can thus describe the wave function everywhere in space by the equation

$$\psi = c_A\phi_A + c_B\phi_B. \quad (6.19)$$

What this says is that the matter wave described by ψ is constructed by superposition (adding together the amplitudes) of two waves corresponding to states of atomic hydrogen. We say that the molecular orbital ψ is formed by *linear combination of atomic orbitals*, abbreviated LCAO. The atomic orbitals are what are called *basis functions*.

What can we say about the constants c_A and c_B ? In accordance with Eq. 6.16, $|\psi|^2$ must be unaffected by interchange of the nuclei. This means that ϕ_A and ϕ_B must be the same function (e.g., both $1s$ functions), and that we must have $|c_A|^2 = |c_B|^2 \equiv |c|^2$. If we restrict the constants to real values, there are only two possible combinations, $c_A = c_B$ and $c_A = -c_B$, and ψ must have the form $c(\phi_A \pm \phi_B)$. The constant c is readily evaluated by normalizing the wave function, that is, setting the integral of $|\psi|^2$ over all space equal to unity:

$$\begin{aligned} \int |\psi|^2 d\tau &= 1 = c^2 \int |\phi_A \pm \phi_B|^2 d\tau \\ &= c^2 \left(\int |\phi_A|^2 d\tau \pm \int \phi_A^* \phi_B d\tau \right. \\ &\quad \left. \pm \int \phi_A \phi_B^* d\tau + \int |\phi_B|^2 d\tau \right). \end{aligned} \quad (6.20)$$

In the limit $R \rightarrow \infty$, either ϕ_A or ϕ_B is negligibly small at every point in space; we can thus write

$$\int \phi_A^* \phi_B d\tau = \int \phi_A \phi_B^* d\tau = 0, \quad (6.21)$$

since the integrands are everywhere effectively zero. We defined ϕ_A and ϕ_B as normalized wave functions, so we have

$$\int |\phi_A|^2 d\tau = \int |\phi_B|^2 d\tau = 1. \quad (6.22)$$

Substituting these results into Eq. 6.20, we find that

$$1 = c^2 (1 + 0 + 0 + 1) = 2c^2 \quad \text{or} \quad |c| = \frac{1}{\sqrt{2}}. \quad (6.23)$$

Thus $|\psi|^2$ around each nucleus is half as much as in a lone hydrogen atom, in agreement with our premise that the electron is equally likely to be around either nucleus.

What we have said thus far applies to any state of the H₂⁺ molecule. The only restriction we have placed on ϕ_A and ϕ_B is that they must describe the same state of the hydrogen atom. The ground state of the molecule will of course be one in which ϕ_A and ϕ_B are $1s$ functions. The ground-state wave function at $R = \infty$ must thus be either

$$\begin{aligned} \psi_0(R = \infty) &= \frac{\phi_A(1s) + \phi_B(1s)}{\sqrt{2}} \quad \text{or} \\ \psi_1(R = \infty) &= \frac{\phi_A(1s) - \phi_B(1s)}{\sqrt{2}}. \end{aligned} \quad (6.24)$$

These two functions are in fact degenerate, with the energy

$$\begin{aligned} E_0(\infty) &= \int_{\text{all space}} \psi^* H \psi d\tau \\ &= \int_{\text{near } A} \frac{\phi_A^*(1s)}{\sqrt{2}} H_A \frac{\phi_A(1s)}{\sqrt{2}} d\tau \\ &\quad + \int_{\text{near } B} \frac{\phi_B^*(1s)}{\sqrt{2}} H_B \frac{\phi_B(1s)}{\sqrt{2}} d\tau \\ &= \frac{1}{2} E_H(1s) + \frac{1}{2} E_H(1s) = E_H(1s), \end{aligned} \quad (6.25)$$

where H_A , H_B are defined as in Eq. 6.18 and $E_H(1s)$ is the energy of a $1s$ hydrogen atom; just as in Eq. 6.20, the cross terms vanish. The ground-state energy of H₂⁺ at $R = \infty$ is thus the same as that of H(1s) + H⁺ in the same limit, the energy we defined to be zero for the molecule. Similarly, each higher-energy atomic wave function $\phi(nl)$ gives rise to a degenerate pair of molecular wave functions with the energy $E_H(nl)$.

Thus, we have a complete solution—both wave functions and energies—for the H₂⁺ molecule at infinite R . This is all very well, but what does it tell us about the real molecule at finite R ? The answer is that it gives us a starting point for an approximate solution. For large but finite R , the wave function near each atom is very much like a hydrogen orbital, so we write the molecular wave function in the form of Eq. 6.19, which is exactly correct only in the limit $R \rightarrow \infty$. At finite R , however, it seems plausible that the wave function is still *something* like a sum of atomic orbitals. Suppose, then, that we retain the LCAO approach and assume

the molecular wave function to be still given by Eq. 6.19, but with constants that vary with R . Since $|\psi|^2$ must be symmetric, we continue to have $|c_A|^2 = |c_B|^2$. The two functions formed from $1s$ orbitals are thus

$$\psi_0 = c_0 [\varphi_A(1s) + \varphi_B(1s)] \quad (6.26)$$

and

$$\psi_1 = c_1 [\varphi_A(1s) - \varphi_B(1s)], \quad (6.27)$$

corresponding to Eqs. 6.24. Unlike Eqs. 6.24, however, these are only *approximate* wave functions; later we shall see how good the approximation is.

The LCAO approximation is by far the most widely used method of constructing molecular orbitals. It has the advantage of combining maximum simplicity with reasonable accuracy. The use of atomic orbitals as a basis not only has a natural and intuitive appeal, but also greatly simplifies the calculations that must be made. This is because the atomic orbitals have already been computed with considerable accuracy, even for quite complex atoms; they merely have to be looked up and substituted into the appropriate equations. More fundamental is the fact that the formation of chemical bonds between atoms constitutes only a small perturbation of the electronic structures of those atoms, so the wave functions around atoms in molecules are very much like those around free atoms. After all, atoms generally retain their individual identities when they are constituents of molecules. The obvious exceptions are the atoms that become ions when they go into molecules, atoms such as Na and Cl when they make rocksalt, NaCl. We shall see that the LCAO method also yields an important insight into how chemical bonds are (or are not) formed, emphasizing the way in which constructive or destructive interference develops between the atomic wave functions. But remember that it is only an approximation. If one calculates molecular orbitals as accurately as possible, one finds that, even near nuclei, the functions are not really quite like atomic orbitals. In complex molecules, particularly in regions midway between nuclei, the molecular orbitals responsible for chemical bonds simply do not look like superpositions such as Eq. 6.19. Nevertheless, the LCAO method is nearly always adequate for an approximate understanding of chemical bonding. After all, the origin of the chemical bond lies in the fact that an electron can be in a region where it simultaneously attracts two nuclei closer together. Crudely, it is like an atomic electron held simultaneously in the field of each nucleus, and this is just what the LCAO approximation describes.

Analysis of the LCAO wave functions can give us a simple way of looking at how chemical bonds are formed. Consider the form of Eq. 6.26. Since s functions have no nodes, both $\varphi_A(1s)$ and $\varphi_B(1s)$ are everywhere positive. The sum of two positive numbers is a larger positive number. This means that the function ψ_0 corresponds to *constructive interference* of the two atomic wave functions. In any

molecular orbital of this type the electron density is proportional to

$$\begin{aligned} |\varphi_A + \varphi_B|^2 &= |\varphi_A|^2 + |\varphi_B|^2 + \varphi_A^* \varphi_B + \varphi_B^* \varphi_A \\ &= |\varphi_A|^2 + |\varphi_B|^2 + 2 \operatorname{Re}(\varphi_A^* \varphi_B) \end{aligned} \quad (6.28)$$

("Re" \equiv real part of a complex quantity). For $1s$ functions, $\varphi_A^* \varphi_B$ is a positive real number, and Eq. 6.28 is everywhere greater than $|\varphi_A|^2 + |\varphi_B|^2$ (which would give the electron density if there were no interaction between the atoms). The increase is greatest where φ_A and φ_B both have appreciable magnitude; this occurs mainly in the region between the nuclei. Thus a higher fraction of the total electronic charge is found between the nuclei than would be there if the atoms did not interact. Since the molecular wave function is normalized ($\int |\psi|^2 d\tau = 1$), this effect must be balanced by a relatively lower electron density in the region beyond the nuclei; in that region the increase in $|\varphi_A + \varphi_B|^2$ is outweighed by the decrease in the normalization constant c (which we shall evaluate later).

In contrast, let us now look at Eq. 6.27. Here the wave function ψ_1 is the difference of two positive numbers, and corresponds to *destructive interference* of the atomic orbitals. The electron density is proportional to

$$|\varphi_A - \varphi_B|^2 = |\varphi_A|^2 + |\varphi_B|^2 - 2 \operatorname{Re}(\varphi_A^* \varphi_B), \quad (6.29)$$

which is everywhere less than $|\varphi_A|^2 + |\varphi_B|^2$; again the effect is greatest between the nuclei. Thus the electron density is decreased between the nuclei and increased beyond the nuclei, relative to the density in noninteracting atoms. In fact, since φ_A and φ_B are identical, they exactly cancel each other at all points where $r_A = r_B$; this means that the function ψ_1 has a nodal plane midway between the nuclei, a surface on which the value of ψ_1 is zero.

What is the significance of all this? Recall the bonding and antibonding regions of Fig. 6.3. We have shown that the wave function ψ_0 has a relatively high electron density in the bonding region between the nuclei, whereas ψ_1 has excess electron density in the antibonding region beyond the nuclei. It is thus clear that ψ_0 describes a "more bonding" state than ψ_1 , that on the average the bonding force is greater in the state ψ_0 . The Hellmann-Feynman theorem, Eq. 6.12, thus requires that $dE(R)/dR$ be greater for ψ_0 than for ψ_1 . The two states have the same $E(\infty)$, Eq. 6.25, so ψ_0 must have a lower energy than ψ_1 for all finite values of R : $E_0(R) < E_1(R)$. We can reach the same conclusion by considering the potential energy curve of Fig. 6.4b. Since the electron in state ψ_1 is more likely to be found in the high- V regions beyond the nuclei, its total energy is higher in this state. We said earlier that one of the states ψ_0 and ψ_1 (which were degenerate at $R = \infty$) must be the ground state of the H_2^+ molecule. Now we have established that ψ_0 is the true ground state (or rather an approximation to it), whereas ψ_1 is an excited state of higher energy.

Note that we still have not proved that H₂⁺ is a stable molecule. Although ψ_0 describes the state in which the bonding force is greatest, we do not yet know if that bonding force is sufficient to overcome the internuclear repulsion—if there is *enough* excess charge in the bonding region. To put it another way, we know that ψ_0 corresponds to the lowest $E(R)$ curve; but does that curve have the minimum necessary for a stable molecule (cf. Fig. 6.2)? To answer these questions, one must actually solve the Schrödinger equation for $E(R)$.

6.4 H₂⁺: Obtaining the Energy Curve

First we must evaluate the normalization constants in our wave functions. It is convenient to define the integral

$$S_{AB} \equiv \int \varphi_A^* \varphi_B d\tau, \quad (6.30)$$

called the *overlap integral* of the orbitals φ_A and φ_B . We pointed out earlier that this integral vanishes when A and B are infinitely far apart. The principal contribution to the integral comes only from the regions where φ_A and φ_B are both appreciable, that is, the regions that dominate the bonding. Note that $S_{AB} = S_{BA}^*$ for any φ_A, φ_B .

We can normalize the ground-state wave function ψ_0 , defined by Eq. 6.26. Integrating over all space, we have

$$\begin{aligned} \int |\psi_0|^2 d\tau &= 1 = c_0^2 \left(\int |\varphi_A|^2 d\tau + \int |\varphi_B|^2 d\tau \right. \\ &\quad \left. + \int \varphi_A^* \varphi_B d\tau + \int \varphi_A \varphi_B^* d\tau \right) \\ &= c_0^2 (1 + 1 + S_{AB} + S_{AB}^*) \\ &= 2c_0^2 (1 + S_{AB}). \end{aligned} \quad (6.31)$$

The first two terms equal unity because we choose φ_A, φ_B to be normalized. We have $S_{AB} = S_{AB}^*$ in this case because $1s$ orbitals are real functions, so that S_{AB} is also real. Solving for the constant c_0 gives

$$c_0 = [2(1 + S_{AB})]^{-1/2}, \quad (6.32)$$

and our ground-state molecular orbital is

$$\psi_0 = \frac{\varphi_A(1s) + \varphi_B(1s)}{[2(1 + S_{AB})]^{1/2}}. \quad (6.33)$$

If we carry out a similar calculation with Eq. 6.27, we obtain

$$\psi_1 = \frac{\varphi_A(1s) - \varphi_B(1s)}{[2(1 - S_{AB})]^{1/2}} \quad (6.34)$$

for the first-excited-state orbital.

Let us compare these results with our earlier discussion of bonding. In a hypothetical “nonbonded” molecule with

no interaction between the atomic orbitals, the electron density would be simply $\frac{1}{2}(|\varphi_A|^2 + |\varphi_B|^2)$, as in the long-range case. By contrast, in the ground state, Eqs. 6.28 and 6.33 give

$$|\psi_0|^2 = \frac{|\varphi_A|^2 + |\varphi_B|^2 + 2\varphi_A\varphi_B}{2(1 + S_{AB})}, \quad (6.35)$$

since $\text{Re}(\varphi_A^* \varphi_B) = \varphi_A \varphi_B$ for $1s$ orbitals. In this case S_{AB} is also necessarily positive, and the effect of division by $1 + S_{AB}$ is to lower the electron density everywhere. Counteracting this, however, is the positive term $2\varphi_A\varphi_B$ in the numerator, which tends to increase the electron density. The latter effect is dominant between the nuclei, where $|\psi_0|^2$ is higher than the nonbonded value. This reinforces our earlier conclusion that ψ_0 corresponds to excess electron density in the bonding region. We need not repeat the argument for ψ_1 . These conclusions are illustrated by Fig. 6.5, which compares the actual electron densities.

Given the normalized LCAO wave functions, one can determine the corresponding energies $E(R)$. If ψ_0 were a true wave function, its energy (for a given R) would be given exactly by $\int \psi_0^* H \psi_0 d\tau$, where H is the electronic Hamiltonian of Eq. 6.17. But in fact our ψ_0 and ψ_1 are only approximations to the true wave functions; we can still carry out the integration, but we must realize that the result will be an approximate energy. The variation principle, Eq. 5.11, tells us that this energy must be higher than the true value; thus if we obtain a minimum in the $E(R)$ curve, we can be sure that there is really an even deeper minimum. Bearing this in mind, let us proceed.

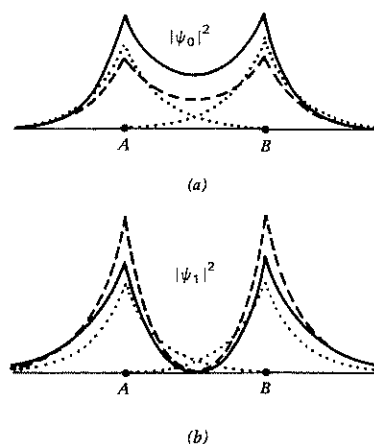


Figure 6.5 Electron density $|\psi|^2$ along the internuclear axis for the two lowest states of H₂⁺. (a) The bonding ground state, ψ_0 . (b) The antibonding excited state, ψ_1 . The wave functions are calculated for the true equilibrium distance, $R_e = 2.00a_0$, noninteracting $1s$ atomic orbitals, $|\psi|^2 = (\frac{1}{2}|\varphi_A|^2 + |\varphi_B|^2)$; ----, LCAO approximation, Eqs. 6.33 and 6.34; —, exact solution.

It is useful to define another kind of integral,

$$H_{ij} \equiv \int \varphi_i^* H \varphi_j d\tau, \quad (6.36)$$

where H is the electronic Hamiltonian and the i, j stand for nuclei; when H is real, we have $H_{ji} = H_{ij}^*$. For a given internuclear distance, the energy corresponding to ψ_0 is

$$\begin{aligned} E_0(R) &= \int \psi_0^* H \psi_0 d\tau \\ &= \frac{\int \varphi_A^* H \varphi_A d\tau + \int \varphi_A^* H \varphi_B d\tau + \int \varphi_B^* H \varphi_A d\tau + \int \varphi_B^* H \varphi_B d\tau}{2(1 + S_{AB})} \\ &= \frac{H_{AA} + H_{AB} + H_{BA} + H_{BB}}{2(1 + S_{AB})} \\ &= \frac{H_{AA} + H_{AB}}{1 + S_{AB}}. \end{aligned} \quad (6.37)$$

Since H is symmetric in A and B , we must have $H_{AA} = H_{BB}$ and $H_{AB} = H_{BA}$. Evaluating the H_{ij} with H from Eq. 6.17, we have⁷

$$\begin{aligned} H_{AA} &= \int \varphi_A^* \left(\frac{\mathbf{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r_A} \right) \varphi_A d\tau + \frac{e^2}{4\pi\epsilon_0 R} \int \varphi_A^* \varphi_A d\tau \\ &\quad - \int \frac{e^2}{4\pi\epsilon_0 r_B} \varphi_A^* \varphi_A d\tau \\ &= E_H(1s) + \frac{e^2}{4\pi\epsilon_0 R} + J \end{aligned} \quad (6.38)$$

and

$$\begin{aligned} H_{AB} &= \int \varphi_A^* \left(\frac{\mathbf{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r_B} \right) \varphi_B d\tau + \frac{e^2}{4\pi\epsilon_0 R} \int \varphi_A^* \varphi_B d\tau \\ &\quad - \int \frac{e^2}{4\pi\epsilon_0 r_A} \varphi_A^* \varphi_B d\tau \\ &= \int \varphi_A^* E_H(1s) \varphi_B d\tau + \frac{e^2}{4\pi\epsilon_0 R} S_{AB} + K \\ &= S_{AB} \left[E_H(1s) + \frac{e^2}{4\pi\epsilon_0 R} \right] + K, \end{aligned} \quad (6.39)$$

where we define the two integrals

$$\begin{aligned} J &\equiv - \int \frac{e^2}{4\pi\epsilon_0 r_B} \varphi_A^* \varphi_A d\tau \quad \text{and} \\ K &\equiv - \int \frac{e^2}{4\pi\epsilon_0 r_A} \varphi_A^* \varphi_B d\tau; \end{aligned} \quad (6.40)$$

⁷ The first terms in Eqs. 6.38 and 6.39 are, respectively, $\int \varphi_A^* H_A \varphi_A d\tau$ and $\int \varphi_A^* H_B \varphi_B d\tau$, where H_A and H_B are hydrogen-atom Hamiltonians. We can thus substitute $H_A \varphi_A = E_H \varphi_A$ and $H_B \varphi_B = E_H \varphi_B$ and take the constant E_H outside the integrals.

J is called the *Coulomb integral* (it gives the Coulomb interaction between the orbital around one atom and the nucleus of the other atom) and K the *exchange integral*. Substituting in Eq. 6.37, we obtain

$$\begin{aligned} E_0(R) &= \frac{E_H(1s) + e^2/4\pi\epsilon_0 R + J + S_{AB}[E_H(1s) + e^2/4\pi\epsilon_0 R] + K}{1 + S_{AB}} \\ &= E_H(1s) + \frac{e^2}{4\pi\epsilon_0 R} + \frac{J + K}{1 + S_{AB}}. \end{aligned} \quad (6.41)$$

The first term is the ground-state energy of a hydrogen atom, which we have taken as the energy zero for the H_2^+ molecule, the second term is simply the internuclear repulsion at distance R , and the third term gives the electronic bonding energy. A similar calculation for the first excited state gives

$$\begin{aligned} E_1(R) &= \frac{H_{AA} - H_{AB}}{1 - S_{AB}} \\ &= E_H(1s) + \frac{e^2}{4\pi\epsilon_0 R} + \frac{J - K}{1 - S_{AB}}. \end{aligned} \quad (6.42)$$

To obtain the $E(R)$ curves, one must evaluate the integrals S_{AB} , J , K for each value of R and substitute the results in the above equations. This is a straightforward calculation, and we shall not bother with the details.⁸ The results for $E_0(R)$ and $E_1(R)$ are plotted in Fig. 6.6, with the terms in Eqs. 6.41 and 6.42 shown separately. In the ground state the electron has a net bonding effect at all values of R , and at moderate distances this is enough to overcome the nuclear repulsion. Thus there is a shallow potential well, and H_2^+ can indeed exist as a stable molecule.⁹ As R grows smaller, the electronic bonding energy increases, but only to a finite value; at the same time the nuclear repulsion increases without limit, so that the total energy curve must become repulsive. As for the excited state ψ_1 , it is interesting that the electron still has a net bonding effect over most of the range, even though there is less charge in the bonding region. Here, however, the nuclear repulsion is greater for all values of R ; thus the $E_1(R)$ curve is everywhere repulsive, and the excited state cannot be stable.

⁸ If $\rho \equiv R/a_0$, one obtains

$$\begin{aligned} S_{AB} &= e^{-\rho} \left(1 + \rho - \frac{\rho^2}{3} \right), \\ J &= -\frac{e^2}{4\pi a_0} \left[\frac{1}{\rho} - e^{-2\rho} \left(1 + \frac{1}{\rho} \right) \right], \\ K &= -\frac{e^2}{4\pi a_0} e^{-\rho} (1 + \rho). \end{aligned}$$

⁹ Stability is relative, of course. The reason one cannot keep H_2^+ around is that it reacts very readily to form some more stable species. For example, if one brings H_2^+ into collision with H_2 , the system immediately yields $\text{H}_3^+ + \text{H}$.

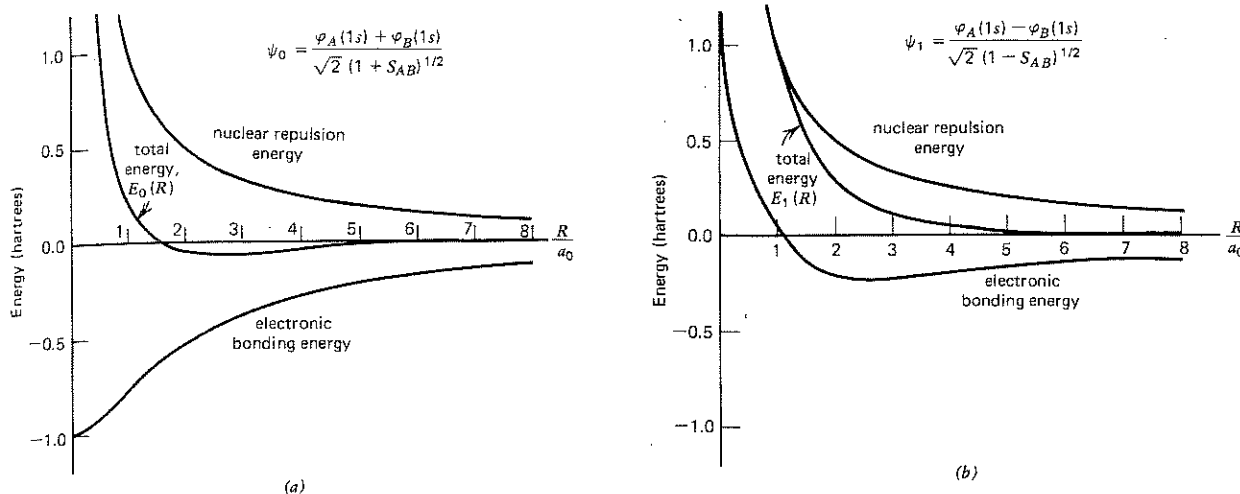


Figure 6.6 Energy of H₂⁺ in the LCAO approximation. (a) The ground state. (b) The first excited state. In each graph we show the nuclear repulsion energy, $e^2/4\pi\epsilon_0 R$; the electronic bonding energy, the last term in Eqs. 6.41 and 6.42; and the total energy $E(R)$, the sum of the previous two. The energy zero is the energy of H(1s) + H⁺ at infinite separation.

The eigenfunctions ψ_0 and ψ_1 are orthogonal, the functional equivalent to being “at right angles” or, more precisely, mutually exclusive. The mathematical condition for this is $\int \psi_1^* \psi_0 dV = 0$ analogous to the scalar product of vectors **a** and **b** to vanish; i.e., that **a** · **b** = 0. This property of orthogonality is general; any two solutions of the Schrödinger equation (or, for that matter, of many differential equations) with different eigenvalues are orthogonal. Physically, this means that the states corresponding to those wave functions, which are necessarily states with different constants of motion and different quantum numbers, are mutually exclusive. If a system is in state 0, then it is certainly not in state 1. Appendix 6A discusses this property in more detail. Some methods of describing electronic states of molecules, and we shall discuss one of these, the Valence Bond method, use sets of wave functions that are not orthogonal and hence work conceptually to describe the physical system in terms of states that are not mutually exclusive. Such methods are sometimes computationally useful but at the expense of some loss of clarity of physical interpretation.

How good is the LCAO approximation? It can be improved by variational methods; for example, one can vary *Z* in the atomic orbitals, as in Eq. 5.13 for the helium atom. However, since there is only one electron to worry about, the H₂⁺ molecule is one of the few quantum mechanical systems for which the Schrödinger equation can be solved exactly (in the Born–Oppenheimer approximation). In Fig. 6.7 we compare the LCAO and exact energies for the first two states; Fig. 6.5 gives the corresponding electron densities along the internuclear axis. In accordance with the variation principle, the exact energy is everywhere lower. The exact solution gives an equilibrium distance $R_e = 2.00a_0$ (1.06 Å) and a dissociation energy $D_e = -0.103$ hartree (−2.79 eV), compared

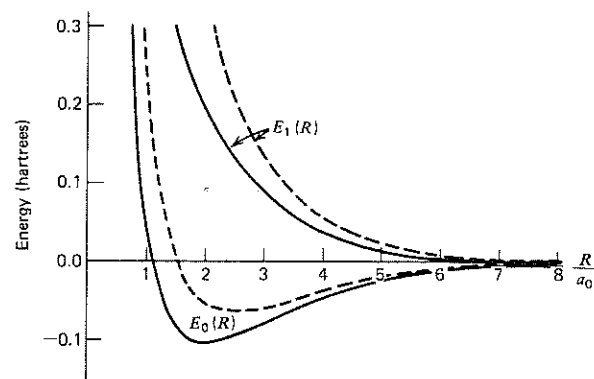


Figure 6.7 Energy curves for the two lowest states of H₂⁺: —, exact solution; ---, LCAO approximation.

to the LCAO values of $2.50a_0$ (1.32 Å) and −0.065 hartree (−1.78 eV). Since the nuclear repulsion is known exactly, the error of the LCAO method is entirely in the electronic binding energy (cf. Fig. 6.5): At $R = 2a_0$, the latter is off by only 8%, but the dissociation energy by 48%. This illustrates the basic problem in calculating dissociation energies, that they are small differences of large quantities. For other molecules the problem is even more difficult, because interactions between the electrons also come into play.

6.5 H₂⁺: Correlation of Orbitals; Excited States

Thus far we have discussed only the lowest two energy levels of the H₂⁺ molecule, but there are many higher levels. Our interest is mainly in how these states, and indeed those of

any diatomic molecule, can be classified. We can best approach this problem by looking at what happens in the long-range and short-range limits.

We have already discussed the long-range or separated-atom limit. As $R \rightarrow \infty$ the molecular wave function goes smoothly into a sum or difference of atomic orbitals; for the two H_2^+ states we have studied, these are hydrogen $1s$ orbitals. At the other extreme, as $R \rightarrow 0$, the two nuclei must eventually collapse into one; this we call the *united-atom limit*. The united atom obtained from the H_2^+ molecule would have a nucleus with charge $+2e$ and a single electron, and would thus be a He^+ ion. (We overlook the fact that there is no bound nucleus composed of two protons; to make the picture truly realistic, we would have to use D_2^+ as our example.) What happens to the wave function in the united-atom limit? In the ground state, the two peaks in the function ψ_0 must coalesce as $R \rightarrow 0$. In the limit we have a nodeless wave function with a single cusp at the united nucleus; this clearly describes the $1s$ state of the hydrogenlike He^+ ion. Since there is a continuous transition of the molecular state from one limit to the other, we say that the ground state *correlates* smoothly with $\text{H}(1s)$ in the separated-atom limit and $\text{He}^+(1s)$ in the united-atom limit.

What about ψ_1 , the first excited state? This also goes into the $\text{H}(1s)$ separated-atom limit, but to what state of He^+ does its united-atom limit correspond? The key is the fact that for all values of R the function ψ_1 has a nodal plane midway between the nuclei, perpendicular to the internuclear axis. This results from the symmetry condition (Eq. 6.16), which for ψ_1 , becomes $\psi_1(A, B) = -\psi_1(B, A)$. The united-atom wave function must thus have a nodal plane through the nucleus, but no other nodes. It is clear from Fig. 4.8 that this must be a $2p$ orbital—more specifically, that $2p$ orbital whose long axis corresponds to the original $A - B$ axis. There is something puzzling here: A p orbital has $l = 1$ and angular momentum $\sqrt{2}\hbar$, yet this orbital was constructed from $1s$ orbitals with zero angular momentum. Since we have only pushed the nuclei together along a straight line, where did the angular momentum come from?

The answer to this question can give us a good deal of insight into the symmetry properties of a diatomic molecule. Recall the principle we stated in Section 3.10: If the energy is independent of some coordinate q_i , the conjugate momentum p_i is a constant of the motion. In an isolated atom the potential energy is spherically symmetric, and thus independent of all the angular coordinates, whose conjugate momenta are components of the angular momentum. In a classical atom, then, the angular momentum and all its components would be constants of the motion. As we showed in Section 3.11, the uncertainty principle makes it impossible for all these components to be known simultaneously, so they cannot all be constants of the motion in a real quantum mechanical system. However, the magnitude of the total angular momentum and any one of its components do remain constants of the motion in a system with spherical symmetry. Corresponding to these we have the two good

quantum numbers l, m_l (for an electron) or L, M_L (for an atom).

In a diatomic system, which has cylindrical rather than spherical symmetry, the above argument no longer applies precisely. The energy of an electron depends very much on angular coordinates like θ_A and θ_B (Fig. 6.1). Thus the components of angular momentum corresponding to these angles cannot be constants of the motion, and neither can the magnitude of the orbital angular momentum: l (or L) is no longer a good quantum number. There is one exception to this breakdown. Since the AB or z axis is an axis of cylindrical symmetry, the energy is independent of the angle ϕ that describes rotation about this axis, and the component of angular momentum along this axis (p_ϕ or L_z) is thus a constant of the motion. The operator corresponding to L_z has the same form as for one component of angular momentum in an atom, $-i\hbar(\partial/\partial\phi)$, and the eigenvalues of L_z are given by

$$L_z = \pm \lambda \hbar \quad (\lambda = 0, 1, 2, \dots), \quad (6.43)$$

where λ is a quantum number corresponding to the absolute value of our earlier m_l . As in the atom, we use lowercase letters for a single electron and capital letters for a many-electron system. The axial angular momentum quantum number is designated by λ for an electron, Λ for a molecule, for which $L_z = \pm \Lambda \hbar$.

In spite of this formal similarity, there is a fundamental difference between L_z in an atom and L_z in a diatomic system. In an atom our choice of a z axis is entirely arbitrary, and L_z is quantized along whatever axis we choose. In the diatomic system this freedom of choice is gone. The z axis must be the system's unique symmetry axis, the axis joining the nuclei. Another difference involves the degeneracy of states. In a spherically symmetric potential the energy depends only on the quantum number l (or L), with $2l + 1$ degenerate states for each value of l . In the cylindrically symmetric potential we no longer have a quantum number l , and only λ (or Λ) is available to classify the energy levels. These levels are either nondegenerate, for $\lambda = 0$ ($\Lambda = 0$), or doubly degenerate, for any other value of λ (or Λ).

Now we can answer our original question, "Where did the angular momentum come from?" In the separated-atom $\text{H}(1s)$ orbitals the angular momentum component is zero along any one axis, including the one that becomes the molecular z axis. Thus the ψ_1 state of H_2^+ has $L_z = 0$ in the separated-atom limit. Since L_z is a constant of the motion, it must also be zero for finite R , and even in the united-atom limit $\text{He}^+(2p)$. This is the case because a $2p$ orbital has zero angular momentum along its long axis, here taken as the z axis; that is, the orbital is $2p_z$, with $m_l = 0$, $L_z = 0$ (cf. Fig. 4.6). The $\sqrt{2}\hbar$ we mentioned above is the total angular momentum of the electron of $\text{He}^+(2p_z)$, which is no longer a constant when the spherical symmetry is removed.

It is customary to use the value of the axial angular momentum quantum number to classify the states of diatomic molecules. Just as atomic orbitals with $l = 0, 1, 2$,

3, . . . are respectively called *s*, *p*, *d*, *f*, . . . , so in diatomic molecules orbitals with $\lambda = 0, 1, 2, 3, \dots$ are designated by analogy, with the corresponding Greek letters $\sigma, \pi, \delta, \phi, \dots$. Capital letters are again used for the molecule as a whole: Molecular states with $\Lambda = 0, 1, 2, 3, \dots$ are called $\Sigma, \Pi, \Delta, \Phi, \dots$ states. The spin multiplicity $(2S + 1)$ of these states is indicated by a left superscript as in atoms. The two states of H₂⁺ we have described both have a single electron in an orbital with $\lambda = 0$, a σ orbital; thus each of these states has $\Lambda = 0, S = \frac{1}{2}$, and can be called a $^2\Sigma$ state. When, as here, the molecule has a center of symmetry, a further distinction must be made. If the wave function is unchanged by inversion through the center of symmetry, that is, if $\psi(x, y, z) = \psi(-x, -y, -z)$, it is said to have *even parity*; if the reflection changes only the sign, $\psi(x, y, z) = -\psi(-x, -y, -z)$, the wave function has *odd parity*. States with even and odd parity are designated by the subscripts *g* and *u* (German *gerade* and *ungerade*), respectively. It is clear from Eqs. 6.26 and 6.27 that ψ_0 is even and describes a σ_g orbital, whereas ψ_1 is odd and describes a σ_u orbital; the corresponding molecular states are $^2\Sigma_g$ and $^2\Sigma_u$, respectively.

A molecular orbital may be labeled by either the united-atom orbital or the separated-atom orbital with which it correlates. The united-atom label precedes the species designation ($\psi_0 \rightarrow 1s\sigma_g$, $\psi_1 \rightarrow 2p\sigma_u$, etc.), whereas the separated-atom label follows it ($\psi_0 \rightarrow \sigma_g 1s$, $\psi_1 \rightarrow \sigma_u 1s$, etc.). This nomenclature is used mainly when one is emphasizing the two limits. For example, the " $\sigma_g 1s$ " notation is appropriate for an LCAO wave function. When discussing the molecule itself, however, one can simply number the orbitals of each species ($\sigma_g, \sigma_u, \pi_g, \dots$) in order of increasing energy. Thus ψ_0 and ψ_1 correspond to the $1\sigma_g$ and $1\sigma_u$ orbitals, respectively. Figure 6.8 gives further examples of all these notations.

Now we are ready to examine the higher-energy orbitals of H₂⁺. For variety, we shall start with the united-atom limit instead of the separated-atom limit. This makes good physical sense since the orbitals in question are very large. They have appreciable magnitudes in regions far beyond the two nuclei, regions in which the electron density must be quite similar to that in a He⁺ ion. For this reason the LCAO approximation, based on the separated atoms, does not give an accurate representation of the excited states.¹⁰ We start with He⁺ in a given state, pull the nucleus apart into two singly charged nuclei, and see what kind of wave function we should obtain. We expect the higher states to be unstable,

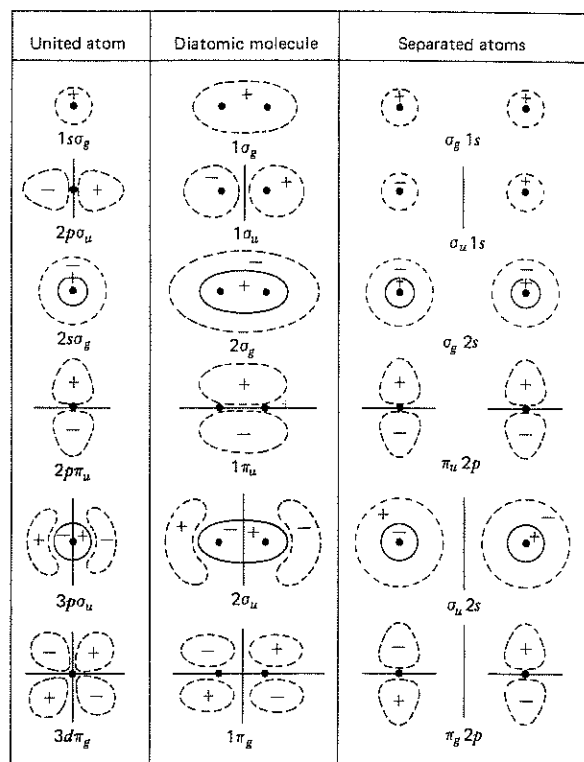


Figure 6.8 Correlation and shapes of orbitals in homonuclear diatomic molecules (for orbitals whose ϕ -dependent factors are real). The diagrams are purely schematic, with dashed lines bounding roughly the regions where the electron density is significant. The solid curves and lines are nodal surfaces; the sign of the wave function is given in each of the regions they separate. Each orbital is labeled by the three systems described in the text. Note that for H₂⁺ the separated-atom limit of $2\sigma_g$ could be either $\sigma_g 2s$ or $\sigma_g 2p$, and that of $2\sigma_u$ either $\sigma_u 2s$ or $\sigma_u 2p$.

that is, to have repulsive $E(R)$ curves (curves with no minima), since they have even less electron density in the binding region of space than the state ψ_1 . (Some states in fact have shallow $E(R)$ minima at large R , but for most practical purposes these are also unstable.)

We know that the $1s$ orbital of He⁺ transforms into the $1\sigma_g$ molecular orbital (ψ_0), which at long range transforms into the sum of two $1s$ orbitals of atomic hydrogen. Into what states do the other united-atom orbitals transform? In speaking of such a "transformation" at all, we are invoking a very general principle of quantum mechanics, the *adiabatic principle*. Let us assume that the energy levels of a system vary smoothly with some parameter R , which, up to this point, we have taken to be the internuclear distance we treated as a parameter for the Born-Oppenheimer method. This gives us a series of $E(R)$ curves, each of which we can label as a particular state of the system. The adiabatic principle states that, if a system is initially in the i th energy level at a particular value of R , then for sufficiently slow changes

¹⁰ For an illustration of how the LCAO approximation breaks down in the united-atom limit, consider the ground state. Since $\phi(\text{H}, 1s)$ varies as e^{-r/a_0} , the LCAO wave function (Eq. 6.33) also approaches e^{-r/a_0} when $R \rightarrow 0$ (and $r_1, r_2 \rightarrow r$). But in this limit the true wave function must approach that of He⁺, which varies as e^{-2r/a_0} (since $Z = 2$). Similarly, at $R = 0$ the LCAO electronic bonding energy is 1.0 hartree (Fig. 6.5), whereas the true value must be

$$E_1(\text{H}) - E_1(\text{He}^+) = -0.5 \text{ hartree} - (-2.0 \text{ hartrees}) = 1.5 \text{ hartrees.}$$

in R it will remain in the same i th level (but as transformed by the change in value of R) unless otherwise disturbed.¹¹ For the particular case of the internuclear distance, this reduces to the Born–Oppenheimer approximation: The $E(R)$ curves calculated for fixed nuclei give the energy of the actual molecule in the limit of sufficiently slow nuclear motion. For rapid nuclear motion, as in a high-speed collision, both the adiabatic approximation and the very concept of an energy curve cease to apply, and transitions between electronic states become likely.

What we wish to know, then, is the behavior of the orbitals when the nuclei are pulled apart very slowly (adiabatically). There should be an $E(R)$ curve connecting each united-atom state with a corresponding separated-atom state; the two limiting states are said to *correlate* with each other. Correlated states, as well as the sequence of molecular states joining them, must be identical in those properties that are constants of the motion; these include the value of λ (or Λ) and the parity of the wave function. Thus σ_g state correlates only with a σ_g state, π_u only with π_u , and so for each class of states. But each limit has many states of each symmetry class; how do we know which ones correlate with each other? The best answer is given by the *noncrossing rule*: Two $E(R)$ curves with the same invariant properties (λ , parity, spin, etc.) never cross each other. This is only another approximation, valid to the same extent as the Born–Oppenheimer approximation (from which it can be derived), but it is sufficiently accurate to be our main tool for analyzing the correlation of states.

Given these assumptions, the analysis of H_2^+ is easy. The lowest σ_g orbital derived from the united atom must correlate with the lowest σ_g orbital formed from the separated atoms, since it can cross no other σ_g curve; this is the ground state, for which we had already tacitly assumed the noncrossing rule. Similarly, the second lowest united-atom σ_g orbital correlates with the second lowest separated-atom σ_g orbital, the third lowest with the third lowest, and so forth. The same applies to each of the other symmetry classes (but note that there is nothing to prevent $E(R)$ curves of *different* symmetry classes— σ_g and π_g , say—from crossing each other).

But now we immediately have a problem: What classes of molecular states do we obtain from each united-atom or separated-atom state? Remember that the quantum number λ corresponds to $|m_l|$ in either limit. For an atomic state with a given value of l , the possible values of $|m_l|$ are 0, 1, . . . , l . Thus a united-atom s orbital ($l = 0$) can only transform into a σ orbital ($\lambda = 0$), a p orbital ($l = 1$) into either a σ or a π orbital ($\lambda = 0, 1$), and so forth; in general the united-atom nl level gives rise to l distinct molecular states. The parity is easily assigned in the united-atom limit: All s

orbitals are even (g), all p orbitals odd (u), all d orbitals even, and so on, as can easily be seen from Fig. 4.6. Combining these rules, we have the following correlations:

$$\begin{array}{lcl} \text{United-atom level:} & s & p & d \\ \text{Molecular orbitals:} & \sigma_g, \sigma_u, \pi_u, \sigma_g, \pi_g, \delta_g, & & \\ & f & & \\ & \sigma_u, \pi_u, \delta_u, \phi_u, \dots & & \end{array}$$

The separated-atom limit is a little more complicated, since we are dealing with *pairs* of atomic orbitals. The relation between λ and $|m_l|$ remains, but now each pair of nl levels combines to form $2(2l + 1)$ molecular orbitals. The molecular orbitals also come in pairs, corresponding in the LCAO approximation to the sum and difference of two identical atomic orbitals. In each such pair of molecular orbitals, one is even (g) and the other odd (u); we have already discussed the example of the $\sigma_g 1s$ and $\sigma_u 1s$ orbitals. We thus have the correlations:

$$\begin{array}{lcl} \text{Separated-atom level:} & s & p & \\ \text{Molecular orbitals:} & \sigma_g, \sigma_u, \sigma_g, \sigma_u, \pi_g, \pi_u, & & \\ & d & & \\ & \sigma_g, \sigma_u, \pi_g, \pi_u, \delta_g, \delta_u, \dots & & \end{array}$$

Later we shall discuss the nature of the molecular orbitals in greater detail, but now we have enough information for a complete description of the orbital correlation.

The simplest way to display such a correlation is with a *correlation diagram*; Fig. 6.9a gives such a diagram for H_2^+ . On the left and right sides of the diagram are the orbitals of the united atom and the separated atoms, respectively, each arranged in order of increasing energy. The energy scale is purely schematic; only the sequence of orbitals is significant. Lines are drawn connecting each united-atom orbital to the separated-atom orbital with which it correlates, following the correlation rules described above. Each of these lines can then be labeled with its appropriate molecular orbital designation; given the noncrossing rule, such designations as $1\sigma_g, 2\sigma_g, \dots$ for the lowest, second lowest, . . . σ_g states can be given unambiguously. Since the two limits correspond to $R = 0$ and $R = \infty$, the vertical sequence of orbitals across the diagram should approximately represent the sequence of orbital energies as a function of R . For H_2^+ it is possible to test this, since the exact $E(R)$ curves have been calculated for many of the molecular states; these are plotted in Fig. 6.9b. The picture is similar to that in the schematic diagram, but there are a number of differences in detail. In particular, the noncrossing rule is apparently violated by a number of the higher energy levels at large R , but this does not affect the correlation, since the states that thus cross are degenerate in one or the other limit.

Degeneracy leads to a special problem in the cases of H_2^+ and H_2 . The $2\sigma_g$ orbital, derived from $\text{He}^+(2s)$, should correlate with the second lowest σ_g orbital of the separated atoms. But σ_g orbitals can be formed from both the $2s$ and

¹¹ "Adiabatic" comes from the Greek word for "uncrossable"; i.e., under adiabatic conditions the system will not "cross" from one $E(R)$ curve to another.

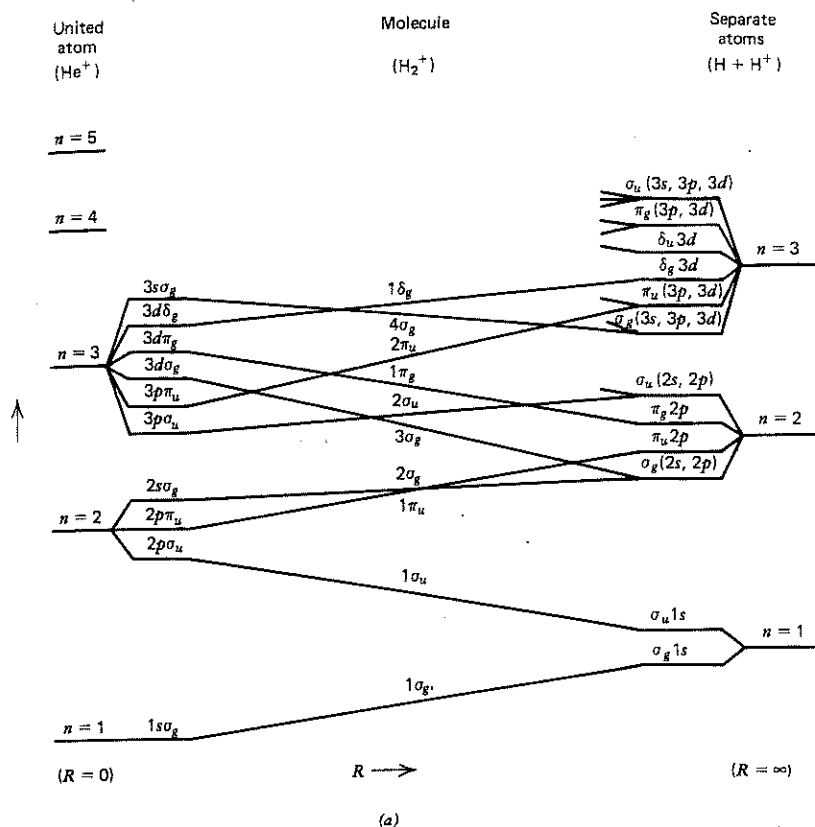
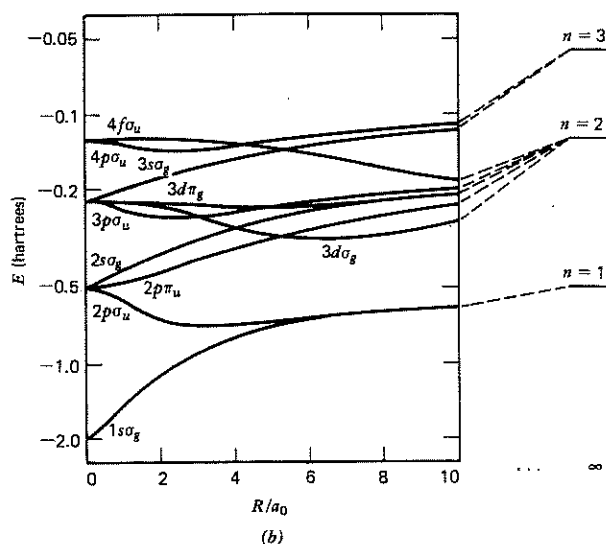


Figure 6.9 Correlation of energy levels for H₂⁺. (a) Schematic correlation diagram, with degenerate energy levels spread apart for clarity. Correlations are shown for all united-atom levels through $n = 3$. See the text for a discussion of separated-atom levels such as " $\sigma_g(2s, 2p)$." (b) Actual $E(R)$ curves for some of the energy levels, as calculated by Bates, Ledsham, and Stewart. The energy is measured relative to the free-electron limit, $H^+ + H^+ + e^-$. Since the calculations have not been carried beyond $R = 10a_0$, the curves are labeled in united-atom notation only.



the $2p$ levels of $H + H^+$, and in the hydrogen atom these levels are degenerate.¹² We have thus used the notation " $\sigma_g(2s, 2p)$ " to label the separated-atom limits of both the $2\sigma_g$ and the $3\sigma_g$ molecular orbitals; similar notation is used

for other such degenerate orbitals of the same species. What this means is that, as far as satisfying the correlation rules goes, the separated-atom limit of the $2\sigma_g$ orbital could be any linear combination of the form $a(\sigma_g 2s) + b(\sigma_g 2p)$. The exact calculations have not been carried far enough to reveal the true nature of this limit. But the simplest approximation

¹² In heavier atoms $2s$ has lower energy than $2p$, so the σ_g orbital correlates with $\sigma_g 2s$; cf. Fig. 7.14.

to the $2\sigma_g$ orbital is an LCAO representation using only the $2s$ atomic orbitals:

$$\psi(\sigma_g 2s) = \frac{\varphi_A(2s) + \varphi_B(2s)}{[2 + 2S_{AB}(2s)]^{1/2}}, \quad (6.44)$$

analogous to Eq. 6.33. This approximation gives a fair description of the actual $2\sigma_g$ orbital at moderate R ; if it is correct, then the $\text{He}^+(2s)$ radial node eventually splits into two $\text{H}(2s)$ radial nodes, but only at very large R (cf. Fig. 6.8).

Let us now look at the nature of some other orbitals. There are two degenerate σ_g orbitals in the $n = 3$ level of He^+ , but here there is no ambiguity. The calculations clearly show that the $3d\sigma_g$ has the lower energy and thus becomes the $3\sigma_g$ molecular orbital. It of course correlates with the other separated-atom orbital formed from the $\sigma_g(2s, 2p)$ degeneracy, which in the simplest LCAO approximation can be represented by $\psi(\sigma_g 2p)$. But the LCAO representations are hardly important for these higher-energy states, which near R_e are better described by the united-atom orbitals. As for the $3s\sigma_g$ level, it becomes the $4\sigma_g$ molecular orbital and correlates with the separated-atom $\sigma_g(3s, 3p, 3d)$ degenerate set of levels.

The first few σ_u orbitals derive from the p orbitals of He^+ —specifically, those p orbitals with $m_l = L_z = 0$ (where the z axis becomes the internuclear axis). We have already described how the $1\sigma_u$ orbital (ψ_1) derives from the $\text{He}^+(2p, m_l = 0)$ orbital and correlates with the difference of two $\text{H}(1s)$ orbitals. The similar $2\sigma_u$ orbital derives from the $\text{He}^+(3p, m_l = 0)$ orbital and correlates with the $\sigma_u(2s, 2p)$ degeneracy. Its simplest LCAO representation is $\sigma_u 2s$, the difference of two $\text{H}(2s)$ orbitals.

Thus far we have described only σ orbitals, with $L_z = 0$. In order to construct H_2^+ orbitals with nonzero angular momentum about the axis, we must begin with He^+ orbitals having such angular momentum themselves. For $\lambda = 1$ ($L_z = \pm\hbar$), the simplest such orbitals are obviously the p orbitals with $m_l = \pm 1$ relative to the internuclear axis. Since the real and imaginary parts of each of these orbitals must have a nodal plane including the axis, symmetry requires that such nodal planes also exist in the molecule and the separated atoms; the separated atom limit must thus also consist of p orbitals with $m_l = \pm 1$. The simplest molecular orbitals of this kind are formed from the $\text{He}^+(2p, m_l = \pm 1)$ orbitals, and can be given the LCAO representation

$$\begin{aligned} \psi(\pi_u 2p, \lambda = 1) \\ = \frac{\varphi_A(2p, m_l = \pm 1) + \varphi(2p, m_l = \pm 1)}{[2 + 2S_{AB}(2p, m_l = \pm 1)]^{1/2}}. \end{aligned} \quad (6.45)$$

Since the value of λ is 1, this is a π orbital— $1\pi_u$ to be specific. It is an odd (u) orbital because it is formed from the sum of two p orbitals. If the orbitals are chosen real, or if we consider only their real or imaginary parts, the two atomic orbitals have their positive lobes on the same side of the axis, so reflection through the center of symmetry changes

the sign of ψ . The difference of two $2p(m_l = \pm 1)$ atomic orbitals would give a π_g orbital, which turns out to correlate with a $3d$ orbital of the united atom. This may be made clearer by Fig. 6.8, which shows schematically the shapes of these and other orbitals.

Note that Eq. 6.45 defines two orbitals, one with $L_z = +\hbar$ and one with $L_z = -\hbar$. Such a pair of wave functions exists for any molecular state in which $\lambda \neq 0$. Since $\lambda\hbar$ is the magnitude of the angular momentum about the internuclear axis, the states with $L_z = \pm\lambda\hbar$ differ (in classical terms) only in the direction of the electron's rotation about the axis. If we changed our coordinate system from right-handed to left-handed, simply by reversing the direction of the z -axis, we would interchange the functions $\psi(L_z = +\hbar)$ and $\psi(L_z = -\hbar)$. But this would in no way change the physics of the situation, and the two states must thus be physically indistinguishable.¹³ Being indistinguishable, they must have the same energy. In short, for every nonzero value of λ in a diatomic molecule there are two degenerate states, with identical energies and with wave functions differing only in orientation. This degeneracy, like that of the hydrogen atom's three $2p$ states, derives directly from the symmetry of space.

As usual when we have degenerate wave functions, we can take linear combinations of them to define new orbitals. For example, we can take the sum and difference of $\psi(L_z = +\hbar)$ and $\psi(L_z = -\hbar)$ to give functions analogous to Eqs. 3.145. These vary respectively as $\cos \lambda\phi$ and $\sin \lambda\phi$, where ϕ is the angle of rotation about the z axis, while the original functions varied as $e^{\pm i\lambda\phi}$. The new orbitals are no longer eigenfunctions of even one component of angular momentum, but they still have the same degenerate energy as the original orbitals. For axially symmetric molecules we are at liberty to use either description. As usual, the real functions are more convenient for graphic purposes, and have been shown in Fig. 6.8. Only in molecules that have no axis of cylindrical symmetry does the difference become physically significant. As for nomenclature, in common usage any linear combination of, say, π_u orbitals is still called a π_u orbital.

This completes our study of the H_2^+ molecule-ion. What have we learned that can be applied to other molecules? Like the electron in a hydrogen atom, that in H_2^+ has a series of distinct quantum states or orbitals, with wave functions and energies that vary with the internuclear distance. Only in the ground state is the electron density in the bonding region high enough to produce a very stable molecule. We have introduced the remarkably simple and useful LCAO approximation, which represents the molecular orbitals as

¹³ This would not be true if we had a way of measuring the sign of L_z , that is, the direction of the electron's rotation. One can do this, for example, with a magnetic field, which can sense the direction of an electric current in a loop. Such a field would remove the degeneracy of the two states. However, we take it for granted in our discussion that external fields are absent. (There is a weak field from the various magnetic moments of the atoms, and this as usual produces a fine-structure splitting of energy levels.)

sums or differences of atomic orbitals, and shown how it can be used to obtain the $E(R)$ curve. But we have also seen that the LCAO method has its limitations for even this simplest of molecules. Finally, we have outlined how molecular orbitals can be classified according to their symmetry and angular momentum, and how they can be organized in a correlation diagram. Next we must find out what complications arise when a molecule has more than one electron.

6.6 The H₂ Molecule: Simple MO Description

The H₂⁺ molecule-ion served as a simple example to help us grasp the physical concepts associated with chemical bonding. However, it is a rather exotic molecule compared with most of those we meet in everyday chemistry. (This is often the case in science: The most useful or familiar examples of a phenomenon are often terribly complex—water waves, for example—whereas those easiest to interpret tend to be rather abstruse.) The hydrogen molecule, H₂, is quite another matter. This is a perfectly stable species that exists as isolated gaseous molecules over a wide range of temperatures. Indeed, it is the most abundant molecule in the universe. Its physical and chemical properties are thoroughly known from experiment, and it is second only to H₂⁺ in simplicity, having only two electrons. Thus it should be relatively easy both to apply a theory of molecular structure to H₂ and to test the results.

The H₂ molecule is similar in several ways to H₂⁺. The symmetry is the same, the potential energy due to the nuclei is the same for a given R , and the molecule still resembles two H atoms in the limit $R \rightarrow \infty$. The fundamental difference is that there are two electrons rather than one. It is natural to make the same initial assumption as in a many-electron atom: that each electron in a molecule sees only the average field of the other electron(s), and that one can describe such an electron by a one-electron wave function (molecular orbital). This corresponds to the central-field approximation in an atom. Here, however, the field is no longer central, and we must do without the advantages of spherical symmetry. As before, the best approximate wave functions in this model are obtained by self-consistent-field methods; to improve on these results, one must apply corrections for the correlation between electrons.

Assume that we can get one-electron wave functions; how do we combine them to get the total molecular wave function? The simplest assumption is that one can assign to each electron a unique orbital, the aggregate of such assignments defining a unique electronic configuration of the molecule. For example, just as the boron atom has the configuration $1s^2 2s^2 2p$, we shall see (in Chapter 7) that the B₂ molecule has the ground-state configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2$. Even in an atom this is only an approximation, though quite a good one, as we pointed out at the end of Section 5.7. Strictly, the interactions between electrons prevent the energy and angular momen-

tum of a single electron from being conserved. One would not expect the single-configuration model to work any better for molecules. However, we can certainly use this model as a first approximation; later we shall introduce an approximation involving more than one configuration.

To the extent that electronic configurations are meaningful in molecules, the Pauli exclusion principle holds for individual electrons: If the electron spin is taken into account, only one electron can be assigned to a given quantum state. Each distinct spatial molecular orbital can then contain only two electrons, which must have opposite spins. One can thus apply the Aufbau principle, filling each orbital in turn in the order of increasing energy. Since H₂ has only two electrons, these rules would not seem to concern us here; yet the law behind them does entail a serious restriction on the possible wave functions of H₂, as we shall see in the next section.

The simplest kind of molecular wave function made up of one-electron orbitals is a Hartree product like Eq. 5.15. For a given state of H₂ such a wave function would have the form

$$\psi_{\text{MO}}(1,2) = \phi_i(1)\phi_j(2), \quad (6.46)$$

where i, j designate orbitals and 1, 2, electrons; each ϕ must include both spatial and spin coordinates. Spectroscopy tells us¹⁴ that the ground state of H₂ is $^1\Sigma_g$. We thus say that the lowest-energy orbital is $1\sigma_g$ (as in H₂⁺) and the ground-state configuration is $(1\sigma_g)^2$, with the two electrons assigned opposite spins. If we use the orbital designation to stand for the spatial part of the wave function, Eq. 6.46 for the ground state becomes

$$\psi_{\text{MO}}[(1\sigma_g)^2] = 1\sigma_g(1)\alpha(1)1\sigma_g(2)\beta(2), \quad (6.47)$$

where α and β are the two different Pauli spin wave functions introduced briefly in Chapter 5: α for $m_s = +\frac{1}{2}$ and β for $m_s = -\frac{1}{2}$. Because we are neglecting electron correlation, each of the spatial orbitals must be identical to the corresponding H orbital, and in the LCAO approximation will be given by Eq. 6.33. Combining these assumptions, we have

$$\begin{aligned} \psi_{\text{MO}}[(\sigma_g 1s)^2] &= \sigma_g 1s(1)\sigma_g 1s(2)\alpha(1)\beta(2) \\ &= \frac{[1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)]\alpha(1)\beta(2)}{2(1 + S_{AB})}. \end{aligned} \quad (6.48)$$

¹⁴ We know it is a $^1\Sigma$ state because it exhibits no Zeeman splitting at all in a magnetic field and thus must have both zero orbital angular momentum (so $\Lambda = 0$) and zero spin angular momentum (so $S = 0$, $2s + 1 = 1$). The g character is actually inferred from the intensities of spectral lines associated with specific rotational states, but we shall not pursue this point. For details, see G. Herzberg, *Molecular Spectra and Molecular Structure, Volume I, Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand, Reinhold, New York, 1950).

Here $1s_A$, $1s_B$ is a shorthand for our earlier $\phi_A(1s)$, $\phi_B(1s)$, normalized hydrogen atom eigenfunctions: $1s_A(1) = (\pi a_0^3)^{-1/2} e^{-r_{A1}/a_0}$, where r_{A1} is the distance from nucleus A to electron 1.

Equation 6.48 is the simplest molecular orbital wave function for the ground state of the H_2 molecule. Note that in its second form, this function can be interpreted as a product of two superpositions of atomic wave functions. The full wave function can be used to obtain an approximate $E(R)$ curve by the same method as in Section 6.4. In this case one evaluates $\iint \psi^* H \psi \, d\tau_1 \, d\tau_2$ for each value of R , with the electronic Hamiltonian of Eq. 6.1 (including the $1/r_{12}$ term); the integration is lengthy but feasible. The calculated $E(R)$ is shown as curve 1 in Fig. 6.10. One obtains $R_e = 1.57a_0$ (0.84 Å) and $D_e = 0.0974$ hartree (2.65 eV), the latter relative to two $1s$ H atoms. The experimental values are $1.40a_0$ (0.74 Å) and 0.1744 hartree (4.75 eV). The electron density looks quite similar to that in the ground state of H_2^+ (Fig. 6.7), multiplied by 2. In the energy at least, this solution gives appreciably worse agreement than does the LCAO solution for H_2^+ . This is not surprising, since here the flaws of the LCAO approach are combined with those of the one-electron-orbital and single-configuration assumptions.

One can improve upon this solution and still remain within the framework of the molecular orbital model. The greatest single improvement can be made by the technique we illustrated in Eq. 5.13, inserting a scale factor in the atomic orbitals. In this case one still uses Eq. 6.48 but sets $1s_A(1) = (\alpha^3/\pi)^{1/2} e^{-\alpha r_{A1}}$, and so on; α is then varied to minimize the energy for each value of R . This solution is shown as curve 2 in Fig. 6.10, and is obviously a considerable improvement over the initial, naive LCAO solution. One obtains $R_e = 1.38a_0$, $D_e = 0.1282$ hartree, with $\alpha(R_e) = 1.197/a_0$. The best possible wave function of the form of Eq. 6.46 is, of course, the self-consistent-field solution, which yields curve 3 of Fig. 6.10; but the SCF molecular orbitals can be represented only by complicated functions with no simple analytic relationship to atomic orbitals, and the $E(R)$ curve is only slightly improved over the scaled LCAO solution. We are still left with a correlation energy of 0.04 hartree (1.1 eV) at R_e , illustrating the limitations of the orbital assumption.

The hydrogen molecule illustrates a fundamental flaw that sometimes appears in the molecular orbital method, as we can see by looking at the separated-atom limit for H_2 . What happens to the molecular orbital wave function as $R \rightarrow \infty$? The overlap integrals vanish, and Eq. 6.48 reduces to

$$\begin{aligned} \lim_{R \rightarrow \infty} \psi_{\text{MO}} &= \frac{\alpha(1)\beta(2)}{2} [1s_A(1)1s_A(2) + 1s_A(1)1s_B(2) \\ &\quad + 1s_B(1)1s_A(2) + 1s_B(1)1s_B(2)]. \end{aligned} \quad (6.49)$$

In this limit, of course, there is negligible probability of finding an electron anywhere but near one of the two nuclei. If we square Eq. 6.49, each of the cross terms contains a fac-

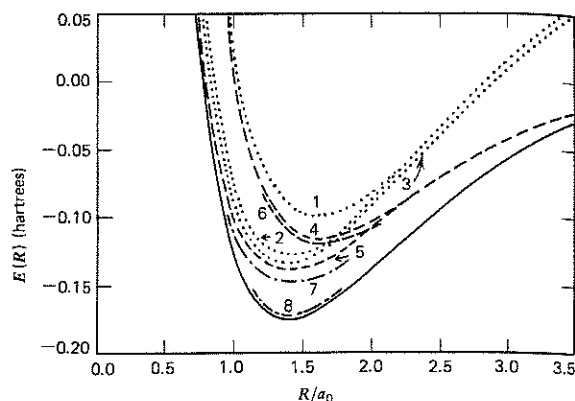


Figure 6.10 Potential energy curves for the ground state of H_2 , calculated by various approximations; the energy zero corresponds to $\text{H}(1s) + \text{H}(1s)$. The heavy solid line is the experimental $E(R)$ curve. Molecular orbital calculations (.....):

1. Simple LCAO, Eq. 6.48, with $1s = (\pi a_0^3)^{-1/2} e^{-r/a_0}$.
 2. Same with scaled atomic orbitals: $1s = (\alpha^3/\pi)^{1/2} e^{-\alpha r}$, with α varied to minimize $E(R)$.
 3. Self-consistent-field solution.
- Valence bond calculations (---):
4. Heitler-London, Eq. 6.72,
 5. Same with scaled atomic orbitals.
- Other calculations (-----):
6. Mixed MO and VB, Eq. 6.76,
 7. Same with scaled atomic orbitals,
 8. Eleven-term variation function, including terms in r_{12} .

tor like $1s_A(1)1s_B(1) \propto e^{-r_{A1}/a_0} e^{-r_{B1}/a_0}$, which vanishes since everywhere either r_{A1} or r_{B1} must be very large. Thus, all the cross terms drop out, and we have

$$\begin{aligned} \lim_{R \rightarrow \infty} (\psi_{\text{MO}})^2 &= [1s_A(1)]^2 [1s_A(2)]^2 + [1s_A(1)]^2 [1s_B(2)]^2 \\ &\quad + [1s_B(1)]^2 [1s_A(2)]^2 + [1s_B(1)]^2 [1s_B(2)]^2. \end{aligned} \quad (6.50)$$

We have assumed that the location of each electron is independent of that of the other. The probability that two independent events occur simultaneously is the product of the probabilities of the two events. Thus, in the integral of Eq. 6.50, $\iint \psi^2 \, d\tau_1 \, d\tau_2$, the first term gives the probability that both electrons are in atom A ; the next two terms give the probability that one electron is in each atom; and the fourth term gives the probability that both electrons are in atom B . Since all the $1s$ functions have the same form, each of the four terms contributes the same amount to the integral, and each of the four electron arrangements has the same probability, 25%. This means that the wave function describes a state in which one is equally likely to observe two neutral atoms, $\text{H}(1s) + \text{H}(1s)$, or a negative ion and a bare proton, $\text{H}^-(1s^2) + \text{H}^+$.

But for two hydrogen atoms infinitely far apart, the state of lowest energy is clearly one in which each atom is in its

ground state, $H(1s) + H(1s)$. It takes 13.60 eV or 0.5 hartree, the ionization potential, to remove an electron from a hydrogen atom, and only 0.75 eV, the electron affinity, is gained by adding that electron to another neutral hydrogen atom. Thus the state $H^-(1s^2) + H^+$ has an energy 12.85 eV higher than $H(1s) + H(1s)$, and the mixed state described by Eq. 6.49 should have an energy halfway between the two, +6.42 eV. If one extends the $E(R)$ curve obtained from the LCAO function (Eq. 6.48) to $R = \infty$, one in fact obtains an energy 8.50 eV (0.312 hartree) higher than the ground state; the 2.08-eV discrepancy is half the correlation energy of H^- , for which the Hartree function $1s(1)1s(2)$ is only an approximation. As one can guess from Fig. 6.10, the SCF solution is not much better; it also approaches an unphysical limit at large R . The molecular orbital approach is thus clearly inadequate because of its behavior at the separated-atom limit. A wave function of this type may be reasonably accurate when R is near its equilibrium value,¹⁵ but it certainly does not describe the ground state—or any stationary state—of two distant H atoms.

What, then, is the wave function really like in the adiabatic, separated-atom limit? Since the electron densities on the two atoms are independent there, we might expect to find a simple product of two atomic orbitals like

$$\lim_{R \rightarrow \infty} \psi[(\sigma_g 1s)^2] \propto 1s_A(1)1s_B(2). \quad (6.51)$$

This wave function will obviously give the correct energy for two separated 1s H atoms. It describes a state in which there is a very high degree of correlation between the two electrons: The probability density $|\psi|^2$ has a significant magnitude only when electron 1 is near nucleus A and electron 2 is simultaneously near nucleus B. This is in contrast to a molecular orbital wave function like Eq. 6.48, in which there is by definition no correlation between the electrons.

Here we have two mathematical descriptions representing sharply contrasting physical situations, yet each is a reasonably good description of the H_2 molecule in one range of R . The MO description (Eq. 6.48) is never exactly correct, but for small R it does give a qualitatively correct $E(R)$ curve; as $R \rightarrow \infty$ it becomes completely wrong. Equation 6.51 is an exact solution at $R = \infty$ (apart from the considerations discussed in the next section), but is inadequate to describe bonding at finite R . The real ground-state wave function must somehow make a transition between these two extremes, and we wish to find a function that behaves in the same way. Before we begin this search, however, we must study the consequences of an apparently trivial fact—that all electrons are identical.

¹⁵ The wave function near R_e does have a significant amount of ionic character (contribution of terms corresponding to H^-H^+), because Coulomb attraction drastically lowers the energy of the ionic state. Cf. Section 6.9.

6.7 Symmetry Properties of Identical Particles

We have several times discussed the importance of symmetry in quantum mechanics. The constants of motion of a system are directly determined by the symmetry of the Hamiltonian; thus in diatomic molecules the equivalence of all orientations about the z axis requires that L_z be conserved. In H_2 , as in H_2^+ , the indistinguishability of the two nuclei means that $|\psi|^2$ must be symmetric about a plane midway between the nuclei. It should not be surprising that the indistinguishability of the electrons also has important consequences. We suggested some of these consequences in our discussion of atoms (which also contain identical electrons); now we shall look at the fundamental principles involved.

Here is the situation that confronts us. All electrons are absolutely indistinguishable. The same is true for all protons, and for all particles of any particular kind. The value of any real (measurable) physical quantity must thus be independent of the way we name or number such identical particles. Now, the physical description of a system depends only on the absolute square of the wave function. This means that, if $\psi(1, 2)$ is a wave function involving the identical particles 1 and 2, we must have

$$|\psi(1, 2)|^2 = |\psi(2, 1)|^2, \quad (6.52)$$

where $\psi(2, 1)$ is obtained from $\psi(1, 2)$ by interchanging particles 1 and 2—that is, rewriting the wave function with the names of particles 1 and 2 exchanged. Equation 6.16 says the same thing for the special case of identical nuclei.

What limitations does Eq. 6.52 place on the wave function? It tells us that $\psi(2, 1)$ must differ from $\psi(1, 2)$ by no more than a phase factor of the form $e^{i\delta}$, where δ is a constant. This is the only kind of factor that has no effect on $\psi^* \psi$, in that $(e^{i\delta})^* e^{i\delta} = e^{-i\delta} e^{i\delta} = e^0 = 1$. We can be more specific about the value of $e^{i\delta}$. If we define an operator P_{12} to mean “permute (exchange) particles 1 and 2,” then by what we have just said we must have

$$\psi(2, 1) = P_{12}\psi(1, 2) = e^{i\delta}\psi(1, 2). \quad (6.53)$$

If we carry out the permutation of 1 and 2 a second time, we must be back where we started. We can thus write

$$\begin{aligned} \psi(1, 2) &= P_{12}\psi(2, 1) = P_{12}[e^{i\delta}\psi(1, 2)] \\ &= e^{i\delta}P_{12}\psi(1, 2) \\ &= e^{2i\delta}\psi(1, 2). \end{aligned} \quad (6.54)$$

This means that

$$e^{2i\delta} = 1 \quad \text{or} \quad e^{i\delta} = \pm 1, \quad (6.55)$$

or, in terms of the wave functions,

$$\psi(2, 1) = \pm \psi(1, 2). \quad (6.56)$$

This argument is completely general: It holds for systems with not just two, but any number of identical particles, because we can always interchange them two at a time.

According to Eq. 6.56, the wave function for any system containing identical particles must either remain unchanged or change sign if we interchange two of the identical particles. There are two physically distinct cases here. If the wave function is unchanged, $\psi(2, 1) = \psi(1, 2)$, we say that it is *symmetric* with respect to particles of the type in question; if the wave function changes sign, $\psi(2, 1) = -\psi(1, 2)$, we say it is *antisymmetric* with respect to those particles. The particles found in nature are sharply divided into two classes, those with symmetric and those with antisymmetric wave functions. A given particle never changes from one class to the other (unless the phenomenon called “super-symmetry” allows a bit of crossover under very high-energy conditions, as in the big bang). The names of these classes are based on the statistical behavior of the particles, which we shall discuss in Part II. Those with symmetric wave functions obey what is called Bose–Einstein statistics, and are thus named *bosons*. These include photons, deuterons, α particles, and all other particles with integral spin (photons have spin 1). The particles with antisymmetric wave functions obey Fermi–Dirac statistics, and are called *fermions*. These include electrons, protons, neutrons, and all other particles with half-integral spin.

We are concerned principally with the wave functions describing electrons. Since the electron is a fermion, any wave function $\psi(1, 2, \dots)$ involving two or more electrons must change sign if we interchange the numbers on any two of the electrons. This is clearly not true of our molecular orbital wave functions for the H_2 molecule. Equations 6.47 through 6.49 all contain the factor $\alpha(1)\beta(2)$, specifically describing a state in which electron 1 has the spin wave function α and electron 2 has the spin wave function β . If we interchange the electrons we get a new wave function, containing $\alpha(2)\beta(1)$, rather than the same wave function with reversed sign. Since α and β here correspond to different spins, $\alpha(1)\beta(2)$ and $\alpha(2)\beta(1)$ describe what appear to be physically distinct states. Thus these wave functions are not really physically admissible descriptions of a two-electron system.

Very well, then, let us write a wave function that is antisymmetric with respect to interchange of electrons. We assume that the spatial and spin coordinates are separable, so that $\psi = \psi_{\text{spatial}} \psi_{\text{spin}}$. (For a two-electron system, this can always be done.) For the product to be antisymmetric, if one of the two factors is symmetric the other must be antisymmetric. We already have symmetric spatial functions, such as $1\sigma_g(1)1\sigma_g(2)$ in Eq. 6.47; thus we must look for an antisymmetric spin function. The trouble with our original

$\alpha(1)\beta(2)$ was that interchange of electrons transformed it to the quite different function $\alpha(2)\beta(1)$. But suppose that we try a linear combination of these two functions, with opposite signs to give the antisymmetry:

$$\psi_{\text{spin,anti}} = \alpha(1)\beta(2) - \alpha(2)\beta(1). \quad (6.57)$$

This function does indeed change sign when we exchange 1 and 2. We can thus combine it with any symmetric spatial function to give an antisymmetric total wave function. The molecular orbital wave function for the ground state of H_2 then becomes

$$\begin{aligned} \psi_{\text{MO,anti}} [(1\sigma_g)^2] \\ = \frac{1\sigma_g(1)1\sigma_g(2)}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)], \end{aligned} \quad (6.58)$$

in which the $\sqrt{2}$ maintains the normalization. This function is antisymmetric with respect to interchange of the electrons and is thus physically admissible. Unfortunately, since the spatial part is the same as before, it is just as poor an approximation as Eq. 6.47. One can also obtain an antisymmetric wave function by combining an antisymmetric ψ_{spatial} with a symmetric ψ_{spin} ; we shall see that such a function describes the first excited state of H_2 .

What physical interpretation can we give to the wave function of Eq. 6.58? Both $\alpha(1)\beta(2)$ and $\alpha(2)\beta(1)$ are legitimate solutions of the wave equation, each describing a conceivable eigenstate of the system. The principle of superposition assures that a linear combination of such solutions is also a solution, with the squared coefficients of the individual terms giving the relative probabilities of observing the corresponding eigenstates.¹⁶ Here the coefficients of the two terms are equal in magnitude, so the two states should be equally likely. In other words, if we make measurements on an H_2 molecule in its ground state, half the time we should find electron 1 with $m_s = +\frac{1}{2}$ and electron 2 with $m_s = -\frac{1}{2}$; the other half of the time we should find electron 1 with $m_s = -\frac{1}{2}$ and electron 2 with $m_s = +\frac{1}{2}$. Since we cannot tell electrons 1 and 2 apart anyway, this result is just what we should expect. In any case, the function of Eq. 6.58 specifies that we will definitely observe the two electrons to have opposite spins; whichever spin electron 1 may have, electron 2 has the opposite. So long as this function describes the spins, however far apart the electrons may be, they have opposite spins. This is sometimes taken to be a paradox, that observation of $m_s = +\frac{1}{2}$ for electron 1

¹⁶ That is, if for some state of a system $\psi = \sum_i c_i \phi_i$, where the ϕ_i are eigenfunctions of an operator Q , then in that state the probability of observing the i th eigenvalue Q_i is

$$P(Q_i) = |c_i|^2 = c_i^* c_i.$$

in Boston forces electron 2 in Los Angeles to have $m_s = -\frac{1}{2}$, by what is sometimes called "action at a distance." The resolution is of course that (a) if the two electrons are very far apart, it is unrealistic to expect that the function of Eq. 6.58 will describe them properly, but (b) so long as that function does describe the electrons, it specifies that the system of the two of them is in a state in which they always have opposite spins, so, whatever we observe for the spin of one *implies* what the spin of the other must be—not that the physics of measuring one spin in Boston causes a physical effect in Los Angeles. There is no mystery, only a condition set when the electrons are prepared in the state described by the function of Eq. 6.58.

Given the antisymmetry of electrons, one can derive the Pauli exclusion principle, which states that no two electrons can occupy the same quantum state. To see why this is so, let us try writing a wave function for two electrons in exactly the same state. This means that we assign to both electrons the same orbital ϕ_i , including both spatial and spin coordinates; for example, $\phi_i(1)$ might be $1\sigma_g(1)\alpha(1)$. The antisymmetrized orbital-product wave function corresponding to Eq. 6.58 is then

$$\psi_{\text{anti}}(1, 2) = \frac{1}{\sqrt{2}}[\phi_i(1)\phi_i(2) - \phi_i(2)\phi_i(1)] = 0. \quad (6.59)$$

A wave function of zero magnitude describes a state of zero probability; in other words, though the state (Eq. 6.59) satisfies the antisymmetry requirement, it can never be observed. This proves the exclusion principle, which applies not just to electrons, but to all fermions. (It is possible to infer antisymmetry from the exclusion principle as well, but the argument is beyond the scope of this book.) By contrast, there is no such restriction on the quantum states of bosons. Since the wave function for two bosons must be symmetric, suitable spin functions to accompany a symmetric spatial function include

$$\psi_{\text{spin, symm}} = \begin{cases} \alpha(1)\alpha(2), \\ \beta(1)\beta(2), \\ \alpha(1)\beta(2) + \beta(1)\alpha(2). \end{cases} \quad (6.60)$$

The symmetric wave function for two bosons in exactly the same state can thus be written, for example, as

$$\psi_{\text{symm}}(1, 2) = \phi_i(1)\phi_i(2)\alpha(1)\alpha(2). \quad (6.61)$$

Since this function is in general nonzero, there is nothing to prevent two bosons, or indeed any number of bosons, from occupying the same quantum state.

Note that the exclusion principle as we have stated it is meaningful only when electrons can be assigned to individual atomic or molecular orbitals, with the wave function written as a linear combination of orbital products. This is

logical, since only in the orbital approximation does each electron have its own set of quantum numbers. But this form of the exclusion principle is only a special case of the general rule, which we can add to the postulates of Section 3.8:

POSTULATE VII. Any eigenfunction of a many-particle system must be antisymmetric with respect to interchange of any two identical fermions, and symmetric with respect to interchange of any two identical bosons.

Which particles are fermions and which bosons is intimately connected to their spins: Particles with integral values of spin are bosons and particles with half-integral spin are fermions. The connection is well established, and within the context of chemistry appears to be rigorous. However, in the realm of physics of elementary particles, there are conjectures that under extreme conditions, it may be possible to observe mixed fermion-boson behavior; such mixing is called "supersymmetry."

How does one write a wave function for more than two electrons? We again use the orbital approximation, with ϕ_i including both spatial and spin coordinates. The antisymmetric wave function for two electrons in the orbitals ϕ_i and ϕ_j , respectively, must be of the form

$$\begin{aligned} \psi_{\text{anti}}(1, 2) &= \frac{1}{\sqrt{2}}[\phi_i(1)\phi_j(2) - \phi_i(2)\phi_j(1)] \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_i(1) & \phi_j(1) \\ \phi_i(2) & \phi_j(2) \end{vmatrix}, \end{aligned} \quad (6.62)$$

equivalent to a determinant of the orbital functions, in which the orbitals fix the row indices and the electrons the column indices. This can be generalized to any number of electrons: The appropriate wave function for N electrons in N orbitals is

$$\begin{aligned} \psi_{\text{anti}}(1, 2, \dots, N) \\ = (N!)^{-1/2} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \cdots & \phi_1(N) \\ \phi_2(1) & \phi_2(2) & \cdots & \phi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \cdots & \phi_N(N) \end{vmatrix}, \end{aligned} \quad (6.63)$$

a determinant in which each row corresponds to a given orbital and each column to a given electron. The $(N!)^{-1/2}$ is needed as a normalization constant, since the expansion of an $N \times N$ determinant has $N!$ terms. This function clearly satisfies the antisymmetry requirement, since any determinant changes sign when two columns are interchanged.

Now we can understand certain cryptic statements in Chapter 5. The trouble with a Hartree wave function like 5.15 is that it is not antisymmetric; instead one writes the determinantal function of expression 6.63. If the orbitals are chosen to give the lowest possible energy, within the approximation that each electron moves in the *average* potential of all the others, the result is called the

Hartree–Fock wave function for N electrons.¹⁷ (Further discussion of the Hartree–Fock method is postponed until Chapter 8.) We can also see why the phenomena associated with the exclusion principle are often called “exchange” effects; the apparent repulsion (“exchange force”) between electrons of the same spin merely expresses the fact that they must have different spatial orbitals, or else the total wave function would vanish by Eq. 6.59. We could have explained all this in Chapter 5, but we preferred to use the two-electron case of H_2 to illustrate the concepts, which are equally applicable to atoms and molecules.

6.8 H_2 : The Valence Bond Representation

Now we can return to the problem of the H_2 molecule. Making the molecular orbital wave function antisymmetric does not keep it from going wrong as $R \rightarrow \infty$, so we still need another approach. Suppose we try to find an approximate wave function that joins smoothly with the separated-atom limit. What is the wave function in this limit? We suggested earlier that it should resemble Eq. 6.51 (which does give the correct energy), but that function is obviously not antisymmetric. Nevertheless, it does illustrate correctly that the wave function at $R = \infty$ must be made up of atomic orbitals. The simplest method of doing this was devised by W. Heitler and F. London in 1927, in what was historically the first quantum mechanical treatment of the chemical bond.

We begin by considering two completely independent hydrogen atoms, with one electron in each atom. Since the electrons are indistinguishable, we may have either electron 1 around nucleus A and electron 2 around nucleus B , or vice versa. Neglecting for the moment the symmetry problem, we have two possible spatial wave functions, $1s_A(1)1s_B(2)$ and $1s_A(2)1s_B(1)$. As for the spin, when the atoms are completely separated, we may assign either spin ($m_s = \pm \frac{1}{2}$) to each electron, independent of the other. This gives us four possible two-electron spin wave functions: $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, $\alpha(1)\beta(2)$, and $\beta(1)\alpha(2)$. But in fact none of these spatial or spin functions is antisymmetric. How can we obtain an antisymmetric total wave function?

Let us write the total wave function as a product of spatial and spin functions. As in our molecular orbital functions, this form is chosen for mathematical and physical simplicity;¹⁸ it certainly is not a correct form for the true

wave function. For the product of spatial and spin functions to be antisymmetric, one must be symmetric and the other antisymmetric. As before, let us make symmetric and antisymmetric linear combinations of our simple functions. For the spatial functions we have

$$\psi_{\text{spat,symm}} = 1s_A(1)1s_B(2) + 1s_A(2)1s_B(1) \quad (6.64)$$

and

$$\psi_{\text{spat,anti}} = 1s_A(1)1s_B(2) - 1s_A(2)1s_B(1). \quad (6.65)$$

There are three simple symmetric spin functions,

$$\psi_{\text{spin,symm}} = \begin{cases} \alpha(1)\alpha(2), & (6.66a) \\ \beta(1)\beta(2), & (6.66b) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1), & (6.66c) \end{cases}$$

and one antisymmetric spin function,

$$\psi_{\text{spin,anti}} = \alpha(1)\beta(2) - \alpha(2)\beta(1). \quad (6.67)$$

Combining these to give an antisymmetric product, we have, in this approximation, four possible wave functions generated from hydrogen $1s$ orbitals:

$$\psi_1 = C_1 [1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)] \quad (6.68)$$

$$[\alpha(1)\beta(2) - \alpha(2)\beta(1)],$$

$$\psi_2 = C_2 [1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)] \quad (6.69)$$

$$\alpha(1)\alpha(2),$$

$$\psi_3 = C_3 [1s_A(1)1s_B(2) - 1s_B(2)1s_B(1)] \quad (6.70)$$

$$\beta(1)\beta(2),$$

$$\psi_4 = C_4 [1s_A(1)1s_B(2) - 1s_B(2)1s_B(1)] \quad (6.71)$$

$$[\alpha(1)\beta(2) + \alpha(2)\beta(1)].$$

The C_i 's are normalization constants; for $R = \infty$ one readily evaluates them as $C_1 = C_4 = 1/2$, $C_2 = C_3 = 1/\sqrt{2}$.

What is the significance of the four functions 6.68–6.71? They are all satisfactory wave functions for two $1s$ hydrogen atoms infinitely far apart—satisfactory in that they both give the correct energy and are antisymmetric. There are other such functions, but these are the only simple ones that are constructed from $\text{H}(1s)$ orbitals and can be factored into spatial and spin parts. Now we make the *approximation* that these exact solutions for $R = \infty$ can be applied to the H_2 molecule at finite R , with appropriate normalization constants. This is exactly analogous to the reasoning by which we wrote the MO wave functions of Eqs. 6.26 and 6.27 for H_2^+ . Obviously the present wave functions cannot be factored into one-electron molecular orbitals. They are basically two-electron functions, and were specifically designed by Heitler and London to represent the electron-pair bond. Their purpose was to find a quantum mechanical basis for G. N. Lewis' concept that chemical bonds consist of electron pairs

¹⁷ In an open-shell atom or molecule, with N electrons in more than N orbitals, one must replace Eq. 6.63 by a linear combination of determinants, one for each possible distribution of the electrons among the orbitals.

¹⁸ In fact, this is possible only for the two-electron system. For three or more electrons there is no way to write an antisymmetric total wave function that can be factored into spin and spatial parts. There are systematic methods for dealing with such cases, but we need not consider them here.

shared between two atoms. Similar approximations can be made for more complicated molecules if one assumes that the molecular wave function is a product of two-electron functions, each representing a conventional chemical bond. Wave functions of this type are called *valence bond* (VB) functions, since only the valence electrons and their bonds are taken into account.

The functions of Eqs. 6.68 through 6.71 all correspond to the same energy at $R = \infty$, but this can no longer be true at finite R . The spatial functions of Eqs. 6.64 and 6.65 obviously correspond to different electron densities at any given point in space, and thus to different energy levels. We can neglect the effect of the electron spins on the energy. We conclude that, of our four wave functions, ψ_1 corresponds to one state of the H₂ molecule, whereas ψ_2 , ψ_3 , and ψ_4 all correspond to a single other state, or rather to three degenerate states. Two 1s hydrogen atoms thus give rise to both a singlet and a triplet term of the H₂ molecule.

We can analyze these terms in much the same way that we treated atomic terms in Section 5.6. Let α correspond to $m_s = +\frac{1}{2}$, so that in the state corresponding to ψ_2 the molecule has $M_S = \sum m_s = 1$. Similarly, ψ_3 describes a state in which each electron has $m_s = -\frac{1}{2}$ and the molecule $M_S = -1$. These two wave functions differ only in the direction of the spin vector, which is not physically significant in the absence of an external field. Thus they are degenerate, corresponding to the same energy at any value of R . Since a two-electron system can never have $|M_S| > 1$, the states described by ψ_2 and ψ_3 must be components of a term with $S = 1$. This is, of course, a triplet term, with $2S + 1 = 3$, and must thus have a third component.

The three components of a triplet have $M_S = 1, 0, -1$ ($S_z = \hbar, 0, -\hbar$). The third component must therefore be a state with $M_S = 0$, corresponding to one electron with $m_s = +\frac{1}{2}$ and one with $m_s = -\frac{1}{2}$. Since both the electrons and the atoms are indistinguishable, the wave function for this state should logically contain an equal mixture of $\alpha(1)\beta(2)$ and $\alpha(2)\beta(1)$. This condition is satisfied by the function ψ_4 , which is also degenerate with ψ_2 and ψ_3 since it has the same spatial wave function. According to our approximate wave functions, then, the components of this triplet are exactly degenerate if one neglects spin-orbit interactions. To complete our term analysis, we are left with the function ψ_1 , which also has $M_S = 0$; this can obviously describe the single component of a singlet term ($S = 0$).

Which of these two terms, the triplet or the singlet, has the lower energy? One could, of course, find out by solving for the $E(R)$ curves, but we can deduce the answer without doing this. Note that the spatial part of ψ_1 is the sum of two positive terms, which add constructively at every point in space. In contrast, the spatial part of the triplet wave functions has a nodal plane midway between the nuclei. Thus the singlet state has excess electron density in the bonding region, and can be assumed to have a minimum in the $E(R)$ curve, whereas the triplet state is certainly antibonding. This conclusion is confirmed by both calculation and

experiment. The ground state is indeed a singlet state, with a fairly deep energy minimum. The first excited state is a triplet state in which the two atoms repel each other very strongly. Because both these states correlate with 1s atomic states, they are both Σ states ($\Lambda = 0$); the singlet is $^1\Sigma_g$ and the triplet is $^3\Sigma_u$. The exact $E(R)$ curves for these states are shown in Fig. 6.11; we shall discuss the excited states of H₂ in Section 6.10.

As for the ground state, one can obtain the valence bond $E(R)$ curve in the usual way. Normalization of Eq. 6.68 gives for the wave function

$$\psi_{\text{VB}} = \frac{[1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]}{2(1 + S_{AB}^2)}, \quad (6.72)$$

where S_{AB} is the overlap integral defined in Eq. 6.30. Evaluating $\iint \psi^* H \psi \, d\tau_1 \, d\tau_2$ for this function, with normal atomic

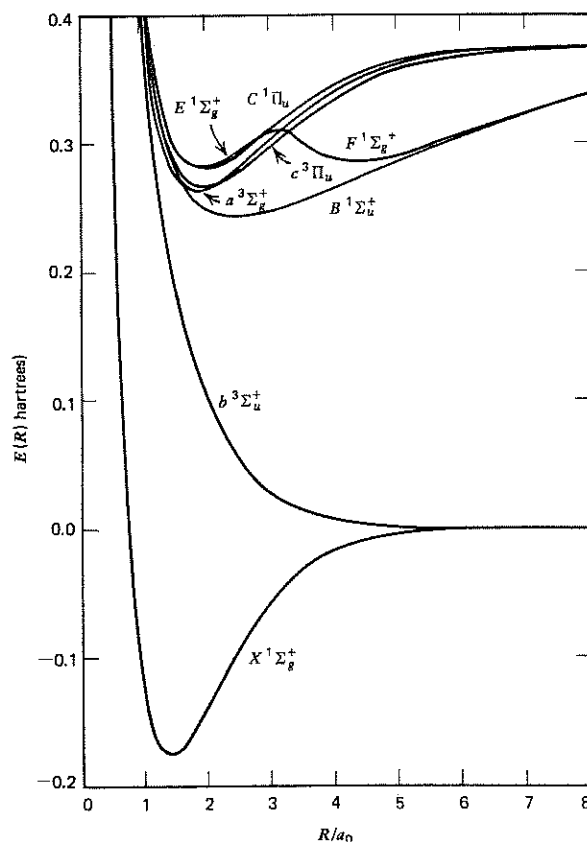


Figure 6.11 Potential energy curves for the ground state and the first few excited states of H₂; the energy zero corresponds to two separated H(1s) atoms. Each state is labeled with its spectroscopic term symbol, the initial letter of which is an arbitrary identifier (X always designates the ground state, excited singlets are usually assigned A, B, . . . , in order of increasing energy, and excited triplets a, b, . . . , similarly).

orbitals, gives curve 4 of Fig. 6.10. This is appreciably better than the simple MO solution (curve 1), and yields $R_e = 1.64a_0$ (0.87 Å) and $D_e = 0.1154$ hartree (3.14 eV). As before, one can obtain considerable improvement by using scaled atomic orbitals. This gives curve 5 of the figure, with $R_e = 1.40a_0$, $D_e = 0.1383$ hartree, $\alpha(R_e) = 1.166$. Since this is better than even the self-consistent-field result, the valence bond method definitely seems preferable to the molecular orbital method in this case. However, the MO method is more easily extended to systems with more than two electrons. But the state of the art has long since gone beyond either approximation in its simple form, as we shall now see.

6.9 H₂: Beyond the Simple MO and VB Approximations

Thus far we have what seem to be two quite distinct kinds of wave function for the H₂ molecule. In the MO method we assume that the molecular wave function is a product of one-electron orbitals, then approximate each of these orbitals by a sum of atomic orbitals. In the VB method we form a two-electron function directly as an antisymmetrized combination of atomic orbital products. Although we have given plausible arguments for both methods, neither gives any more than a crude approximation to the true molecular wave function. In this section we shall look at some of the ways to obtain better approximations.

To begin with, let us examine the relationship between the MO and VB wave functions. For the ground state of H₂ these functions are given by Eqs. 6.58 and 6.72, respectively. Let us disregard the spin functions, which are the same in both cases, and concentrate on the atomic orbitals from which the spatial functions are composed. Expanding the molecular orbitals according to Eq. 6.33, we have

$$\begin{aligned}\psi_{\text{MO,spat}} &= \frac{[1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)]}{2(1 + S_{AB})} \\ &= \frac{1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) + [1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)]}{2(1 + S_{AB})},\end{aligned}\quad (6.73)$$

whereas the corresponding VB function is

$$\psi_{\text{VB,spat}} = \frac{1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)}{\sqrt{2}(1 + S_{AB})}.\quad (6.74)$$

To understand the physical and essential mathematical content of these equations, we can ignore their denominators, which are merely normalization constants. If we compare the two functions, we see at once that the numerator of Eq. 6.74 is identical to the two terms in brackets in the numerator of Eq. 6.73. Thus the MO function contains the

VB function. But the MO function contains two other terms that do not appear in the VB function.

How can we interpret this relationship? Each of the first two terms in Eq. 6.73 (and not in Eq. 6.74) describes a state in which both electrons are on the same atom, H⁻ + H⁺, whereas the two terms in brackets describe states with one electron on each atom. It is customary to call these “ionic” and “covalent” terms, respectively. Since all the terms in each function have equal coefficients, one says that the MO function is an equal mixture of covalent and ionic terms, whereas the VB function contains only the covalent terms. We have gone through this argument before, in discussing Eq. 6.50: At $R = \infty$ the MO function literally describes a state that is 50% covalent and 50% ionic. This is *not* true at finite R , since the ionic-covalent cross terms in $(\psi_{\text{MO}})^2$ do not vanish. At finite distances, especially at the atomic scale, the atomic wave functions on A and B are not *orthogonal*: $\int \phi_A^*(1)\phi_B(1) d\tau_1 \neq 0$, which is a mathematical expression of the physical condition that the one-electron states $\phi_A(1)$ and $\phi_B(1)$ are not mutually exclusive states. (See Appendix 6A.) This in turn means that states represented by such product functions as $\phi_A(1)\phi_B(2)$ and $\phi_A(1)\phi_A(2)$ are also not mutually exclusive. Thus in this approximation one cannot divide the bond (i.e., the electron density) in any unique way into “covalent” and “ionic” parts. If we say that the wave function is 50% ionic, this is merely a convenient shorthand to describe the mathematical form of our approximate function.

To compare the two approximations further, let us consider how they treat the correlation between the positions of the two electrons. The valence bond function (Eq. 6.74) is highly correlated. For $R \gg R_e$, ψ_{VB} is negligibly small unless the two electrons are near different nuclei; as we pointed out in connection with Eq. 6.51, this indeed describes the correct long-range behavior. But even at values of R near R_e , ψ_{VB} is quite small whenever the two electrons are close to each other.¹⁹ In contrast to this, the ionic terms in Eq. 6.73 ensure that ψ_{MO} has appreciable magnitude even when both electrons are near the same nucleus. In fact, writing ψ as an orbital product explicitly assumes that there is *no* Coulombic correlation between the electrons. (On the other hand, both wave functions do contain what we have called exchange correlations between electrons of the same spin, as a direct result of the wave functions’ being antisymmetric.) So one approximation to the singlet state contains no Coulombic correlation, whereas the other assumes strong correlation that becomes absolute at long range. A naive but sensible guess would say that the true extent of correlation is somewhere between these extremes.

¹⁹ Each term in the VB function has the form $e^{-\alpha r_{1A}}e^{-\alpha r_{2B}}$, or its equivalent with 1 and 2 exchanged. If the nuclei are not close together, then at any point space either r_A or r_B (or both) must be large, and the corresponding $e^{-\alpha r}$ small. So if both electrons are near the same point, at least one of the factors in $e^{-\alpha r_{1A}}e^{-\alpha r_{2B}}$ is small.

Assuming that this is so, can we devise a wave function intermediate between the two extreme representations? This is quite easy to do. If we define

$$\begin{aligned}\psi_{\text{covalent}} &\equiv 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2), \\ \psi_{\text{ionic}} &\equiv 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2),\end{aligned}\quad (6.75)$$

then it is immediately clear that both ψ_{MO} and ψ_{VB} are of the form

$$\psi_{\text{mixed}} = a(R)\psi_{\text{covalent}} + b(R)\psi_{\text{ionic}}, \quad (6.76)$$

where $a(R)$ and $b(R)$ are constants for any given value of R . In the MO approximation we impose the condition $a(R) = b(R)$; in the VB approximation we set $b(R) = 0$. But in accord with the variation principle, we can obviously obtain a better wave function by varying the ratio of $a(R)$ to $b(R)$ until $E(R)$ is minimized. As usual, the more variable parameters one introduces into the wave function, the more closely one can approximate the true solution of the Schrödinger equation. The results of this calculation are shown in Fig. 6.10 as curve 6 (using normal atomic orbitals) and curve 7 (using scaled atomic orbitals). The latter gives $R_e = 1.415a_0$ (0.749 Å), $D(e) = 0.1470$ hartree (4.00 eV), our closest approach yet to the true values. The ratio $b(R)/a(R)$ for curve 7 is 0.256 at R_e , and of course approaches zero as $R \rightarrow \infty$.

We are still a long way from the true wave function, but already we have gone beyond the simple MO and VB approaches. However, one can extend the language of either method to cover mixed functions like Eq. 6.76. In VB language, one describes the wave function as a linear combination of functions corresponding to hypothetical "structures," a structure being a particular arrangement of electrons and bonds. Thus ψ_{covalent} describes the covalent structure written as H:H or H—H, ψ_{ionic} is a combination of the ionic structures $H_A^+H_B^-$ and $H_A^-H_B^+$ (which must be equally likely), and ψ_{mixed} combines all three structures.

We can also reach Eq. 6.76 by an extension of the MO method. In the LCAO approximation, the ground state is one in which both electrons are in the orbital $1\sigma_g$, defined by Eq. 6.33 as a sum of $1s$ orbitals. But the difference of the same atomic orbitals gives rise to the excited (and antibonding) orbital $1\sigma_u$, defined by Eq. 6.34. Consider a state in which both electrons are in the orbital $1\sigma_u$. The LCAO molecular wave function, corresponding to Eq. 6.48, is then

$$\begin{aligned}\psi_{\text{MO}}[(\sigma_u 1s)^2] &= \frac{[1s_A(1) - 1s_B(1)][1s_A(2) - 1s_B(2)]}{2(1 + S_{AB})} \\ &\quad \times \frac{[\alpha(1)\beta(2) - \alpha(2)\beta(1)]}{\sqrt{2}}.\end{aligned}\quad (6.77)$$

As in the ground state, the spatial function is symmetric in the electrons, so the spin function must be antisymmetric. Expanding the spatial function as in Eq. 6.73, we have

$$\begin{aligned}\psi_{\text{MO,spat}}[(\sigma_u 1s)^2] &= \frac{[1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) - 1s_A(1)1s_B(2) - 1s_B(1)1s_A(2)]}{2(1 + S_{AB})} \\ &= \frac{\psi_{\text{ionic}} - \psi_{\text{covalent}}}{2(1 + S_{AB})},\end{aligned}\quad (6.78)$$

which is again of the form of Eq. 6.76. Like the ground state, the state described by Eq. 6.77 is $^1\Sigma_g$, the product of two odd (u) functions giving an even (g) function. Since functions 6.58 and 6.77 have the same electronic symmetry, either *could* describe the ground state—and so, of course, could any linear combination of the two,

$$\begin{aligned}\psi_{\text{MO,mixed}} &= x(R)\psi_{\text{MO}}[(\sigma_g 1s)^2] \\ &\quad + y(R)\psi_{\text{MO}}[(\sigma_u 1s)^2].\end{aligned}\quad (6.79)$$

We can again improve the wave function by varying the ratio $x(R)/y(R)$ to minimize $E(R)$. But substitution of Eqs. 6.73 and 6.78 in Eq. 6.79 gives

$$\begin{aligned}\psi_{\text{MO,mixed}} &= \frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{2\sqrt{2}(1 + S_{AB})} \\ &\quad [x(R)(\psi_{\text{ionic}} + \psi_{\text{covalent}}) + y(R)(\psi_{\text{ionic}} - \psi_{\text{covalent}})] \\ &= \frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{2\sqrt{2}(1 + S_{AB})} \\ &\quad \{[x(R) + y(R)]\psi_{\text{ionic}} + [x(R) - y(R)]\psi_{\text{covalent}}\} \\ &= a'(R)\psi_{\text{covalent}} + b'(R)\psi_{\text{ionic}},\end{aligned}\quad (6.80)$$

an equation of the same form as Eq. 6.76. So since ψ_{covalent} and ψ_{ionic} are exactly the same functions in both cases, the variation to minimize $E(R)$ must give identical results in both cases: $a(R) = a'(R)$, $b(R) = b'(R)$. Thus the mixed wave function obtained is the same whether it is derived according to Eq. 6.76 or Eq. 6.79. It is purely a matter of taste and convenience which form one chooses for computation.

In MO language, a wave function like Eq. 6.79 or Eq. 6.80 is said to involve *configuration interaction* (CI). A "configuration" here has the same meaning as in our theory of atomic structure,²⁰ a particular distribution of electrons among orbitals. In this case our ground-state wave function is a mixture of the two configurations $(\sigma_g 1s)^2$ and $(\sigma_u 1s)^2$. One can improve the wave function still further by adding

²⁰ One can also carry out CI calculations on atoms, writing the total wave function as a sum of determinantal functions. This is the usual way of improving on the ordinary SCF calculations. As we saw in Chapter 5, however, the single-configuration model works rather well for atoms—at least for those with closed shells or a single electron outside closed shells.

additional configurations, as long as they have the correct symmetry properties. Given enough configurations, one may approach arbitrarily close to the true wave function, although after the first few important configurations are included, this convergence is usually rather slow. One is not restricted to LCAO orbitals, of course, and it is possible to define other orbitals that give more rapid convergence.

With orbitals chosen to give the most rapid convergence of a CI series, the so-called *natural* orbitals, the wave function for H_2 accounts for over 90% of the energy associated with electron correlation.²¹ By using wave functions containing the interelectronic distance explicitly, it is possible to predict energies of dissociation and ionization for H_2 that lie within about 10^{-4} eV or less of the experimental values.²²

There were, for a period, extended controversies over whether MO or VB wave functions were better for any particular molecule. In retrospect these arguments lose their force, because the two methods converge with the next approximation. This was recognized very early, of course, but for molecules larger than H_2 people thought, until the mid-1950s, that the next level would be too difficult to carry out. Since about 1960, however, computers have made quite extensive CI calculations feasible. Yet there are still many instances—in large molecules, or when only an approximate result is needed—in which the simple MO and VB approximations are used. Each has its advantages, and we shall use both approaches in the next few chapters. The simple VB method gives more accurate results in cases where correlation is very important; the MO calculations are much easier, and offer convenient ways to interpret spectra and bonding pictorially. Excited states are quite awkward to handle by VB methods. The “structures” of the VB method are easily visualizable chemical species, so that one can often use “chemical intuition” to guess the properties of the ground states of molecules that involve several such structures. Used naively, the VB method can cause misunderstandings because one can, in general, draw many more “structures” than the number of independent wave functions. Moreover the functions that represent different “structures” in the sense of representing each bond by a pair of electrons with opposite spins, are almost never orthogonal to one another. This means that different “structures” do not represent different, mutually-exclusive states. On the side of the MO method, electronic spectra are more easily interpreted in terms of single-electron transitions between molecular

orbitals. The choice of method thus depends on what one wants to know, how accurate a result one wants, and how much work one is prepared to do.

Before leaving the ground state of H_2 , we should say something about the most accurate calculations that have been performed. The best available CI calculations account for only about 97% of the correlation energy. One can do better by writing a function that explicitly contains electron correlation in the form of r_{12} terms, like Eq. 5.14 for the He atom. Given enough adjustable parameters to vary, one can get quite close to the true $E(R)$ curve, and thus presumably to the true wave function. Curve 8 of Fig. 6.10 was obtained by varying an 11-parameter function. Calculations have been made with as many as 50 parameters, giving an $E(R)$ curve that is correct within experimental error. Just as in atoms, unfortunately, it is impractical to extend calculations of this type to more than a few electrons.

6.10 H_2 : Excited Electronic States

Thus far we have examined in detail only the ground state of the H_2 molecule. We have mentioned two excited states: the $^3\Sigma_u$ state whose VB approximation is given by Eqs. 6.69–6.71, and the $^1\Sigma_g$ state whose MO approximation is given by Eq. 6.77. In this section we shall consider the excited states of H_2 more systematically; $E(R)$ curves for the ground state ($X^1\Sigma_g^+$) and several excited states are given in Fig. 6.11.²³

To begin with, let us find the MO representation of the first excited state. This is obviously a state in which one electron is in the lowest-energy orbital, $\sigma_g 1s$, whereas the other electron is in the lowest excited orbital, $\sigma_u 1s$. Previously we have considered the configurations $(\sigma_g 1s)^2$ (the ground state) and $(\sigma_u 1s)^2$, both of which can give only singlet states. The exclusion principle tells us that if both electrons are in the same orbital they must have opposite spins, giving $S = 0$. However, for the configuration $(\sigma_g 1s)(\sigma_u 1s)$ both singlet and triplet states are possible. The symmetries of these states follow the same rules as we developed in Section 6.8: The singlet state has a symmetric spatial function and antisymmetric spin function, the triplet states the reverse. The singlet state is thus represented by

$$\begin{aligned}\psi_1 [(\sigma_g 1s)(\sigma_u 1s)] \\ = C_1 [\sigma_g 1s(1)\sigma_u 1s(2) + \sigma_g 1s(2)\sigma_u 1s(1)] \\ [\alpha(1)\beta(2) - \alpha(2)\beta(1)],\end{aligned}\quad (6.81)$$

²¹ S. Hagstrom and H. Shull, *Rev. Mod. Phys.* **35**, 624 (1963); E. R. Davidson and L. L. Jones, *J. Chem. Phys.* **37**, 2966 (1962); W. D. Lyons and J. O. Hirschfelder, *J. Chem. Phys.* **46**, 1788 (1967).

²² W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **41**, 3663, (1964); **43**, 2429 (1965); **49**, 404 (1968); **51**, 1417 (1969); **45**, 509 (1966); **48**, 3672 (1968); *Chem. Phys. Lett.* **24**, 457 (1974).

²³ The superscript + in the Σ term symbols means that the wave function is unchanged by reflection in a plane containing the internuclear axis. We shall say more about this symmetry property in the next chapter.

and the triplet state by

$$\begin{aligned}
 \psi_2[(\sigma_g 1s)(\sigma_u 1s)] &= C_2[\sigma_g 1s(1)\sigma_u 1s(2) - \sigma_g 1s(2)\sigma_u 1s(1)]\alpha(1)\alpha(2), \\
 \psi_3[(\sigma_g 1s)(\sigma_u 1s)] &= C_3[\sigma_g 1s(1)\sigma_u 1s(2) - \sigma_g 1s(2)\sigma_u 1s(1)]\beta(1)\beta(2), \\
 \psi_4[(\sigma_g 1s)(\sigma_u 1s)] &= C_4[\sigma_g 1s(1)\sigma_u 1s(2) - \sigma_g 1s(2)\sigma_u 1s(1)] \\
 &\quad [\alpha(1)\beta(2) + \alpha(2)\beta(1)]. \quad (6.82)
 \end{aligned}$$

These functions are analogous to Eqs. 6.68–6.71, but with the atomic orbitals of the latter replaced by molecular orbitals. In fact, if we expand the spatial part of Eqs. 6.82 in atomic orbitals, we obtain

$$\begin{aligned}
 &\sigma_g 1s(1)\sigma_u 1s(2) - \sigma_g 1s(2)\sigma_u 1s(1) \\
 &\quad [1s_A(1) + 1s_B(1)][1s_A(2) - 1s_B(2)] \\
 &\quad - [1s_A(2) + 1s_B(2)][1s_A(1) - 1s_B(1)] \\
 &= \frac{2(1 + S_{AB})}{1 + S_{AB}}, \quad (6.83)
 \end{aligned}$$

which differs only by a constant multiplier from the spatial part of Eqs. 6.69–6.71; all the “ionic” terms like $1s_A(1)1s_A(2)$ cancel out. In short, for the first excited state of H₂ the simplest MO and VB wave functions turn out to be identical.

As we pointed out earlier, this first excited state has the symmetry ${}^3\Sigma_u$. Its $E(R)$ curve, labeled $b\ {}^3\Sigma_u^+$ in Fig. 6.11, is everywhere repulsive. Like the ground state it gives $H(1s) + H(1s)$ in the limit $R \rightarrow \infty$. The repulsive nature of this state is vividly exhibited by a hydrogen discharge lamp, the ultraviolet light from which consists largely of continuous radiation. Any state with a minimum in the potential energy curve is a bound state, and thus has quantized energy levels (in this case vibrational–rotational energy levels, which we shall discuss in the next chapter); but a state with no minimum is free and unquantized. Electrons dropping from higher orbitals into the $\sigma_u 1s$ orbital to give this triplet state thus produce continuous emission.

What about the singlet state represented by $(\sigma_g 1s)(\sigma_u 1s)$? If we expand the spatial part of Eq. 6.81 in atomic orbitals, we obtain

$$\begin{aligned}
 &\sigma_g 1s(1)\sigma_u 1s(2) + \sigma_g 1s(2)\sigma_u 1s(1) \\
 &= \frac{1s_A(1)1s_A(2) - 1s_B(1)1s_B(2)}{1 + S_{AB}}, \quad (6.84)
 \end{aligned}$$

here the “covalent” terms cancel out, and we have the odd-parity equivalent of the ψ_{ionic} of Eq. 6.75. This state has the

symmetry ${}^1\Sigma_u$ and is labeled $B\ {}^1\Sigma_u^+$ in Fig. 6.11. Its energy is relatively high: Eq. 6.84 predicts that it should give $H^-(1s^2) + H^+$ in the long-range limit. Actually, it gives $H(1s) + H(2s)$, the energy of which is lower than that of two ions, but still quite high. Nevertheless, there is a minimum in the $E(R)$ curve, so that this configuration can exist as a stable excited state.

As for the ${}^1\Sigma_g$ state whose simplest MO representation is the doubly excited $(\sigma_u 1s)^2$, its energy is obviously still higher. The simple MO expansion (Eq. 6.78) again gives the wrong energy as $R \rightarrow \infty$, in fact the same wrong energy as we obtained for the ground state. The lowest excited ${}^1\Sigma_g$ state actually has two minima in the $E(R)$ curve, which appear spectroscopically to be distinct states (since each has its own set of vibrational–rotational levels); these are labeled $E\ {}^1\Sigma_g^+$ and $F\ {}^1\Sigma_g^+$ in Fig. 6.11. A single MO configuration cannot give a complicated curve like this; a much better representation is obtained by taking a mixture of the configurations $(\sigma_g 1s)(\sigma_g 2s)$ and $(\sigma_u 1s)^2$. If we wrote such a wave function in a form like Eq. 6.79, we would find that the coefficients $x(R)$ and $y(R)$ are rather rapidly varying functions of R . States of this type are fairly rare and can be considered as pathological cases. In most such cases, including this one, the outer minimum is described by a wave function with a large amount of ionic character—in this case the configuration $(\sigma_u 1s)^2$ which like $(\sigma_g 1s)^2$ is half “ionic” at long range.

We have now described the ground state and three excited states (one of them a triplet), and these are only the states that can be constructed from $1s$ atomic orbitals. This by no means exhausts the excited states of the H₂ molecule; there are, in fact, an infinite number of such states. Obviously we can also construct molecular states from H atoms one or both of which are themselves in excited states. Each combination of atomic orbitals can give two or more distinct molecular wave functions, corresponding to all the possible symmetric and antisymmetric combinations of electrons and nuclei.²⁴ Thus there are many more possible electronic states

²⁴ For example, consider the states formed from $H(1s) + H(2s)$. There are four possible spatial wave functions, which in the valence bond approximation can be written:

$$\begin{aligned}
 &1s_A(1)2s_B(2) + 1s_A(2)2s_B(1) + 1s_B(1)2s_A(2) + 1s_B(2)2s_A(1) \\
 &\quad (\text{symmetric in both electrons and nuclei, } {}^1\Sigma_g), \\
 &1s_A(1)2s_B(2) - 1s_A(2)2s_B(1) + 1s_B(1)2s_A(2) - 1s_B(2)2s_A(1) \\
 &\quad (\text{symmetric in nuclei, antisymmetric in electrons, } {}^3\Sigma_g), \\
 &1s_A(1)2s_B(2) + 1s_A(2)2s_B(1) - 1s_B(1)2s_A(2) - 1s_B(2)2s_A(1) \\
 &\quad (\text{symmetric in electrons, antisymmetric in nuclei, } {}^1\Sigma_u), \\
 &1s_A(1)2s_B(2) - 1s_A(2)2s_B(1) - 1s_B(1)2s_A(2) + 1s_B(2)2s_A(1) \\
 &\quad (\text{antisymmetric in both electrons and nuclei, } {}^3\Sigma_u).
 \end{aligned}$$

Each of these describes a physically distinct state of the molecule (three degenerate states for the triplets).

of the molecule than of the H atom. Of course, only a limited number of the excited states have actually been observed, and not all of those have been fully analyzed.

To the extent that the molecular orbital approximation is valid, we can speak of singly and doubly excited states of H_2 , the singly excited states being those in which one electron remains in the lowest ($1\sigma_g$) orbital. We have seen that the first excitation requires a large amount of energy, even for the lowest stable excited states. Just as in the helium atom (Section 5.3), a doubly excited state would have an energy well above the ionization limit, which in this case is the ground-state energy of $\text{H}_2^+ + e^-$. On the scale of Fig. 6.11, the minimum in the H_2^+ $E(R)$ curve lies at +0.397 hartree. Since all the stable singly excited states have energies not much below this,²⁵ one would expect them to bear some resemblance to the H_2^+ molecule-ion. In fact the $1\sigma_g$ orbital is very like the H_2^+ wave function, extending over a quite small region of space around the nuclei, whereas the excited electron occupies a very large orbital, which must resemble an excited orbital of the helium atom.²⁶ The higher the excitation, the less the orbitals overlap and the better the orbital approximation works. In effect, one has an H_2^+ ion with an electron orbiting it at long range. A highly excited electron must see the H_2^+ core as something close to a point charge. The orbital energies are then given reasonably well by a "Rydberg formula" like Eq. 2.68, and we speak of these highly excited states as molecular *Rydberg states*. There must be an infinite number of Rydberg states for any molecule having a stable molecule-ion like H_2^+ . The excited electron is far from the nuclei, so it has very little effect on the

bonding force between them. Thus the $E(R)$ curves for excited states of H_2 are often quite similar to that for H_2^+ , as can be seen by comparing Figs. 6.6 and 6.11.

What about the doubly excited states, in which both electrons are energized? Not just for H_2 but for most molecules, doubly excited states generally have energies higher than the energy needed to remove a single electron. In the case of H_2 , this means that the excited state has an energy higher than at least some states of H_2^+ . Such an excited state can thus lose energy by getting rid of (ionizing) one of its electrons, the excess energy becoming kinetic energy of the ionized electron. This process is called *autoionization* or *preionization*,²⁷ and normally takes place with no emission of radiation. Autoionization thus competes with the various kinds of radiative transitions (Section 4.5) as a way for some excited states to decay. Although the relative efficiency of these decay processes varies widely with the states involved, it is clear that the possibility of autoionization shortens the lifetime of an excited state. In practice, it is mostly doubly excited states that can undergo autoionization, and many such states have very short lifetimes ($\approx 10^{-11} - 10^{-12}\text{s}$) compared with typical singly excited states ($10^{-7} - 10^{-8}\text{s}$). When it can occur, ionization is usually the mode selected by an excited molecule or atom to relieve itself of excess energy.

This completes our discussion of the electronic states of the H_2 molecule. But each of these states encompasses many vibrational and rotational energy levels. In the next chapter we investigate these levels and the spectra to which they give rise, and we extend our analysis to diatomic molecules more complicated than H_2 .

²⁵ Those shown in Fig. 6.11 have $E(\infty) = +0.375$ hartree, corresponding to $\text{H}(1s) + \text{H}(2s \text{ or } 2p)$, whereas H_2^+ has $E(\infty) = +0.500$ hartree, corresponding to $\text{H}(1s) + \text{H}^+ + e^-$.

²⁶ As we pointed out for H_2^+ , highly excited states are best described in terms of the united-atom limit. The united-atom, descriptions of the states in Fig. 6.11 are as follows (cf. Fig. 6.8):

$X^1\Sigma_g^+$	$E^1\Sigma_g^+$	$a^3\Sigma_g^+$	$B^1\Sigma_u^+$	$b^3\Sigma_u^+$	$c^1\Pi_u$	$c^3\Pi_u$
$(1s\sigma_g)^2$	$(1s\sigma_g)$	$(2s\sigma_g)$	$(1s\sigma_g)$	$(2p\pi_u)$	$(1s\sigma_g)$	$(2p\pi_u)$

²⁷ The corresponding process in excited atoms is called the *Auger effect*.

Orthogonality

The concept of orthogonality is a generalization of the geometric concept of perpendicularity. Two vectors **a** and **b** with real components are perpendicular, or orthogonal, if their scalar product is zero:

$$\begin{aligned}\mathbf{a} \cdot \mathbf{b} &= a_x b_x + a_y b_y + a_z b_z \\ &= |\mathbf{a}| |\mathbf{b}| \cos \theta_{ab} \\ &= 0 \quad \text{if and only if (iff) } \mathbf{a} \text{ and } \mathbf{b} \text{ are orthogonal. (6A.1)}\end{aligned}$$

The first of these equations suggests (but does not prove) that the two vectors have no basis vectors in common. The value of a scalar product is independent of the choice of orientation of the coordinate system. If **a** and **b** are orthogonal, one can always choose an orientation for the coordinate system so that **a** and **b** have no common basis vectors; for example, **a** and **b** can be chosen to lie along the *x* and *y* axes.

The generalization of orthogonality from ordinary vectors in three-dimensional space to vectors in an *n*-dimensional abstract space is straightforward: If $\mathbf{a} = \{a_1, a_2, \dots, a_n\}$ and $\mathbf{b} = \{b_1, b_2, \dots, b_n\}$, then $\mathbf{a} \cdot \mathbf{b} = a_1 b_1 + a_2 b_2 + \dots + a_n b_n$; **a** and **b** are orthogonal iff $\mathbf{a} \cdot \mathbf{b} = 0$. If the components of the vectors are complex numbers instead of real numbers, then one writes $\mathbf{a} \cdot \mathbf{b} = a_1^* b_1 + \dots + a_n^* b_n$ for the scalar product. Again, if **a** and **b** are orthogonal, they are built from different, mutually exclusive sets of basis vectors of the space.

To generalize the idea of orthogonality from vectors to functions we replace the summation $a_1 b_1 + \dots + a_n b_n$ with an integration over the continuous variable or variables of the functions. Thus, if $\phi_A(x)$ and $\phi_B(x)$ are real and exist for $-\infty < x < \infty$, then the equivalent of the scalar product of ϕ_A and ϕ_B is the integral of their product over the range of their argument. If *x* ranges from $-\infty$ to ∞ ,

$$S_{AB} = \int_{-\infty}^{\infty} \phi_A(x) \phi_B(x) dx. \quad (6A.2)$$

If $\phi_A(x)$ and $\phi_B(x)$ are complex and $-\infty < x < \infty$, then we write, for the equivalent of their scalar product, Eq. 6.30:

$$S_{AB} = \int_{-\infty}^{\infty} \phi_A^*(x) \phi_B(x) dx \quad (6.30)$$

The functions $\phi_A(x)$ and $\phi_B(x)$ are orthogonal if and only if $S_{AB} = 0$.

Sometimes the range of the argument is finite. For example, consider $\phi_A = \sin mx$ and $\phi_B = \sin nx$, for $0 \leq x \leq 2\pi$:

$$\begin{aligned}S_{AB} &= \int_0^{2\pi} \sin mx \sin nx dx = 0 \quad \text{if } m \neq n, \\ &= \frac{1}{2} \quad \text{if } m = n, \quad (6A.3)\end{aligned}$$

so $\sin mx$ and $\sin nx$ are orthogonal on the interval $0 \leq x \leq 2\pi$.

The second equality of Eq. 6A.1 shows that $\mathbf{a} \cdot \mathbf{b}$ is the projection of the vector **a** on the vector **b**, which, as the first equality shows, is the same as the projection of **b** on **a**. We can likewise think of Eq. 6A.1 or Eq. 6.30 as the projection of function ϕ_A on ϕ_B . The projection of one vector or function on another is the same, geometrically, as the overlap of one vector or function with the other. But the overlap of functions has a physical interpretation that goes beyond the simple geometric model. In physical terms, if two functions representing states of a system are orthogonal, then the states are mutually exclusive: A 1*s* state and a 2*s* state of the hydrogen atom represent two mutually exclusive states of that atom. The wave functions ψ_0 and ψ_1 of Eqs. 6.26 and 6.27 or 6.33 and 6.34 are orthogonal, and correspond to mutually exclusive states of an electron in the H_2^+ molecule.

Hermitian Operators

In Section 3.8, Postulate III supposes that every variable of classical mechanics can be represented by a linear mathematical operator. The statement of that postulate now needs to be made a bit stricter: To every variable of classical mechanics there corresponds a linear *Hermitian* operator (after the French mathematician of the nineteenth century, Charles Hermite). The reason: Hermitian operators have two properties that we would like observables to exhibit. For Hermitian operators, the eigenvalues, which correspond to the values the property can assume (Postulate IV), are *real*, and the eigenfunctions corresponding to different eigenvalues are *orthogonal*. Thus the observables are real rather than complex numbers, as we want them to be, and, from the interpretation of orthogonality in Appendix 6A, the eigenstates with different eigenvalues must be mutually exclusive states of the system.

An operator R is Hermitian iff (if and only if)

$$\int \phi_A^* R \phi_B d\tau = \int (R \phi_A)^* \phi_B d\tau. \quad (6B.1)$$

To give this a physical interpretation, note that $R\phi_B$ is some new function ϕ_C , corresponding to the state of the system initially described by ϕ_B but then acted upon by the process represented by the operator R . Hence $\int \phi_A^* R \phi_B d\tau$ is the projection of the state of the system in state C , represented by ϕ_C , onto the state A , represented by ϕ_A . If C and A are mutually exclusive, $\int \phi_A^* \phi_C d\tau \equiv \int \phi_A^* R \phi_B d\tau = 0$; otherwise A and C share some aspects and have nonzero overlap.

The state represented by $R\phi_A$ corresponds to a system initially in A and then acted upon by the operation corresponding to the operator R . Call this state D , and represent it with ϕ_D . Then $\int (R\phi_A)^* \phi_B d\tau$ is the same as $\int \phi_D^* \phi_B d\tau$, the projection or overlap of state B onto state D . The operator R is Hermitian if the projection of C on A , $\int \phi_A^* \phi_C d\tau$, is the same as the projection of B on D , $\int \phi_D^* \phi_B d\tau$. In other words, an operator is Hermitian if and only if the same result occurs (but with proper allowance for complex conjugation, where $\sqrt{-1}$ appears) whether the operation R is performed on B and the result is projected onto A , or B is projected onto the result of performing R on A .

Let us show that the eigenvalues of a Hermitian operator are real. If Eq. 6B.1 holds and if $R\phi_A = R_A\phi_A$, so ϕ_A is an eigenfunction of R , then

$$\begin{aligned} \int \phi_A^* R \phi_A d\tau &= R_A \int \phi_A^* \phi_A d\tau \\ &= \int (R \phi_A)^* \phi_A d\tau = R_A^* \int \phi_A^* \phi_A d\tau. \end{aligned} \quad (6B.2)$$

so $R_A = R_A^*$ and R_A must be real. Similarly, if $R\phi_B = R_B\phi_B$, so that both ϕ_A and ϕ_B are eigenfunctions of R , and if $R_A \neq R_B$, then $\int \phi_A^* \phi_B d\tau = 0$, since

$$\begin{aligned} \int \phi_A^* R \phi_B d\tau &= R_B \int \phi_A^* \phi_B d\tau \\ &= \int (R \phi_A)^* \phi_B d\tau = R_A \int \phi_A^* \phi_B d\tau. \end{aligned} \quad (6B.3)$$

The equalities of 6B.3 can hold only if the overlap integral of ϕ_A and ϕ_B vanishes. Therefore the Hermitian operators do indeed have eigenvalues that are real and can correspond to observable properties, and the physical states corresponding to different observable values, that is, to different eigenvalues, are mutually exclusive.

FURTHER READING

- Herzberg, G., *Molecular Spectra and Molecular Structure, Volume I, Spectra of Diatomic Molecules*, 2nd Ed. (Van Nostrand Reinhold, New York, 1950).
- Hurley, A. C., *Introduction to the Electron Theory of Small Molecules* (Academic, London, 1976).
- Karplus, M., and Porter, R. N., *Atoms and Molecules* (Benjamin, Menlo Park, Calif., 1970), esp. Chapters 5, 6 and 7.
- Kauzmann, W., *Quantum Chemistry* (Academic, New York, 1957), Chapter 11A, B.
- Kondratyev, V., *The Structure of Atoms and Molecules* (Noordhoff, Groningen, The Netherlands, 1964), Chapter 7.
- Mulliken, R. S., and Ermler, W. C., *Diatomic Molecules, Results of ab initio Calculations* (Academic, New York, 1977), esp. Chapters I–III.
- Slater, J. C., *Quantum Theory of Molecules and Solids, Volume I* (McGraw-Hill, New York, 1963), esp. Chapters 1–4.

PROBLEMS

1. In making the Born–Oppenheimer approximation, one supposes that the molecular wave function is separable

- (Eq. 6.2), and thus that the electronic wave function $\psi_{\text{elec}}(r; R)$ is an eigenfunction of an electronic Hamiltonian H_{elec} for each fixed R . If one supposes that R is a quantum mechanical variable, then H_{nuc} can act on $\psi_{\text{elec}}(r; R)$ as well as on $\psi_{\text{nuc}}(R)$. When $\psi(r; R)$ is separable but H_{nuc} is allowed to act on ψ_{elec} , what terms occur in $\int \psi^*(r; R) H \psi(r; R) d\tau$ that do not appear if H_{nuc} is only allowed to act on $\psi_{\text{nuc}}(R)$?
- The binding energy of the deuteron, ${}^2\text{H}$ (D), is 2.2 MeV. The binding energy of the α particle is approximately 28.5 MeV. The first ionization potential of He is 24.5 eV; the second is 54.14 eV. Using a logarithmic scale for the energy, draw a curve of the total energy, including the nuclear binding energy, for the D_2 molecule going from the equilibrium internuclear distance down to $R = 0$. Follow the nuclear repulsion up to $R \sim 10^{-6} R_e$ and sketch the rest of the curve schematically. You may wish to put R on a nonlinear scale.
 - Show that if, in the diatomic molecule AB, the nuclear charges Z_A and Z_B are unequal, with $Z_A > Z_B$, then the region far enough from the molecule and out beyond B is a bonding region. At what distance beyond B is any electronic charge on the internuclear axis exactly non-bonding?
 - Construct the surfaces on which the bonding force is zero for the diatomic molecule LiF, that is, for $Z_A = 3$, $Z_B = 9$.
 - Figure 6.3 shows contours on which the bonding force of Eq. 6.8 is zero. For the system of two protons, calculate enough points to sketch contours for curves on which the bonding force is not zero; develop the curves for two negative (antibonding) values of F_{bonding} and two positive values of F_{bonding} . Express your values in terms of $F_{\text{bonding}} \times (4\pi\epsilon_0/eq)$; give the value of $(4\pi\epsilon_0/eq)$, so a reader could translate your plot into SI units of force. (Eliminate one distance, r_A or r_B and one cosine, $\cos \theta_A$ or $\cos \theta_B$, from Eq. 6.8. You may want to use a programmable calculator or computer to map F_{bonding} , and then construct contours from the map.)
 - Compute the charge density in electrons per cubic angstrom and the expectation value of the electron's kinetic energy in the neighborhood of a nucleus and at the midpoint of the H—H axis in H_2^+ for the two normalized molecular orbitals Eqs. 6.33 and 6.34. Estimate the local kinetic energy from the slopes of the functions at their cusps and at $R/2$.
 - A proton B approaches a hydrogen atom A. At what internuclear distance R is the most probable electron-nuclear distance r_A of an undisturbed hydrogen atom equal to R ? Where is the distance R equal to the mean value of r_A ? (You may wish to look back to Chapter 4.)
 - The graphs of Fig. 6.7 show the charge density of the orbitals of Eqs. 6.33 and 6.34 along the internuclear axis. Construct similar curves for a line parallel to the internuclear axis but a distance $0.1a_0$ away from it.
 - The overlap integral of Eq. 6.30 can be evaluated easily by making the coordinate transformation $\lambda = (r_A + r_B)/R$, $\mu = (r_A - r_B)/R$.
 - Show that surfaces of constant λ are ellipses and surfaces of constant μ are hyperbolas.
 - Show that Eq. 6.33 and 6.34 take the forms

$$\psi_0 = \text{constant} \times e^{-\lambda R/2} (e^{\mu R/2} + e^{-\mu R/2})$$
 and

$$\psi_1 = \text{constant} \times e^{-\lambda R/2} (e^{\mu R/2} - e^{-\mu R/2}),$$
 or

$$\psi_0 = \text{constant} \times e^{-\lambda R/2} \cosh\left(\frac{\mu R}{2}\right)$$
 and

$$\psi_1 = \text{constant} \times e^{-\lambda R/2} \sinh\left(\frac{\mu R}{2}\right).$$
 - Show that the variable λ ranges from 1 to ∞ , and that μ ranges from -1 to $+1$.
 - Show that the overlap integral

$$S_{AB} = \frac{1}{\pi} \int_{\text{all space}} e^{-\alpha r_A} e^{-\alpha r_B} d\tau$$

$$= e^{-\alpha R} \left(1 + \alpha R + \frac{1}{3} \alpha^2 R^2\right).$$
 Use the fact that

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}};$$
 to evaluate the term involving $e^{-\alpha(r_A + r_B)}$, use the transformation of Problem 9 and the fact that the volume element $dx dy dz$, when transformed to the coordinates λ, μ, ϕ , is $(R^3/8)(\lambda^2 - \mu^2) d\lambda d\mu d\phi$.
 - Show that atomic orbitals follow the rule that they are even (g) with respect to their nuclei if l is zero or even,

- and odd (u) if l is odd. In an H_2^+ molecule we can construct both g and u molecular orbitals from sums and differences of $p\sigma$ orbitals on the separated atoms. Resolve this apparent paradox.
- Draw a correlation diagram connecting the orbital energies of the separated-atom limit with those of the united-atom limit for the one-electron molecule HeH^{2+} .
 - Write the analogs of Eqs. 6.58, 6.62, 6.68, and 6.69 if particles 1 and 2 are bosons.
 - What are the charge densities of the molecular orbital wave function, Eq. 6.73, and the valence bond wave function, Eq. 6.74, at the midpoint between A and B and at the nucleus A , when R has the value $1.415a_0$? Which function would you say delocalizes the charge more?
 - The molecule-ion HeH^+ has been studied both experimentally and theoretically. Its equilibrium internuclear distance is $1.4632a_0$. Construct a potential curve for the electrons along the $\text{He}-\text{H}$ axis analogous to Fig. 6.4a and indicate the energies of the ground-state ($1s$) levels of the separated atoms. Sketch the free-atom $1s$ orbitals of H and of He^+ , each centered at its appropriate nucleus. The lowest molecular orbital of HeH^+ is *not* well expressed by the form $\text{constant} \times [\phi_{\text{H}}(1s) + \phi_{\text{He}^+}(1s)]$. Explain in physical terms why the lowest state of this species contains much more of one $1s$ orbital than of the other. Which predominates? What are the energies of the orbitals of He^+ with $n = 2$? What atomic orbitals of hydrogen and of the helium ion are likely to be important in the first excited state of HeH^+ ?
 - Draw a curve of the interference term of Eq. 6.28, $2 \text{Re}(\phi_A^* \phi_B)$, for the midpoint between the two nuclei in H_2^+ , as a function of the internuclear distance R .
 - From Eqs. 6.41 and 6.42, and footnote 8 on page 223, compute the internuclear distance at which $E_0(R) = 0$, and the distances at which $E_0(R) = +1$ eV and $E_1(R) = +1$ eV. The latter correspond to the classical distances of closest approach for a proton colliding with a hydrogen atom along the $1\sigma_g$ and $1\sigma_u$ potential curves, respectively.
 - One of the dissociation limits of H_2 is the ion pair $\text{H}^+ + \text{H}^-$. Locate this dissociation limit on an energy scale, relative to the neutral states of the form $\text{H}(1s) + \text{H}(nl)$ and $\text{H}(2s) + \text{H}(nl)$. Where does the ionic curve of $-e^2/4\pi\epsilon_0 R$ fall on the diagram of Fig. 6.11? Can you associate any of the potential curves or portions of the curves of Fig. 6.11 with an electrostatic attraction $E(R)$ in Eq. 6.11?
 - If two nuclei move at a relative velocity of order 1% or more of the average speed of the electrons attached to them, one can be concerned about the validity of the adiabatic or Born–Oppenheimer approximation. What energy must a proton have, in its motion relative to a hydrogen atom, to achieve roughly 1% of the average speed of the electron in the transient H_2^+ molecule? Use the energy of the H_2^+ molecule at its equilibrium distance to estimate the electron's speed. (For a particle bound by Coulomb forces, $\langle \text{K.E.} \rangle = -\frac{1}{2} \langle \text{P.E.} \rangle$.)
 - Recall from Section 5.5 that the hydrogen atom forms a stable negative ion, H^- , and that the electron affinity of the hydrogen atom is approximately 0.75 eV. The H_2 molecule in its ground electronic and vibrational state does not form a stable negative ion. Give a physical interpretation of why no stable H_2^- can be made by attaching a slow electron to H_2 , and explain what occurs when a hydride ion (H^-) and a hydrogen atom undergo a close, slow collision. Sketch a potential curve for $\text{H}^- + \text{H}$ together with the curve for the ground state of $\text{H}^- + \text{H} + e^-$ as given in Fig. 6.11.
 - By using the curves of Fig. 6.11, assuming that electronic excitation of a molecule of H_2 in its ground state occurs from the lowest point of the ground-state potential and that neither the position nor the momentum of the nuclei can change during the excitation process, estimate the wavelengths at which one might expect to observe transitions to the $b^3\Sigma_u^+$ and the $B^1\Sigma_u^+$ states.
 - From your knowledge of the spatial dimensions of the $1\sigma_g$ orbital of H_2 and of the atomic orbitals of the hydrogen atom, estimate at approximately what principal quantum number n the excited-state orbitals of H_2 could be well represented by atomic orbitals. How will the accuracy of this representation depend on the angular momentum lh ?
 - Perform a HF–SCF calculation for the ground electronic state of H_2 to investigate the effect of the basis set representation on computed values of D_e and R_e . Use the (a) STO–3G, (b) 3–21G, and (c) 6–31G basis sets. (See Problem 5.26 for basis set descriptions and software packages.)
 - In the HF–SCF method, the wave function is represented by a single electronic configuration. In Configuration Interaction (CI) methods, the wave function is represented by a sum of different configurations. A singly-excited configuration (single excitation) is formed by promoting a single electron from an occupied orbital to a previously unoccupied orbital. A doubly excited configuration (double excitation) is

formed by promoting two electrons to previously unoccupied orbitals. The CISD method expresses the wave function as a sum of the Hartree-Fock configuration and all single and double excitations. Use the CISD method along with the (a) STO-3G, (b) 3-21G, and (c) 6-31G basis sets to calculate the values of D_e and R_e for the ground electronic state of the H_2 molecule.

25. An alternative approach (to CI) for estimating the correlation energy is perturbation theory. While perturbation theory calculations are size consistent, they are not variational (as are CI methods). Use the MP2 (second-

order Møller-Plesset perturbation theory) method along with the (a) STO-3G, (b) 3-21G, and (c) 6-31G basis sets to calculate the values of D_e and R_e for the ground electronic state of H_2 .

26. The potential energy surface (PES) of the excited electronic state $B\ ^1\Sigma_u^+$ of the hydrogen molecule possesses a minimum, which can support bound states (see Fig. 6.11). Use the CISD method along with the (a) STO-3G, (b) 3-21G, and (c) 6-31G basis sets to calculate the values of D_e and R_e for this excited electronic state of H_2 .