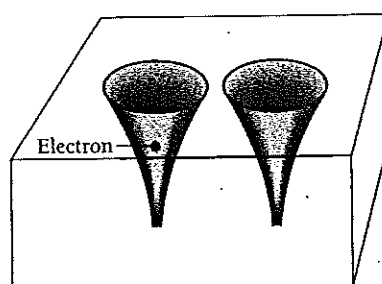


(a)



(b)

Figure 8.4 (a) Potential energy of an electron in the electric field of two nearby protons. The total energy of a ground-state electron in the hydrogen atom is indicated. (b) Two nearby protons correspond quantum-mechanically to a pair of boxes separated by a barrier.

shared by two protons is less confined than one belonging to a single proton, which means that it has less kinetic energy. The total energy of the electron in  $\text{H}_2^+$  is therefore less than that of the electron in  $\text{H} + \text{H}^+$ . Provided the magnitude of the proton-proton repulsion in  $\text{H}_2^+$  is not too great, then,  $\text{H}_2^+$  ought to be stable.

### 8.3 THE $\text{H}_2^+$ MOLECULAR ION

#### *Bonding requires a symmetric wave function*

What we would like to know is the wave function  $\psi$  of the electron in  $\text{H}_2^+$ , since from  $\psi$  we can calculate the energy of the system as a function of the separation  $R$  of the protons. If  $E(R)$  has a minimum, we will know that a bond can exist, and we can also determine the bond energy and the equilibrium spacing of the protons.

Solving Schrödinger's equation for  $\psi$  is a long and complicated procedure. An intuitive approach that brings out the physics of the situation is more appropriate here. Let us begin by trying to predict what  $\psi$  is when  $R$ , the distance between the protons, is large compared with  $a_0$ , the radius of the smallest Bohr orbit in the hydrogen atom. In this event  $\psi$  near each proton must closely resemble the 1s wave function of the hydrogen atom, as pictured in Fig. 8.5. The 1s wave function around proton  $a$  is called  $\psi_a$  and that around proton  $b$  is called  $\psi_b$ .

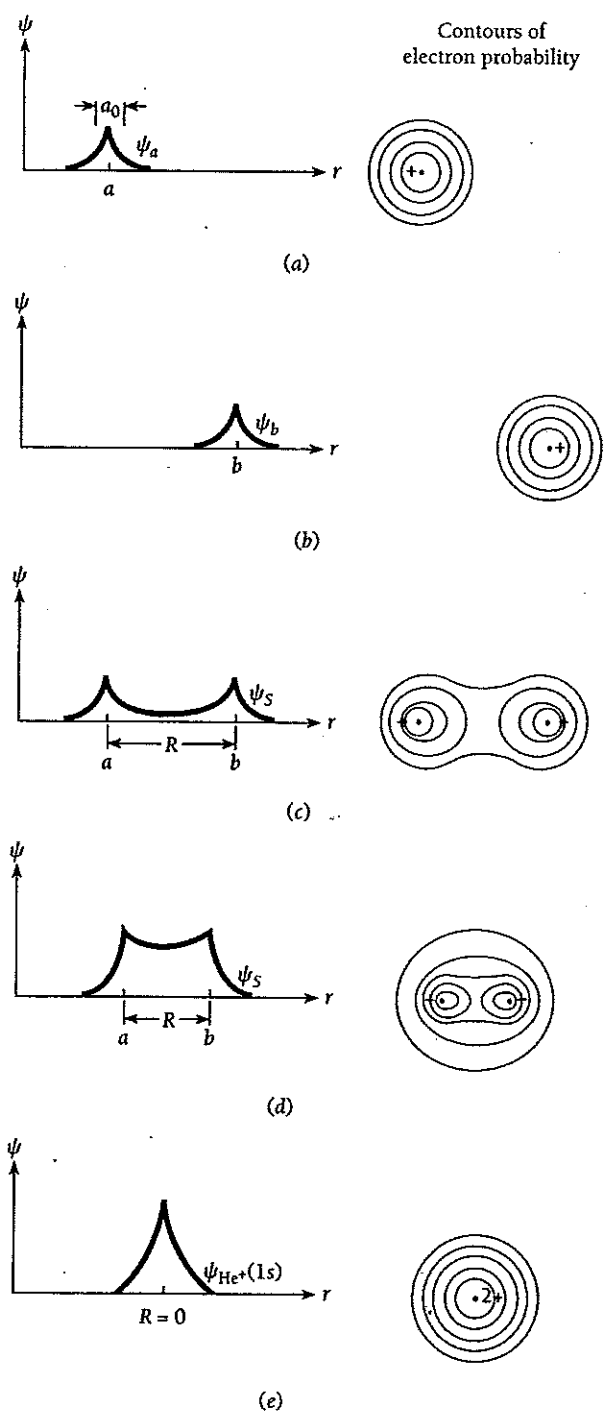


Figure 8.5 (a)–(d) The combination of two hydrogen-atom 1s wave functions to form the symmetric  $\text{H}_2^+$  wave function  $\psi_s$ . The result is a stable  $\text{H}_2^+$  molecular ion because the electron has a greater probability of being between the protons than outside them. (e) If the protons could join together, the resulting wave function would be the same as the 1s wave function of a  $\text{He}^+$  ion.

We also know what  $\psi$  looks like when  $R$  is 0, that is, when the protons are imagined to be fused together. Here the situation is that of the  $\text{He}^+$  ion, since the electron is now near a single nucleus whose charge is  $+2e$ . The  $1s$  wave function of  $\text{He}^+$  has the same form as that of  $\text{H}$  but with a greater amplitude at the origin, as in Fig. 8.5e. Evidently  $\psi$  is going to be something like the wave function sketched in Fig. 8.5d when  $R$  is comparable with  $a_0$ . There is an enhanced likelihood of finding the electron in the region between the protons, which corresponds to the sharing of the electron by the protons. Thus there is on the average an excess of negative charge between the protons, and this attracts the protons together. We have still to establish whether this attraction is strong enough to overcome the mutual repulsion of the protons.

The combination of  $\psi_a$  and  $\psi_b$  in Fig. 8.5 is symmetric, since exchanging  $a$  and  $b$  does not affect  $\psi$  (see Sec. 7.3). However, it is also conceivable that we could have an *antisymmetric* combination of  $\psi_a$  and  $\psi_b$ , as in Fig. 8.6. Here there is a node between  $a$  and  $b$  where  $\psi = 0$ , which implies a reduced likelihood of finding the electron between the protons. Now there is on the average a deficiency of negative charge between the protons and in consequence a repulsive force. With only repulsive forces acting, bonding cannot occur.

An interesting question concerns the behavior of the antisymmetric  $\text{H}_2^+$  wave function  $\psi_A$  as  $R \rightarrow 0$ . Obviously  $\psi_A$  does not become the  $1s$  wave function of  $\text{He}^+$  when  $R = 0$ . However,  $\psi_A$  *does* approach the  $2p$  wave function of  $\text{He}^+$  (Fig. 8.6e), which has a node at the origin. But the  $2p$  state of  $\text{He}^+$  is an excited state whereas the  $1s$  state is the ground state. Hence  $\text{H}_2^+$  in the antisymmetric state ought to have more energy than when it is in the symmetric state, which agrees with our inference from the shapes of the wave functions  $\psi_A$  and  $\psi_S$  that in the former case there is a repulsive force and in the latter, an attractive one.

### System Energy

A line of reasoning similar to the preceding one lets us estimate how the total energy of the  $\text{H}_2^+$  system varies with  $R$ . We first consider the symmetric state. When  $R$  is large, the electron energy  $E_S$  must be the  $-13.6\text{-eV}$  energy of the hydrogen atom, while the electric potential energy  $U_p$  of the protons,

$$U_p = \frac{e^2}{4\pi\epsilon_0 R} \quad (8.1)$$

falls to 0 as  $R \rightarrow \infty$ . ( $U_p$  is a positive quantity, corresponding to a repulsive force.) When  $R \rightarrow 0$ ,  $U_p \rightarrow \infty$  as  $1/R$ . At  $R = 0$ , the electron energy must equal that of the  $\text{He}^+$  ion, which is  $Z^2$ , or 4 times, that of the  $\text{H}$  atom. (See Exercise 35 of Chap. 4; the same result is obtained from the quantum theory of one-electron atoms.) Hence  $E_S = -54.4\text{ eV}$  when  $R = 0$ .

Both  $E_S$  and  $U_p$  are sketched in Fig. 8.7 as functions of  $R$ . The shape of the curve for  $E_S$  can only be approximated without a detailed calculation, but we do have its value for both  $R = 0$  and  $R = \infty$  and, of course,  $U_p$  obeys Eq. (8.1).

The total energy  $E_S^{\text{total}}$  of the system is the sum of the electron energy  $E_S$  and the potential energy  $U_p$  of the protons. Evidently  $E_S^{\text{total}}$  has a minimum, which corresponds to a stable molecular state. This result is confirmed by the experimental data on  $\text{H}_2^+$  which indicate a bond energy of  $2.65\text{ eV}$  and an equilibrium separation  $R$  of  $0.106\text{ nm}$ . By "bond energy" is meant the energy needed to break  $\text{H}_2^+$  into  $\text{H} + \text{H}^+$ . The *total*

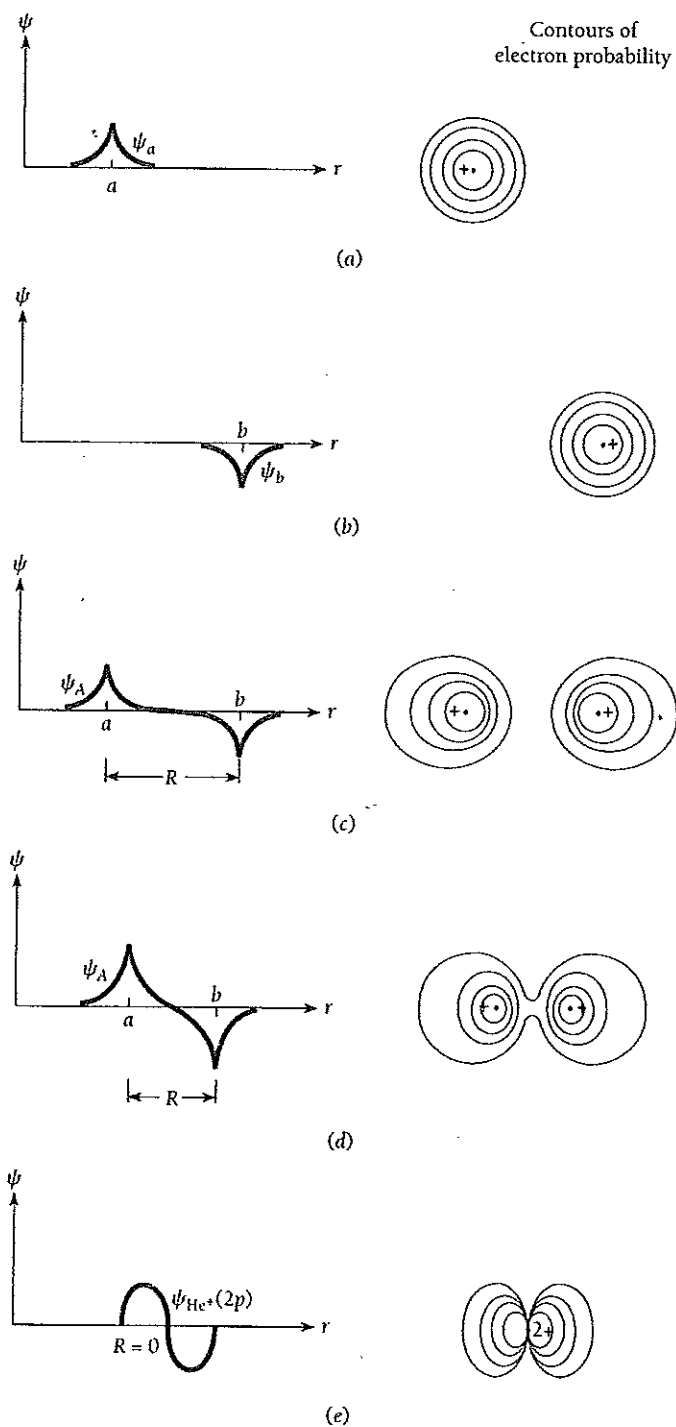


Figure 8.6 (a)–(d) The combination of two hydrogen-atom 1s wave functions to form the antisymmetric  $\text{H}_2^+$  wave function  $\psi_A$ . A stable  $\text{H}_2^+$  molecular ion is not formed because now the electron has a smaller probability of being between the protons than outside them. (e) If the protons could join together, the resulting wave function would be the same as the  $2p$  wave function of a  $\text{He}^+$  ion. In the  $2p$  state a  $\text{He}^+$  ion has more energy than in the  $2s$  state.

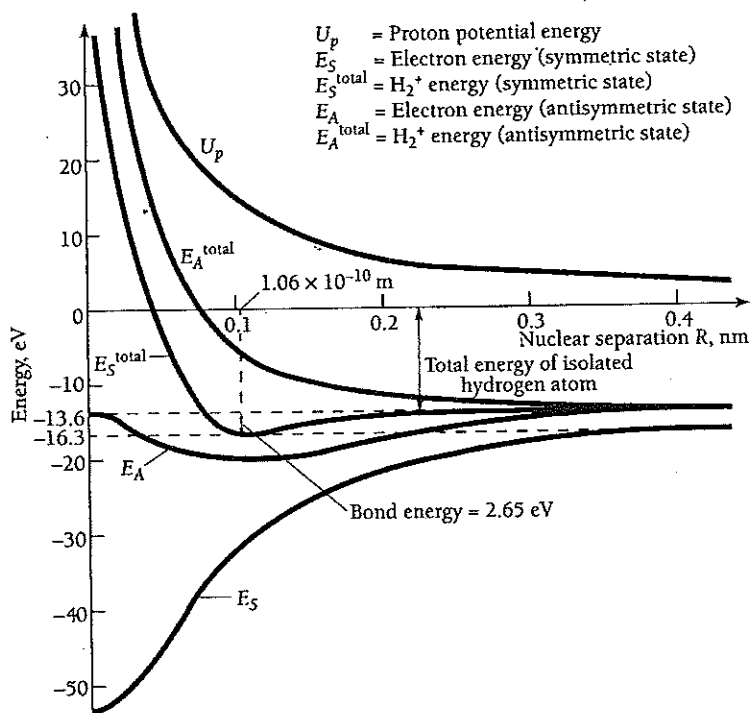


Figure 8.7 Electron, proton repulsion, and total energies in  $H_2^+$  as a function of nuclear separation  $R$  for the symmetric and antisymmetric states. The antisymmetric state has no minimum in its total energy.

energy of  $H_2^+$  is the  $-13.6$  eV of the hydrogen atom plus the  $-2.65$ -eV bond energy, or  $-16.3$  eV in all.

In the case of the antisymmetric state, the analysis proceeds in the same way except that the electron energy  $E_A$  when  $R = 0$  is that of the  $2p$  state of  $He^+$ . This energy is proportional to  $Z^2/n^2$ . With  $Z = 2$  and  $n = 2$ ,  $E_A$  is just equal to the  $-13.6$  eV of the ground-state hydrogen atom. Since  $E_A \rightarrow -13.6$  eV also as  $R \rightarrow \infty$ , we might think that the electron energy is constant, but actually there is a small dip at intermediate distances. However, the dip is not nearly enough to yield a minimum in the total energy curve for the antisymmetric state, as shown in Fig. 8.7, and so in this state no bond is formed.

## 8.4 THE HYDROGEN MOLECULE

*The spins of the electrons must be antiparallel*

The  $H_2$  molecule has two electrons instead of the single electron of  $H_2^+$ . According to the exclusion principle, both electrons can share the same orbital (that is, be described by the same wave function  $\psi_{nlm_l}$ ) provided their spins are antiparallel.

With two electrons to contribute to the bond,  $H_2$  ought to be more stable than  $H_2^+$ —at first glance, twice as stable, with a bond energy of  $5.3$  eV compared with

2.65 eV for  $H_2^+$ . However, the  $H_2$  orbitals are not quite the same as those of  $H_2^+$  because of the electric repulsion between the two electrons in  $H_2$ , a factor absent in the case of  $H_2^+$ . This repulsion weakens the bond in  $H_2$ , so that the actual energy is 4.5 eV instead of 5.3 eV. For the same reason, the bond length in  $H_2$  is 0.074 nm, which is somewhat larger than the use of unmodified  $H_2^+$  wave functions would indicate. The general conclusion in the case of  $H_2^+$  that the symmetric wave function  $\psi_S$  leads to a bound state and the antisymmetric wave function  $\psi_A$  to an unbound one remains valid for  $H_2$ .

In Sec. 7.3 the exclusion principle was formulated in terms of the symmetry and antisymmetry of wave functions, and it was concluded that systems of electrons are always described by antisymmetric wave functions (that is, by wave functions that reverse sign upon the exchange of any pair of electrons). However, the bound state in  $H_2$  corresponds to both electrons being described by a symmetrical wave function  $\psi_S$ , which seems to contradict the above conclusion.

A closer look shows that there is really no contradiction. The *complete* wave function  $\Psi(1, 2)$  of a system of two electrons is the product of a spatial wave function  $\psi(1, 2)$  which describes the coordinates of the electrons and a spin function  $s(1, 2)$  which describes the orientations of their spins. The exclusion principle requires that the complete wave function

$$\Psi(1, 2) = \psi(1, 2) s(1, 2)$$

be antisymmetric to an exchange of both coordinates and spins, not  $\psi(1, 2)$  by itself. An antisymmetric complete wave function  $\Psi_A$  can result from the combination of a symmetric coordinate wave function  $\psi_S$  and an antisymmetric spin function  $s_A$  or from the combination of an antisymmetric coordinate wave function  $\psi_A$  and a symmetric spin function  $s_S$ . That is, only

$$\Psi(1, 2) = \psi_S s_A \quad \text{and} \quad \Psi(1, 2) = \psi_A s_S$$

are acceptable.

If the spins of the two electrons are parallel, their spin function is symmetric since it does not change sign when the electrons are exchanged. Hence the coordinate wave function  $\psi$  for two electrons whose spins are parallel must be antisymmetric:

Spins parallel  $\Psi(1, 2) = \psi_A s_S$

On the other hand, if the spins of the two electrons are antiparallel, their spin function is antisymmetric since it reverses sign when the electrons are exchanged. Hence the coordinate wave function  $\psi$  for two electrons whose spins are antiparallel must be symmetric:

Spins antiparallel  $\Psi(1, 2) = \psi_S s_A$

Schrödinger's equation for the  $H_2$  molecule has no exact solution. In fact, only for  $H_2^+$  is an exact solution possible, and all other molecular systems must be treated approximately. The results of a detailed analysis of the  $H_2$  molecule are shown in Fig. 8.8 for the case when the electrons have their spins parallel and the case when their spins are antiparallel. The difference between the two curves is due to the exclusion principle, which leads to a dominating repulsion when the spins are parallel.

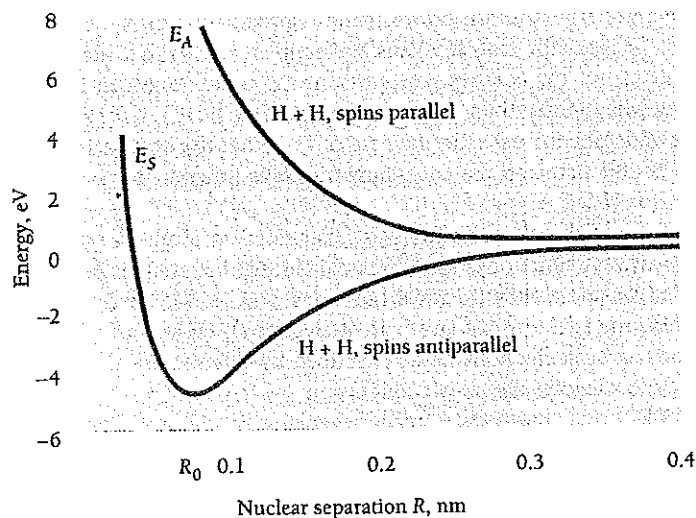


Figure 8.8 The variation of the energy of the system  $H + H$  with their distances apart when the electron spins are parallel and antiparallel.

## 8.5 COMPLEX MOLECULES

*Their geometry depends on the wave functions of the outer electrons of their atoms*

Covalent bonding in molecules other than  $H_2$ , diatomic as well as polyatomic, is usually a more complicated story. It would be yet more complicated but for the fact that any alteration in the electronic structure of an atom due to the proximity of another atom is confined to its outermost, or **valence**, electron shell. There are two reasons for this:

- 1 The inner electrons are much more tightly bound and hence less responsive to external influences, partly because they are closer to their parent nucleus and partly because they are shielded from the nuclear charge by fewer intervening electrons.
- 2 The repulsive interatomic forces in a molecule become predominant while the inner shells of its atoms are still relatively far apart.

The idea that only the valence electrons are involved in chemical bonding is supported by x-ray spectra that arise from transitions to inner-shell electron states. These spectra are virtually independent of how the atoms are combined in molecules or solids.

We have seen that two  $H$  atoms can combine to form an  $H_2$  molecule; and, indeed, hydrogen molecules in nature always consist of two  $H$  atoms. The exclusion principle is what prevents molecules such as  $He_2$  and  $H_3$  from existing, while permitting such other molecules as  $H_2O$  to be stable.

Every  $He$  atom in its ground state has a  $1s$  electron of each spin. If it is to join with another  $He$  atom by exchanging electrons, each atom will have two electrons with the same spin for part of the time. That is, one atom will have both electron spins up ( $\uparrow\uparrow$ ) and the other will have both spins down ( $\downarrow\downarrow$ ). The exclusion principle, of course,