T E N

MOLECULES

*I*n previous chapters we have studied the properties of the atom, that is, a single nucleus surrounded by a cloud of electrons. In our everyday dealings with matter, including that making up our own bodies, it would seem that such isolated atoms are rather rare and are encountered considerably less frequently than are *molecules*, which are the aggregates of two or more atoms. Indeed, all of our bodily processes, including breathing air, digesting food, and the formation of DNA in the cell, include chemical reactions that involve taking apart one molecule and recombining its constituent atoms to form other molecules. Our very existence is as inextricably linked to the nature of molecules as it is to that of atoms or nuclei.

Chemistry is the science of molecules. The various forces that hold molecules together include the covalent, ionic, and van der Waals interactions as manifestations of the *chemical bond*. All these forces are basically electromagnetic in nature but also involve, as we see in this chapter, some rather subtle quantum mechanical effects.

The simplest molecular form is the diatomic hydrogen molecular ion H_2^+, consisting of two protons and a single electron. The next in order of increasing complexity is H_2, with one more electron than H_2^+. These two molecules illustrate some of the basic principles involved in molecular structure, including in the case of H_2 the *covalent bond* in which the two nuclei "share" the two electrons equally. Other molecules, such as NaCl in which one nucleus steals an electron from the other, are held together by a somewhat different force known as the *ionic bond*. Atoms with closed shells such as argon attract each other with only a much weaker force known as the *van der Waals interaction*.

As with atoms, the most fruitful way to probe the structure of molecules is by spectroscopy. Not surprisingly, molecular spectra are often more complicated than those of atoms. This additional complexity arises because, in addition to electronic transitions, there are energy changes involving the relative motions of the nuclei that make up the molecule. Such motions are classified as *rotational* and *vibrational*. Because the rotational transitions involve relatively small energy changes, the spectra occur in characteristic groupings of very closely spaced lines called *bands*.

While the most mundane features of our lives depend on molecular processes, molecules are by no means restricted to our local environment. Astronomical observations at radio-wave frequencies have shown in recent years that molecular clouds are spread throughout the universe. Molecules that do not occur naturally on Earth have been discovered in space. Molecular clouds are found to be closely associated with regions giving birth to stars in galaxies. It would seem that molecules may be equally fundamental to our understanding of nature on every scale from the cosmological to the biological.

10-1   Binding by Quantum Tunneling: H_2^+

A molecule is a collection of two or more nuclei and their associated electrons with the whole complex bound together by electromagnetic forces. Solving the problem of a complex atom is difficult enough; here we have an even more complicated multicenter problem so that the electrons can be associated with one or more of several nuclei. To simplify the difficulties inherent in studying molecules we look primarily at the diatomic (two-atom) system. Furthermore, we begin our discussion with the simplest of these, H_2^+, which consists of two protons and just a single electron.

Electrons are considerably less massive than protons so that electron rearrangements occur much more rapidly than those of the more ponderous nuclei. This fact results in a useful technique, introduced by Born and J. R. Oppenheimer and known as the *Born–Oppenheimer approximation*. The nuclei are assumed to be at fixed points and the electron energies and wave functions are then found as functions of the fixed nuclear positions. The total electronic energy is then used, together with the direct internuclear forces, to form an effective potential energy for the nuclear motion.

Figure 10-1 shows the arrangement of the two protons in H_2^+; both are on the z axis, one at $-R/2$ and one at $R/2$, so the distance between them is R. The electron is at arbitrary position r. The nuclear positions are taken as fixed so we need write the

Figure 10-1

Molecular coordinates for H_2^+. The protons are at $-R/2$ and $R/2$; the electron is at r. The z axis is taken along the internuclear line.
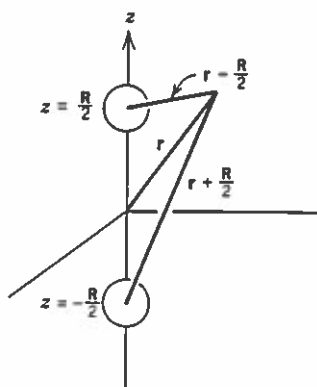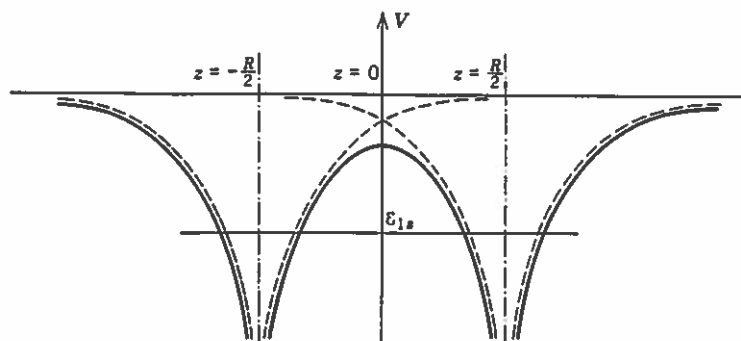
Figure 10-2

Potential energy seen by the electron in H_2^+ as it moves along the z axis. The dotted line gives that part of the potential arising just from the proton at $z = -R/2$. The dashed line shows the same for the proton at $z = R/2$.

Schrödinger equation for only the *electronic* eigenfunction $\psi_e(r)$:

$$\left\{ -\frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{ke^2}{|r + R/2|} - \frac{ke^2}{|r - R/2|} + \frac{ke^2}{R} \right\} \psi_e(r) = \varepsilon_e \psi_e(r), \quad (10\text{-}1)$$

where m_e is the electron mass, $k = 1/4\pi\varepsilon_0$, and ε_e is an energy eigenvalue of the electron. The first term in curly brackets is the electron kinetic energy operator. The second and third terms are the attractive potential energies caused by the protons at $-R/2$ and $R/2$. We have also included the last term, the proton–proton repulsion, as a part of the electronic potential energy for convenience.

Figure 10-2 shows a cut through the potential energy function as one travels along the z axis. The potential energy diverges at $z = -R/2$ and $z = R/2$ as it must for the Coulomb force. Near $z = 0$ the function is a bit lower than it would be if there were only one atomic potential energy curve. The potential energy is symmetric about this point. This double-welled potential energy function is analogous to that considered in Chapter 5 (Figure 5-25) and the wave functions have properties similar to those found there.

Suppose that only one of the potential wells is present (e.g., the one around $z = R/2$ as indicated by the dashed curve). Then the problem is quite familiar and the ground-state wave function is just $\phi_{1s}(r - R/2)$, the hydrogenic 1s state centered at $r = R/2$. Similarly, a particle in the potential well centered at $r = -R/2$ has wave function $\phi_{1s}(r + R/2)$. Because both potential wells are the same, just shifted in space, the energy levels in each are identical and equal to ε_{1s}.

Now consider the situation in the combined problem represented by the solid line in Figure 10-2. While the electron is in the neighborhood of $r = R/2$ we expect the ground-state wave function to be approximately equal to $\phi_{1s}(r - R/2)$ because in much of that region the dashed line and the solid line coincide. While the electron is in the neighborhood of $r = -R/2$, the wave function is approximately $\phi_{1s}(r + R/2)$. A further necessary property of the wave function arises from the symmetry of the potential energy about the point $r = 0$. We expect the probability $P(r)$ of a particle

being around $r = -R/2$ to be equal to that of it being around $r = R/2$. More precisely, we require parity invariance $P(-r) = P(r)$. In terms of the eigenfunction this is equivalent to

$$\psi(-r) = \pm\psi(r). \tag{10-2}$$

Molecular wave functions that are even under a parity change (the upper sign) are said to be *gerade*; those that are odd are *ungerade*. (These are the German words for "even" and "odd.")

Eigenfunctions that satisfy both of the above sets of requirements are given by

$$\psi_+(r) = \frac{1}{\sqrt{2}}\left(\phi_{1s}(r - R/2) + \phi_{1s}(r + R/2)\right) \tag{10-3a}$$

and

$$\psi_-(r) = \frac{1}{\sqrt{2}}\left(\phi_{1s}(r - R/2) - \phi_{1s}(r + R/2)\right). \tag{10-3b}$$

When r is near $R/2$, $\phi_{1s}(r + R/2) \approx \phi_{1s}(R)$ is small and $\psi_\pm(r) \approx (1/\sqrt{2})\phi_{1s}(r - R/2)$ as required. (The $1/\sqrt{2}$ is just an approximate normalization factor.) To see the parity property of $\psi_\pm(r)$ we note that

$$\psi_\pm(-r) = \frac{1}{\sqrt{2}}\left(\phi_{1s}(-r - R/2) \pm \phi_{1s}(-r + R/2)\right).$$

From Chapter 7 we know that the $1s$ state for hydrogen is also even under parity inversion, that is,

$$\phi_{1s}(-r) = \phi_{1s}(r),$$

so that Equation (10-2) is satisfied as well. A graph of the functions $\psi_\pm$ is shown in Figure 10-3.

Note that the $\psi_\pm$ of Equations (10-3) are not exact solutions of Equation (10-1), even though they behave reasonably. They are *approximations* to the two lowest states

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Figure 10-3

Graph along the z axis of the approximate eigenfunctions $\psi_\pm(r)$ (Equations (10-3)) for H_2^+.
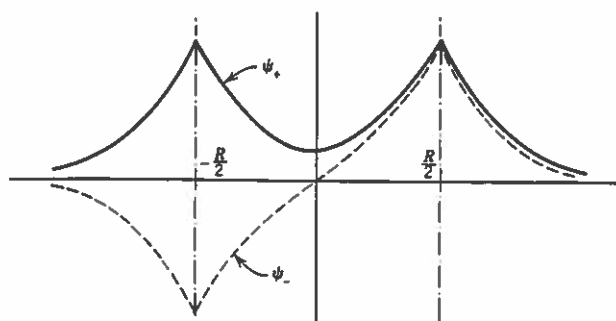
of H_2^+. An exact solution of Equation (10-1) is possible but the complications involved in finding it do not offer as much physical insight into the problem.

The energies associated with these wave functions are found by computing the expectation value

$$\langle \varepsilon \rangle \equiv \varepsilon_{\pm} = \int \psi_{\pm}^* \left[-\frac{\hbar^2}{2m_e} \nabla_r^2 + V(\mathbf{r}) \right] \psi_{\pm} \, dr. \tag{10-4}$$

This quantity is a simple generalization to three dimensions of the one-dimensional energy expectation value given by Equation (5-65) in Section 5-7. The quantity $-(\hbar^2/2m)\nabla_r^2$ is the three-dimensional kinetic energy operator that replaces the one-dimensional form $-(\hbar^2/2m) \, \partial^2/\partial x^2$, and $V(\mathbf{r})$ is the sum of the three potential energy terms in Equation (10-1).

To simplify the calculation of the energies we establish the following shorthand notation:

$$T = -\frac{\hbar^2}{2m_e}\nabla_r^2;$$

$$V_a = -\frac{ke^2}{|\mathbf{r} - \mathbf{R}/2|}; \qquad V_b = -\frac{ke^2}{|\mathbf{r} + \mathbf{R}/2|}; \qquad V_R = \frac{ke^2}{R^2};$$

$$\phi_a = \phi_{1s}(\mathbf{r} - \mathbf{R}/2); \qquad \phi_b = \phi_{1s}(\mathbf{r} + \mathbf{R}/2).$$

The total potential energy is then

$$V(\mathbf{r}) = V_a + V_b + V_R.$$

Note that the $\psi_{\pm}$ are real because ϕ_a and ϕ_b are real. Putting the $\psi_{\pm}$ of Equations (10-3) into Equation (10-4) gives for the energy estimate

$$\varepsilon_{\pm} = \frac{1}{2} \int (\phi_a \pm \phi_b)[T + V_a + V_b + V_R](\phi_a \pm \phi_b) \, dr$$

$$= \frac{1}{2} \int (\phi_a \pm \phi_b)[(T + V_a)\phi_a \pm (T + V_b)\phi_b] \, dr$$

$$+ \frac{1}{2} \int \phi_a^2(V_b + V_R) \, dr + \frac{1}{2} \int \phi_b^2(V_a + V_R) \, dr$$

$$\pm \frac{1}{2} \int \phi_a(V_a + V_R)\phi_b \, dr \pm \frac{1}{2} \int \phi_b(V_b + V_R)\phi_a \, dr.$$

The fact that ϕ_a and ϕ_b are hydrogenic functions allows us to write

$$(T + V_a)\phi_a = \varepsilon_{1s}\phi_a \quad \text{and} \quad (T + V_b)\phi_b = \varepsilon_{1s}\phi_b.$$

We also note that

$$G \equiv \int \phi_a^2(V_b + V_R) \, dr = \int \phi_b^2(V_a + V_R) \, dr \tag{10-5}$$

corresponds to the average value of the Coulomb interaction between the electron and nucleus on site a (at $\mathbf{R}/2$) and the nucleus on b (at $-\mathbf{R}/2$) or vice versa.

A *quantum interference* or *overlap* term also occurs in the energy. This is

$$S = \int \phi_a (V_a + V_R) \phi_b \, d\mathbf{r} = \int \phi_b (V_b + V_R) \phi_a \, d\mathbf{r}. \qquad (10\text{-}6)$$

This quantity arises as a cross-term in $\varepsilon_{\pm}$ because the electron has probability amplitude for being on either site. The overlap term is extremely important and is the source of the binding of the atoms to form a molecule. Note that the term involves the product $\phi_a \phi_b$. The function ϕ_a is localized about $R/2$ and falls off exponentially as r moves away from $R/2$, and similarly for ϕ_b. The product is appreciable only in the vicinity of $r = 0$ where the two functions overlap. For this reason S is usually a good deal smaller than the *direct energy* terms, such as ε_{1s} or G, which depend on ϕ_a^2 or ϕ_b^2. Classically, a particle is trapped in a potential well (e.g., the electron near $r = R/2$ can not get into the well at $r \approx -R/2$ if its energy is less than the central barrier height as indicated in Figure 10-2). But because of the quantum mechanical barrier penetration effect, the wave function does enter this classically forbidden region, resulting in a nonzero overlap integral. Thus, we obtain

$$\varepsilon_{\pm} = \varepsilon_{1s} + G \pm S \qquad (10\text{-}7)$$

as the final result.

In the limit that the nuclear separation R becomes large, the overlap of ϕ_a and ϕ_b, and hence S, becomes exponentially small. It can be shown that G also becomes exponentially small. Then we have $\varepsilon_{\pm} \to \varepsilon_{1s}$. However, for smaller separations the two energies ε_+ and ε_- are not equal but are split by $2S$. The exchange integral S turns out to be negative so that ε_+ (corresponding to ψ_+, the eigenfunction with no nodes) is lower than ε_- and is the ground-state energy. More importantly, even though G is positive, ε_+ is lower than ε_{1s}, which can be considered to be the energy of the dissociated molecule. Thus, the molecule is bound.

The other state that we have formed, ψ_-, has an energy greater than ε_{1s}. This state turns out not to be bound.

Figure 10-4 shows the two energies ε_+ and ε_- as functions of internuclear separation R. These electronic energies can be interpreted as effective potential energy functions of the two protons. They either cause the protons to be drawn toward each other or repelled from one another. We write

$$V_{\pm} = \varepsilon_{\pm} - \varepsilon_{1s}$$

as the nuclear potential energy functions. Written in this way, the potential energy goes to zero as $R \to \infty$. V_- is always repulsive but V_+ is attractive until R gets so small that the Coulomb repulsion between the protons dominates. There is a minimum in V_+, defining the equilibrium separation of the two protons in the molecule.

The binding of the H_2^+ molecule arises from the exchange integral S in Equation (10-7). The physical origin of this term can be seen from the behavior of $\psi_{\pm}$ in Equations (10-3). From the plot of these two functions in Figure 10-3 we see that ψ_+ is larger than either $\phi_a = \phi_{1s}(r - R/2)$ or $\phi_b = \phi_{1s}(r + R/2)$ in the region between the two protons. The probability density associated with the two functions is

$$|\psi_{\pm}|^2 = \tfrac{1}{2} \left[|\phi_a|^2 + |\phi_b|^2 \pm 2\phi_a \phi_b \right]. \qquad (10\text{-}8)$$

The last term is the contribution from the overlap region. In $|\psi_+|^2$ this extra electron

Figure 10-4

Effective internuclear potential energies for H_2^+ as functions of proton–proton separation R. These functions are related to the electronic energies by $V_\pm = \varepsilon_\pm - \varepsilon_{1s}$. The minimum in V_+ gives R_0, the equilibrium internuclear distance.
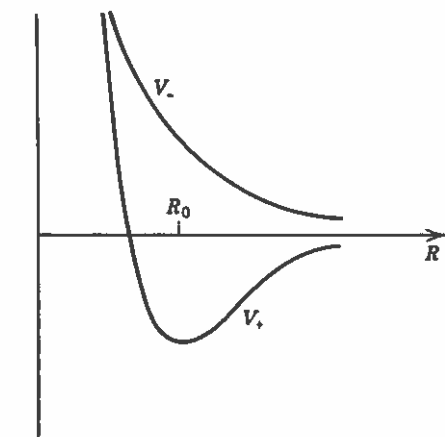
density implies a region of extra negative charge, which attracts each proton to it and partially shields one proton from the repulsion of the other. This is the effect causing molecular binding in H_2^+; hence ψ_+ is said to be a *bonding molecular orbital*. On the other hand, $|\psi_-|^2$ has less electron density than it would have without the overlap term (note ψ_- vanishes at the midpoint between the protons), and ψ_- is said to be *antibonding*.

The explicit calculation of G and S in Equation (10-7) leads to an equilibrium distance of 0.132 nm and a depth of the potential V_+ of 1.77 eV compared to the results obtained from the exact wave function of 0.106 nm and 2.79 eV. The approximate function ψ_+ of Equation (10-3) tends to be inaccurate at small R; the wave functions for the individual atomic wells become quite distorted from $1s$ states at such separations. Indeed, for $R = 0$, ψ_+ ought to transform into the ground state of He^+ but does not in our approximation (see Problem 3 at the end of the chapter).

It is possible to construct other molecular orbitals analogous to those of Equations (10-3) by substituting other atomic functions for the $1s$ states. These orbitals represent excited molecular states, some of which are bonding and some antibonding.

We next examine the angular momentum classification of the molecular orbitals of H_2^+. To do this most easily we shift the molecular coordinate system so that the origin coincides with one of the protons as shown in Figure 10-5. The atomic wave function for the electron centered on the proton at the origin is now $\phi_{1s}(r)$. This function is clearly an eigenstate of electron angular momentum $\ell = 0$. To examine the angular momentum properties of the molecular orbital ψ_+ of Equation (10-3a), we must also look at the atomic function for the electron centered at $r = R$, that is, $\phi_{1s}(r - R)$. Because this latter state is displaced from the origin, it is *not* an eigenfunction of the electron's squared angular momentum L^2. Adding a second center of force at R has

Figure 10-5

Molecular coordinates for H_2^+ with the origin taken at one of the protons.
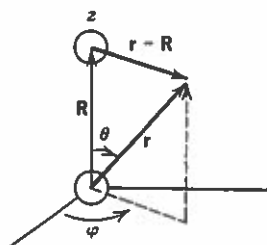
ruined the spherical symmetry of the electron's potential energy. The problem is no longer one having a simple central force. Thus, molecular orbitals cannot be classified according to ℓ values.

Molecular wave functions for diatomic molecules like H_2^+ do have *cylindrical symmetry* and therefore turn out to be eigenstates of the z component of angular momentum L_z. In molecular physics the eigenvalues of L_z for a single electron are denoted by $\lambda \hbar$, where $\lambda = 0, \pm 1, \pm 2, \dots$. Just as hydrogenic atomic orbitals have the letter code $s, p, d, \dots$ representing $\ell = 0, 1, 2, \dots$, molecular orbitals corresponding to $|\lambda| = 0, 1, 2, \dots$ are designated by the Greek letters $\sigma, \pi, \delta, \dots$, respectively. As is shown below, $\psi_{\pm}$ of Equations (10-3) are both σ states.

Detail

We can easily show that ψ_+ is an eigenfunction of L_z. Using the coordinate system of Figure 10-5, write

$$|\mathbf{r} - \mathbf{R}| = \left(r^2 + R^2 - 2rR \cos \theta \right)^{1/2}.$$

This arrangement of ψ_+, and hence ψ_+ itself, depends on r and $\cos \theta$ but not on the azimuthal angle ϕ shown in Figure 10-5. From Chapter 6,

$$L_z \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

so that

$$L_z \psi_+ = 0,$$

and ψ_+ therefore corresponds to $\lambda = 0$.

10-2 Covalent Bonding: H_2

The H_2^+ molecule discussed in Section 10-1 is useful in showing the elements of molecular binding in a reasonably straightforward way. It is the "hydrogen atom" of molecules. However, the simplest *neutral* molecule is H_2, which carries two electrons. We now proceed to treat this fundamental problem.

Figure 10-1 continues to describe the proton configuration for H$_2$. However, there are now two electrons at positions r_1 and r_2. We construct an approximate electronic wave function first introduced by W. Heitler and F. London in 1927. Suppose for a moment that the two protons are at the same point $r = 0$. We then have the charge equivalent of a helium nucleus. The electronic ground state for this system is a $1s^2$ configuration with eigenfunction

$$\psi(1,2) = \phi_{1s}(r_1)\phi_{1s}(r_2)\chi^A(1,2), \tag{10-9}$$

where $\chi^A(1,2)$ is the antisymmetric or singlet spin function given by (see Equation (9-25))

$$\chi^A(1,2) = \frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2). \tag{10-10}$$

The spin function must have one electron with spin up and the other with spin down because both electrons are in the same atomic orbital. In this way eigenfunction $\psi(1,2)$ satisfies the Pauli principle; that is, it is antisymmetric and $\psi(2,1) = -\psi(1,2)$.

Next, let the two protons be drawn apart along the z axis, one to $R/2$ and the other to $-R/2$. We might expect one electron to be dragged along with each proton. Then Equation (10-9) would be transformed into

$$\psi(1,2) = \phi_{1s}(r_1 - R/2)\phi_{1s}(r_2 + R/2)\chi^A(1,2). \tag{10-11}$$

This might seem a good initial guess at a molecular eigenfunction except for two important deficiencies. First, Equation (10-11) has not incorporated the physical features found to be necessary for molecular binding in the H$_2^+$ analysis. Each electron should have a probability of being at *each* proton, thereby spending extra time in the intermediate region between the protons. This extra electron density yields the net attraction that binds the molecule. A second deficiency arises from the fact that the proposed function does not obey the Pauli principle; it is not properly antisymmetric as it must be for fermions.

Fortunately, we can easily solve both problems at once by simply adding on to Equation (10-11) the interchanged state with electron 1 at $-R/2$ and electron 2 at $+R/2$. The result is

$$\psi_S^{HL}(1,2) = \frac{1}{\sqrt{2}}\left[\phi_{1s}(r_1 - R/2)\phi_{1s}(r_2 + R/2) + \phi_{1s}(r_2 - R/2)\phi_{1s}(r_1 + R/2)\right]$$

$$\times\chi^A(1,2), \tag{10-12}$$

where the superscript HL stands for Heitler–London and the subscript S stands for singlet spin state. The factor $1/\sqrt{2}$ is put in to make ψ^{HL} approximately normalized. Because $\chi^A(1,2)$ is antisymmetric under electron interchange, the entire wave function is now antisymmetric. Also, each electron now has a probability of being at each nucleus. Note, however, that the electrons move in a rather coherent way, so that if electron 1 moves from the nucleus at $-R/2$ to that at $+R/2$, electron 2 flips its position in just the opposite way. In this way the wave function never allows both electrons to appear simultaneously on the same nucleus. We might think that this a positive feature because it would tend to minimize electron–electron repulsion; however, we show later that mixing in a little of this double-occupancy state actually improves binding.

There is an alternative antisymmetric wave function that we can form from the $1s$ atomic orbitals. First, we construct triplet spin states from the spin eigenfunctions as done in Chapter 9, Equation (9-26). These are

$$\chi^S_{m_s} = \begin{cases} \chi^S_1 = \uparrow_1 \uparrow_2 & (10\text{-}13) \\[2mm] \chi^S_0 = \dfrac{1}{\sqrt{2}}(\uparrow_1 \downarrow_2 + \downarrow_1 \uparrow_2) & (10\text{-}14) \\[2mm] \chi^S_{-1} = \downarrow_1 \downarrow_2. & (10\text{-}15) \end{cases}$$

Since these states are symmetric under electron exchange, the spatial part of the wave function must be antisymmetric. By analogy with Equation (10-12) we have

$$\psi^{HL}_T = \frac{1}{\sqrt{2}}\big[\phi_{1s}(\mathbf{r}_1 - \mathbf{R}/2)\phi_{1s}(\mathbf{r}_2 + \mathbf{R}/2) - \phi_{1s}(\mathbf{r}_2 - \mathbf{R}/2)\phi_{1s}(\mathbf{r}_1 + \mathbf{R}/2)\big]\chi^S_{m_s}.$$

$$(10\text{-}16)$$

The T subscript stands for triplet spin state.

As with H_2^+, one of the two states formed from $1s$ atomic functions is bonding and the other antibonding. To see which is which, consider the squares of the two spatial portions of the wave functions. The spatial probability densities are

$$P^{(12)}_{S,T} = \tfrac{1}{2}\big[\phi^2_{1s}(\mathbf{r}_1 - \mathbf{R}/2)\phi^2_{1s}(\mathbf{r}_2 + \mathbf{R}/2) + \phi^2_{1s}(\mathbf{r}_2 - \mathbf{R}/2)\phi^2_{1s}(\mathbf{r}_1 + \mathbf{R}/2)$$

$$\pm 2\big(\phi_{1s}(\mathbf{r}_1 - \mathbf{R}/2)\phi_{1s}(\mathbf{r}_1 + \mathbf{R}/2)\big)\big(\phi_{1s}(\mathbf{r}_2 - \mathbf{R}/2)\phi_{1s}(\mathbf{r}_2 + \mathbf{R}/2)\big)\big]. \quad (10\text{-}17)$$

The interference term (the last one, like that of Equation (10-8)) depends on the overlap of electronic wave functions in the region halfway between the nuclei, and implies that there is extra electronic charge there in the singlet case (plus sign) and diminished charge for the triplet (minus sign). While the added charge density of the singlet wave function does enhance electron–electron repulsion, this effect is more than offset by the added attraction between the extra charge and the two protons. It is this effect that provides the *covalent bonding* in the singlet case. The triplet wave function, on the other hand, is antibonding.

In a molecule more complicated than H_2 there is often a closed-shell core of electrons, quite tightly bound to their originating nucleus, which participate weakly or not at all in this exchange phenomenon. The outer electrons that do exchange are known as *valence* electrons. Since these electrons are paired in the sense that they exchange cooperatively from one atom to the other, the bond is called *covalent*.

The energies associated with the two eigenfunctions ψ^{HL}_S and ψ^{HL}_T may be calculated. When this is done, forms analogous to those of Equations (10-7) are found:

$$\varepsilon_{S,T} = 2\varepsilon_{1s} + G' \pm S', \qquad (10\text{-}18)$$

where the upper sign refers to the singlet case and the lower to the triplet. The exchange integral S' depends on *two*-particle overlap integrals and contains terms like

$$\iint \phi_{1s}(\mathbf{r}_1 - \mathbf{R}/2)\phi_{1s}(\mathbf{r}_2 + \mathbf{R}/2)V(\mathbf{r}_1, \mathbf{r}_2)\phi_{1s}(\mathbf{r}_1 + \mathbf{R}/2)\phi_{1s}(\mathbf{r}_2 - \mathbf{R}/2)\, d\mathbf{r}_1\, d\mathbf{r}_2,$$

where $V(\mathbf{r}_1, \mathbf{r}_2)$ can be any one of the various terms occurring in the energy operator. G' is also a two-particle quantity somewhat analogous to the G of Equation (10-5). S' turns out to be negative so that the singlet energy is lower than the triplet. The singlet energy has a minimum as a function of R and exhibits binding while the triplet has no bound state.

As mentioned briefly above, the approximate Heitler–London eigenfunction ψ_S^{HL} can be improved somewhat by including double-occupancy states:

$$\psi_S(1,2) = \psi_S^{HL}(1,2) + \gamma \frac{1}{\sqrt{2}} \left[\phi_{1s}(\mathbf{r}_1 - \mathbf{R}/2)\phi_{1s}(\mathbf{r}_2 - \mathbf{R}/2) \right.$$

$$\left. + \phi_{1s}(\mathbf{r}_1 + \mathbf{R}/2)\phi_{1s}(\mathbf{r}_2 + \mathbf{R}/2) \right] \chi^A(1,2), \quad (10\text{-}19)$$

where γ is an adjustable coefficient. The first term of the new addition has both electrons near the same nucleus at $\mathbf{R}/2$; the second has both near that at $-\mathbf{R}/2$. While each of these terms increases the average value of the electron–electron repulsion, it also gives the system an *ionic structure* in which there is some probability of the formation of the ion combinations (H^+, H^-) or (H^-, H^+). The ions attract one another and add to the molecular binding. At the equilibrium separation of the molecule (the minimum of the electronic energy), it is found that $\gamma \approx 0.2$, implying that only a small percentage of the binding results from this process. Note that the configurations (H^-, H^+), with both electrons on proton 1, and (H^+, H^-), with both on proton 2, are equally likely so that H_2 does not have a permanent electric dipole moment. In Section 10-3 we study systems that owe their bonding to the existence of a permanent separation of charge and the resulting electric dipole configuration.

It is possible to construct bonding or antibonding molecular states from excited atomic orbitals as well as from $1s$ states. For example, simply replace the $1s$ orbitals in Equations (10-12) and (10-16) with $2s$ functions. Excited-state molecular energies vary with internuclear distance R in a manner similar to the ground-state energy as shown schematically in Figure 10-6. The $R \to \infty$ limit of such energies need not be zero or all equal. As $R \to \infty$, G' and S' of Equation (10-18) go to zero and the energy $\varepsilon_S \to 2\varepsilon_{1s}$, which is the electronic energy associated with the two isolated hydrogen atoms. The bonding state constructed of two $2s$ states would have the limit $2\varepsilon_{2s}$ as $R \to \infty$. A bonding excited molecular state such as ε_4 in Figure 10-6 has a minimum at some R value and does not necessarily dissociate (i.e., separate into its atomic constituents) even though its $R \to \infty$ limit is greater than that of the ground state. On the other hand, excitation of the molecule from the ground state to an excited state such as ε_2 or ε_3 in Figure 10-6 would result in dissociation.

As a last topic of this section we consider why a closed shell (noble gas) atom does not interact covalently with any other atom. Consider the case of hydrogen and helium. The bonding molecular wave function has been seen to have a singlet spin configuration with one spin up and one spin down. Consider a covalent bond involving the hydrogen $1s$ electron with spin down, for example, and one of the helium $1s$ electrons with spin up. The wave function involves an exchange term that brings the down electron over to the He, which then has two spins down and violates the Pauli principle. This is a somewhat simplified view; a rigorous argument would construct three-electron wave functions for the two nuclear centers. These wave functions can be shown to vanish because of the Pauli principle for all but antibonding molecular orbitals. Thus, the molecule H—He does not form.

While similar arguments can be made to show that two noble gas atoms, such as He—He or He—Ar, cannot interact covalently, molecules such as Ar_2 do exist.

Figure 10-6
Electronic states for a diatomic molecule as functions of internuclear separation R. Bonding states have minima as in ε_1 or ε_4. Antibonding states do not support bound states.
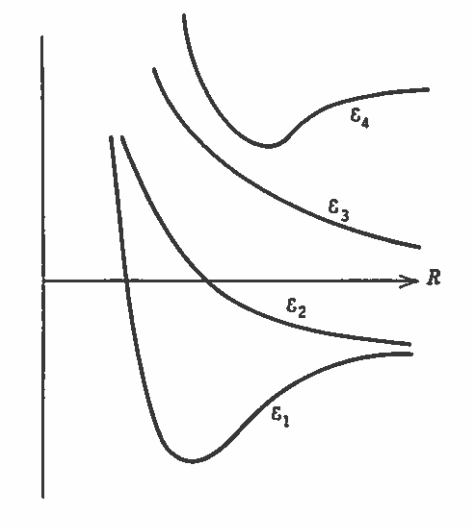
These occur because there is another attractive force mechanism known as the van der Waals interaction, which is discussed in Section 10-4.

10-3   Ionic Bonding: LiF

Hydrogen has a single electron, and the alkalis (Li, Na, Rb, Cs) have a single electron outside a closed shell. When any one of these react with any one of the halogens (F, Cl, Br, I), which are one electron short of completing a shell, they form *ionic bonds*. Basically, what happens is that the single s electron of the alkali element (or of hydrogen) is taken by the halogen to fill its shell; the resulting positive and negative ions attract one another and the molecule becomes bound.

Consider the molecule lithium fluoride, LiF. The primary question to be answered is why an electron would be pulled off the lithium atom to form Li^+ and move over to fluorine to form F^-. The case rests mainly in the fact that all the electrons in a single shell have roughly the same average atomic radius. The electronic structure of fluorine is $1s^2 2s^2 2p^5$. The $n = 1$ shell is complete and the $n = 2$ shell is missing one electron. All the $n = 2$ electrons reside at approximately the same average radius, which, of course, is larger than that corresponding to the $n = 1$ electrons. Each of the seven $n = 2$ electrons is thus screened efficiently from the nucleus by only the two $1s$ electrons. The resulting Z value seen by each of the $n = 2$ electrons is not much less than 7. An extra tenth electron borrowed from the lithium atom sees roughly the same effective Z value and is bound. The binding energy of this electron to form a negative ion is known as the *electron affinity*. This electron affinity, however, is usually smaller than the ionization potential associated with forming the positive ion. In the case of

lithium (whose structure is $1s^2 2s$) it costs 5.4 eV to pull off the $2s$ electron (the ionization potential), and in forming the negative fluorine ion 3.4 eV is released (the electron affinity)—a net cost of energy of 2.0 eV. However, the energy released by the binding of the resulting ions (about 8 eV) more than compensates for this energy expense. This ionization process goes only in the direction indicated, as is easily seen by considering the energy required to form $(Li^- F^+)$. The electron affinity for lithium is 0.6 eV; the ionization potential of fluorine is 17.4 eV. The energy requirement is 16.8 eV, while the net gain through binding of the two ions is the same as for $(Li^+ F^-)$.

Note that homonuclear diatomic molecules (those made up of like nuclei, such as H_2) have constituents with equal attractions for the electrons and so do not form permanent ions within the molecule, although they may have ionic structure in their wave functions as discussed in Section 10-2. Only *heteronuclear* molecules (those made up of unlike nuclei, as HF) can have the permanent charge separation described above.

There is a simple test by which we can judge the accuracy of the above idea of the ionic bond in LiF or in any diatomic molecule. If the lithium's electron spends all its time on the fluorine atom, then the electric dipole moment of the molecule, from Figure 10-7, is

$$p = -e\left(-\frac{R}{2}\right) + e\frac{R}{2} = eR.$$

The interatomic separation in LiF is found to be $R = 0.156$ nm so we expect $p = (1.6 \times 10^{-19}\ C)(1.56 \times 10^{-10}\ m) = 2.5 \times 10^{-29}\ C \cdot m$. The experimental value of the electric dipole moment is $p_{exp} = 2.11 \times 10^{-29}\ C \cdot m$, 85% of the above model value. The lithium's electron does maintain some probability of being on its home-base atom in addition to spending time at the fluorine; this reduces charge separation from the model value. There are also other small effects that tend to reduce the polarization.

The above result indicates the bonding of LiF is only partly ionic; it is also partly covalent. The lithium's $2s$ electron pairs with one of the fluorine's $2p$ electrons to form this covalent bond. To see how this takes place consider the possible angular parts of the $2p$ wave function. There are three degenerate states with angular components

$$Y_{1\pm 1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi} \tag{10-20a}$$

and

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta. \tag{10-20b}$$

(Refer back to Table 6-1.) Figure 6-8 shows how the angular lobes of the probability density corresponding to these states are positioned. Combinations of the $Y_{1\pm 1}$ functions have lobes in the xy plane. The Y_{10} function shown in Figure 10-8 has lobes along the z axis. The upper lobe is positive and the lower one negative. Of the three functions, the one expected to have the largest overlap with a $2s$ function centered at a distance R away along the z axis is Y_{10}. We pair this so-called $2p_z$ function of fluorine with the lithium's $2s$ function for a covalent type of wave function.

Figure 10-7
Model of an ionically bound diatomic molecule. Atom B has the greater electron affinity and takes an electron from atom A. The two atoms form an electric dipole with charges $+e$ and $-e$ separated by distance R.
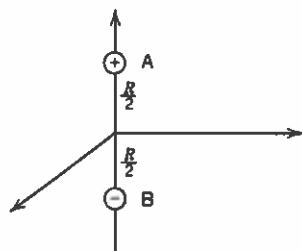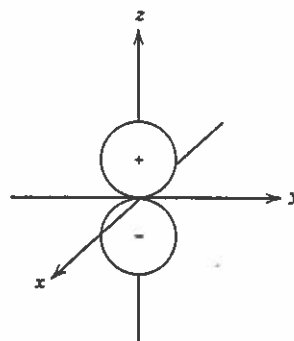

Figure 10-8
Angular function Y_{10} – a factor in the $2p_z$ wave function of fluorine.

The eigenfunction describing the bonding orbitals in this molecule is then a generalization of Equation (10-19). We place the fluorine at $z = -R/2$ and the lithium at $z = +R/2$ so

$$\psi(1,2) = \left\{ A\frac{1}{\sqrt{2}}\left[\phi_{2s}(\mathbf{r}_1 - \mathbf{R}/2)\phi_{2p_z}(\mathbf{r}_2 + \mathbf{R}/2) + \phi_{2s}(\mathbf{r}_2 - \mathbf{R}/2)\phi_{2p_z}(\mathbf{r}_1 + \mathbf{R}/2)\right] \right.$$
$$+ B\phi_{2s}(\mathbf{r}_1 - \mathbf{R}/2)\phi_{2s}(\mathbf{r}_2 - \mathbf{R}/2)$$
$$\left. + C\phi_{2p_z}(\mathbf{r}_1 + \mathbf{R}/2)\phi_{2p_z}(\mathbf{r}_2 + \mathbf{R}/2)\right\}\chi^A(1,2), \tag{10-21}$$

where ψ is normalized by taking $\sqrt{A^2 + B^2 + C^2} = 1$ (see Problem 9 at the end of the chapter). The term with coefficient A is the covalent part of the wave function and those in B and C involve the ionic structures. Unlike the case of H_2, we have no reason to take $B = C$ and indeed the ionic bonding mechanism we have described requires $B \neq C$. Because we know the electrons may double up on fluorine but are very unlikely to do so on lithium, it is reasonable to set $B = 0$ as an approximation.

It can be shown that the electric dipole moment of the molecule may be related to the parameters in Equation (10-21). The result, for the case of arbitrary A, B, and C, is

$$p = eR(C^2 - B^2). \tag{10-22}$$

For H_2, whose eigenfunction is given by Equation (10-19), we have the equivalent of $B = C$ in Equation (10-21) and $p = 0$ as expected. In the present case we have

$$p = eRC^2. \tag{10-23}$$

The experimental ratio of $p/eR = 0.85$ for LiF gives us $C = \sqrt{0.85} = 0.9$, $A = \sqrt{1 - C^2} = 0.4$, the latter equality being the normalization condition. Thus, we see that the percentage of ionic bonding in the total bond of LiF is quite high.

Given the wave function of Equation (10-21) we can determine the average energy as a function of internuclear separation. This result tells us many of the properties of

Figure 10-9
Electronic energy for an ionically bound
molecule as a function of internuclear distance.
The energy is adjusted to $V(\infty) = 0$.
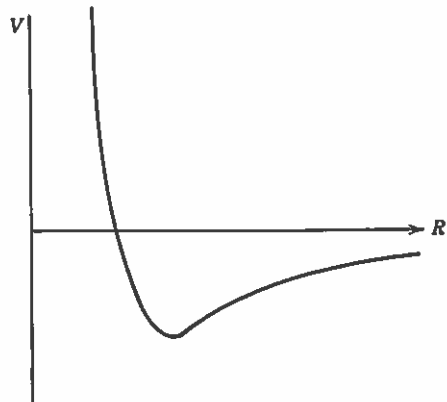
the molecule. However, a more direct approach is one in which we guess the form of
the electronic energy on the basis of general physical principles. Such a "phenomeno-
logical" form contains coefficients that vary from molecule to molecule and are
determined by fitting the predictions derived from the potential energy function to
experiment.

The potential energy function usually chosen for a general ionically bound alkali
halide molecule has the form

$$V(R) = \alpha e^{-aR} - \frac{e^2}{4\pi\varepsilon_0 R}.$$
(10-24)

The second term obviously represents the Coulomb attraction, at large separation R,
between the positive and negative ions. When the ions are so close to each other that
their closed-shell electronic clouds overlap, the electronic energy becomes repulsive
due to the Pauli principle as represented by the first term. The constants α and a,
which control the strength and slope of the repulsive part, are determined from
comparison with experimental data as shown in the example at the end of this section.
A qualitative plot of $V(R)$ is shown in Figure 10-9. While $V(R)$ looks much like V_+ of
Figure 10-4 or ε of Figure 10-6, it falls off at large R as $1/R$, which makes it much
longer ranged than either of those energies, since each drops off exponentially.

The equilibrium separation of the nuclei in the molecule is very near the position
R_0 of the minimum in the potential energy. (Zero-point motion changes this slightly.)
This position satisfies

$$\frac{dV}{dR}\bigg|_{R=R_0} = -a\alpha e^{-aR_0} + \frac{e^2}{4\pi\varepsilon_0 R_0^2} = 0$$

or

$$\alpha = \frac{e^2}{4\pi\varepsilon_0} \frac{e^{aR_0}}{aR_0^2}.$$
(10-25)

The curvature of the potential energy at $R = R_0$ is

$$K = \frac{d^2V}{dR^2}\bigg|_{R=R_0} = a^2\alpha e^{-aR_0} - \frac{2e^2}{4\pi\varepsilon_0 R_0^3}$$

from which it is found that

$$a = \frac{1}{R_0}\left(2 + 4\pi\varepsilon_0 \frac{KR_0^3}{e^2}\right). \tag{10-26}$$

Spectral data give R_0 and K directly, as we see in Section 10-8. Putting these values in Equations (10-25) and (10-26) yields α and a.

The dissociation energy is the work needed to pull the two atoms completely apart into isolated *neutral* atoms. If we were to separate the *ions* to infinity the work needed would be $-V(R_0)$, the depth of the potential energy. The removal of the electron from the negative ion and its return to the positive ion net a positive energy

$$Q = I_0 - A_0, \tag{10-27}$$

where I_0 is the ionization potential and A_0 is the electron affinity. The dissociation energy then is related to the potential energy by

$$D = -V(R_0) - Q \tag{10-28}$$

if we neglect the zero-point energy.

Covalent and ionic forces are the primary molecular bonding mechanisms. There are, however, other physical principles that contribute to interatomic interactions. We consider one of these, the van der Waals attraction, in Section 10-4.

Example

For the molecule lithium fluoride spectral data yield the values of the interatomic separation $R_0 = 0.156$ nm and the potential energy function curvature $K = 248$ J/m^2. From these values Equation (10-26) yields

$$a = \frac{1}{0.156\text{ nm}}\left(2 + \frac{(248\text{ J/m}^2)(1.56 \times 10^{-10}\text{ m})^3}{(8.99 \times 10^9\text{ N}\cdot\text{m}^2/\text{C}^2)(1.6 \times 10^{-19}\text{ C})^2}\right) = \frac{6.13}{0.156\text{ nm}}$$

$$= 39.2\text{ nm}^{-1}.$$

Then the parameter α is found from Equation (10-25) to be

$$\alpha = \frac{(8.99 \times 10^9\text{ N}\cdot\text{m}^2/\text{C}^2)(1.6 \times 10^{-19}\text{ C})^2}{6.13(1.56 \times 10^{-10}\text{ m})}e^{6.13} = 1.1 \times 10^{-16}\text{ J}$$

$$= 688\text{ eV}.$$

Thus, the potential energy in Equation (10-24) for LiF becomes

$$V(R) = \left(688e^{-39.2R} - \frac{1.44}{R}\right)\text{ eV},$$

where R is given in nanometers.

To get the dissociation energy from $V(R)$ we need the value of Q in Equation (10-27). The ionization potential of lithium is 5.4 eV, and the electron affinity of fluorine is 3.4 eV, so

$$Q = 5.4 - 3.4 = 2.0 \text{ eV}.$$

The potential depth at R_0 is

$$V(R_0) = 688e^{-(39.2)(0.156)} - \frac{1.44}{0.156}$$
$$= 1.5 - 9.2 = -7.7 \text{ eV}.$$

From Equation (10-28)

$$D = 7.7 - 2.0 = 5.7 \text{ eV}.$$

The experimental value is 6.0 eV, so our prediction from the phenomenological potential energy function is only about 5% in error. This is quite good considering the fact that there are several small corrections to the potential energy to be taken into account. These refinements include covalent, induced dipole (see Problem 11 at the end of the chapter), and van der Waals (Section 10-4) forces.

10-4 Van der Waals Interaction

Atoms of the noble gases, having closed electronic shells, do not interact with one another via covalent or ionic forces. However, there is a weaker attraction between such atoms, called the *van der Waals force*. This force is also present in molecules that do interact covalently or ionically but it is much weaker and of lesser importance. Despite its relative weakness the heavier noble gas atoms—neon, argon, and so on—are able to form molecules via the van der Waals interaction. Helium liquifies at low temperatures only because of the presence of this force.

The Dutch physicist J. D. van der Waals proposed that all molecules have attractive forces that, at sufficiently low temperatures, can cause liquification. The force we discuss here has thus been named after him. However, it was London who in 1930 first explained the physical origin of this interaction, which is occasionally called the *London force*.

The attraction arises from an induced dipole–dipole effect. We consider here a classical model of the force that is not totally adequate but does have many of the elements of the quantum mechanical picture. Suppose two neutral H atoms approach one another, and assume no covalent force. At any instant in time an electron and the nucleus that it is orbiting form an electric dipole. This dipole creates an electric field, which is felt by the second atom whose positive charge is pulled one way and its negative another. It becomes polarized; that is, it develops an *induced* dipole moment as shown in Figure 10-10.

We can easily find the behavior of the electric field as a function of distance R from the first atom. Consider for simplicity a point A on the perpendicular to the dipole as shown in Figure 10-11. At this position only the vertical components $E_i \sin \theta$ of each field do not cancel. From the figure we see that $\sin \theta$ satisfies $\sin \theta = \frac{1}{2}a/\sqrt{R^2 + (a/2)^2}$. When the field point is far away from the dipole so $R \gg a$, we

Figure 10-10

Electric-dipole behavior of atoms. An atom with an instantaneous dipole moment p_1 creates an electric field that induces a dipole moment p_2 in a second atom.
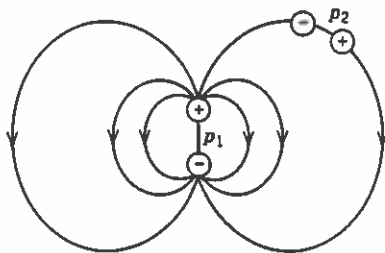
have $\sin\theta \approx a/2R$. The net electric field is then given by

$$E_d = \frac{2Q}{4\pi\varepsilon_0} \frac{\sin\theta}{R^2 + (a/2)^2} \approx \frac{2Qa}{4\pi\varepsilon_0 R^2} \frac{a}{2R} = \frac{p_1}{4\pi\varepsilon_0 R^3}, \qquad (10\text{-}29)$$

where $p_1 = Qa$ is the dipole moment of the first atom. From this we see that E_d drops off as $1/R^3$ as we move away from the dipole, a result that holds even when the point A is not on the perpendicular.

The second atom in the field E_d acquires an induced dipole moment p_2 having size proportional to the electric field that it feels. So

$$\mathbf{p}_2 = \alpha \mathbf{E}_d, \qquad (10\text{-}30)$$

where α is called the *polarizability* of the molecule. This is a kind of Hooke's law approximation in which the separation of the charges is proportional to the applied force. (See Problem 11 at the end of the chapter.)

Figure 10-11

Electric field $\mathbf{E}_d$ due to a dipole $\mathbf{p}_1$. The field is the sum of the electric fields $\mathbf{E}_+$ and $\mathbf{E}_-$ of the individual charges $\pm Q$. Position A in the xy plane at a distance R from the dipole is considered. The charges $\pm Q$ are separated by distance a. The distance from either charge to A is $\sqrt{R^2 + \frac{1}{4}a^2}$.
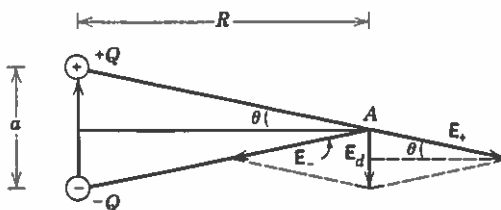
The energy of a dipole p_2 aligned with an electric field E_d is

$$U = -p_2 E_d. \tag{10-31}$$

To derive this note that if a field is along the z axis, then while a dipole rotates from the xy plane into alignment with the field, the field does work $QEa/2$ on the charge $+Q$ and work $-QE(-a/2)$ on the charge $-Q$. Thus, the total dipole energy is $-2Q(a/2)E = -pE$.

If we combine Equations (10-30) and (10-31) and then use Equation (10-29), we find

$$U = -\alpha E_d^2 = -\alpha \frac{p_1^2}{(4\pi\varepsilon_0)^2} \frac{1}{R^6} = -\frac{\alpha Q^2 a^2}{(4\pi\varepsilon_0)^2} \frac{1}{R^6}.$$

We can do some dimensional analysis on α to estimate its size. Equation (10-30) gives $\alpha = p/E$, which *dimensionally* can be written as

$$\alpha = \frac{q\ell}{\dfrac{1}{4\pi\varepsilon_0}\dfrac{q}{\ell^2}} = 4\pi\varepsilon_0\ell^3,$$

where ℓ is some length in the problem. For a dipole the appropriate length is the charge separation a, which in this case is approximately the atomic radius. So we substitute

$$\alpha = 4\pi\varepsilon_0 a^3. \tag{10-32}$$

This result agrees with that of Problem 11. We get

$$U = -\left(\frac{Q^2}{4\pi\varepsilon_0 a}\right)\left(\frac{a}{R}\right)^6. \tag{10-33}$$

The leading factor is of the same order as I_0, the ionization potential of the atom. Thus the van der Waals potential energy function has the form

$$V_{vdW}(R) \sim -I_0\left(\frac{a}{R}\right)^6. \tag{10-34}$$

An accurate calculation for two hydrogen atoms gives

$$V_{vdW}(R) = -13.0 I_0\left(\frac{a}{R}\right)^6 \tag{10-35}$$

instead of Equation (10-34).

This interaction is longer ranged than the exponentially diminishing covalent bond. Atoms such as hydrogen, which do interact covalently, also have the van der Waals attraction acting effectively at distances beyond the range of the covalent force.

Atoms of the noble gases are attracted to one another by only the van der Waals force. When they approach so closely that their electron shells overlap, the Pauli principle causes a repulsive force that increases rapidly with decreasing internuclear

Table 10-1   Parameters of the Lennard-Jones 12-6 Potential

	σ (nm)	ε (eV)
He	0.256	8.79×10^{-4}
Ne	0.275	3.08×10^{-3}
Ar	0.340	1.05×10^{-2}
Kr	0.368	1.44×10^{-2}
Xe	0.407	1.94×10^{-2}

Source: *Data from E. R. Dobbs and G. O. Jones*, Rep. Prog. Phys. **20**: 516 (1957).

separation. In 1925 J. E. Lennard-Jones suggested a phenomenological potential energy function that included both attractive and repulsive effects in a convenient mathematical form. This energy function is

$$V_{LJ}(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^n - \left(\frac{\sigma}{R}\right)^6\right]. \tag{10-36}$$

The constants ε, σ, and n are parameters to be determined to fit gas, liquid, and solid data. (Even though the energy function is sufficiently weak that the so-called noble gases are indeed gases at room pressure and temperature, they do liquify and solidify at sufficiently low temperature.) The most frequently used value of n is 12, in which case we have the *Lennard-Jones 12-6 potential*. It is easy to verify that the potential depth is ε and that σ is the value of R for which $V_{LJ}(R) = 0$ (see Problem 13 at the end of the chapter).

Some values of ε and σ for the 12-6 potential for various noble gases are given in Table 10-1. Note that as one progresses to heavier atoms the polarizability, which depends on atomic volume, increases and the strength of the interaction also increases.

Molecules with one member an alkali atom (which has a high polarizability) and the other a noble gas atom can be bound by the van der Waals interaction and can be observed spectroscopically. Molecules made up completely of noble gas atoms are difficult to observe but have been detected by use of mass spectrometers.

Example

The noble gases neon, argon, krypton, and xenon are able to form molecules because of the van der Waals interaction. However, they are weakly bound by comparison with molecules held together by other forces. For the ionically bound molecule LiF we know that the dissociation energy is about 6 eV. For the heavy noble gases the dissociation energy is approximately equal to the well depth. The Lennard-Jones 12-6 potential has a depth equal to the parameter ε given in Table 10-1. For Xe, $\varepsilon = 0.0194$ eV. A thermal energy equivalent to ε occurs for a temperature approximately equal to $T_{Xe} = (\varepsilon_{Xe}/k_B)$, where k_B is the Boltzmann constant 1.38×10^{-23} J/K or 8.62×10^{-5} eV/K. For xenon this is

$$T_{Xe} = \frac{0.0194 \text{ eV}}{8.62 \times 10^{-5} \text{ eV/K}} = 225 \text{ K}.$$

At this temperature, which is a little below room temperature, most of the