

Electronic Structure of Diatomic Molecules

13.1 The Born–Oppenheimer Approximation

We now begin the study of molecular quantum mechanics. If we assume the nuclei and electrons to be point masses and neglect spin–orbit and other relativistic interactions (Sections 11.6 and 11.7), then the molecular Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 r_{\alpha\beta}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_j \sum_{i > j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (13.1)$$

where α and β refer to nuclei and i and j refer to electrons. The first term in (13.1) is the operator for the kinetic energy of the nuclei. The second term is the operator for the kinetic energy of the electrons. The third term is the potential energy of the repulsions between the nuclei, $r_{\alpha\beta}$ being the distance between nuclei α and β with atomic numbers Z_{α} and Z_{β} . The fourth term is the potential energy of the attractions between the electrons and the nuclei, $r_{i\alpha}$ being the distance between electron i and nucleus α . The last term is the potential energy of the repulsions between the electrons, r_{ij} being the distance between electrons i and j . The zero level of potential energy for (13.1) corresponds to having all the charges (electrons and nuclei) infinitely far from one another.

As an example, consider H_2 . Let α and β be the two protons, 1 and 2 be the two electrons, and m_p be the proton mass. The H_2 molecular Hamiltonian operator is

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m_p} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_p} \nabla_{\beta}^2 - \frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 \\ & + \frac{e^2}{4\pi\epsilon_0 r_{\alpha\beta}} - \frac{e^2}{4\pi\epsilon_0 r_{1\alpha}} - \frac{e^2}{4\pi\epsilon_0 r_{1\beta}} - \frac{e^2}{4\pi\epsilon_0 r_{2\alpha}} - \frac{e^2}{4\pi\epsilon_0 r_{2\beta}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \end{aligned} \quad (13.2)$$

The wave functions and energies of a molecule are found from the Schrödinger equation:

$$\hat{H}\psi(q_i, q_{\alpha}) = E\psi(q_i, q_{\alpha}) \quad (13.3)$$

where q_i and q_{α} symbolize the electronic and nuclear coordinates, respectively. The molecular Hamiltonian (13.1) is formidable enough to terrify any quantum chemist. Fortunately, a very accurate, simplifying approximation exists. Since nuclei are much heavier than electrons ($m_{\alpha} \gg m_e$), the electrons move much faster than the nuclei. Hence, to a good

approximation as far as the electrons are concerned, we can regard the nuclei as fixed while the electrons carry out their motions. Speaking classically, during the time of a cycle of electronic motion, the change in nuclear configuration is negligible. Thus, considering the nuclei as fixed, we omit the nuclear kinetic-energy terms from (13.1) to obtain the Schrödinger equation for electronic motion:

$$(\hat{H}_{\text{el}} + V_{NN})\psi_{\text{el}} = U\psi_{\text{el}} \quad (13.4)$$

where the **purely electronic Hamiltonian** $\hat{H}_{\text{el}}$ is

$$\hat{H}_{\text{el}} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_j \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (13.5)$$

The electronic Hamiltonian including nuclear repulsion is $\hat{H}_{\text{el}} + V_{NN}$. The nuclear-repulsion term V_{NN} is

$$V_{NN} = \sum_{\alpha} \sum_{\beta>\alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 r_{\alpha\beta}} \quad (13.6)$$

The energy U in (13.4) is the **electronic energy including internuclear repulsion**. The internuclear distances $r_{\alpha\beta}$ in (13.4) are not variables, but are each fixed at some constant value. Of course, there are an infinite number of possible nuclear configurations, and for each of these we may solve the electronic Schrödinger equation (13.4) to get a set of electronic wave functions and corresponding electronic energies. Each member of the set corresponds to a different molecular electronic state. The electronic wave functions and energies thus depend parametrically on the nuclear coordinates:

$$\psi_{\text{el}} = \psi_{\text{el},n}(q; q_{\alpha}) \quad \text{and} \quad U = U_n(q_{\alpha})$$

where n symbolizes the electronic quantum numbers.

The variables in the electronic Schrödinger equation (13.4) are the electronic coordinates. The quantity V_{NN} is independent of these coordinates and is a constant for a given nuclear configuration. Now it is easily proved (Prob. 4.52) that the omission of a constant term C from the Hamiltonian does not affect the wave functions and simply decreases each energy eigenvalue by C . Hence, if V_{NN} is omitted from (13.4), we get

$$\hat{H}_{\text{el}}\psi_{\text{el}} = E_{\text{el}}\psi_{\text{el}} \quad (13.7)$$

where the **purely electronic energy** $E_{\text{el}}(q_{\alpha})$ (which depends parametrically on the nuclear coordinates q_{α}) is related to the electronic energy including internuclear repulsion by

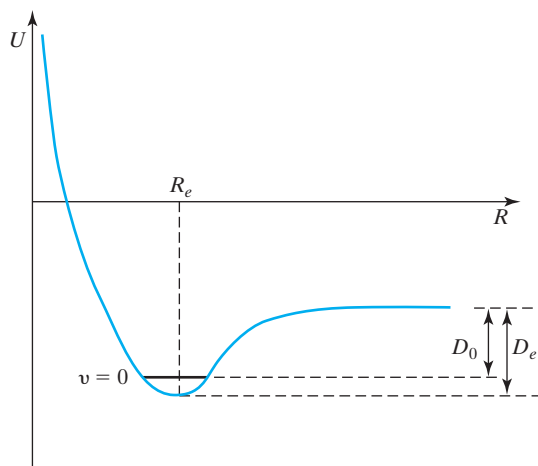
$$U = E_{\text{el}} + V_{NN} \quad (13.8)$$

We can therefore omit the internuclear repulsion from the electronic Schrödinger equation. After finding E_{el} for a particular configuration of the nuclei by solving (13.7), we calculate U using (13.8), where the constant V_{NN} is easily calculated from (13.6) using the assumed nuclear locations.

For H_2 , with the two protons at a fixed distance $r_{\alpha\beta} = R$, the purely electronic Hamiltonian is given by (13.2) with the first, second, and fifth terms omitted. The nuclear repulsion V_{NN} equals $e^2/4\pi\epsilon_0 R$. The purely electronic Hamiltonian involves the six electronic coordinates $x_1, y_1, z_1, x_2, y_2, z_2$ as variables and involves the nuclear coordinates as parameters.

The electronic Schrödinger equation (13.4) can be dealt with by approximate methods to be discussed later. If we plot the electronic energy including nuclear repulsion for a bound state of a diatomic molecule against the internuclear distance R , we find a

FIGURE 13.1 Electronic energy including internuclear repulsion as a function of the internuclear distance R for a diatomic-molecule bound electronic state.



curve like the one shown in Fig. 13.1. At $R = 0$, the internuclear repulsion causes U to go to infinity. The internuclear separation at the minimum in this curve is called the **equilibrium internuclear distance** R_e . The difference between the limiting value of U at infinite internuclear separation and its value at R_e is called the **equilibrium dissociation energy** (or the *dissociation energy from the potential-energy minimum*) D_e :

$$D_e \equiv U(\infty) - U(R_e) \quad (13.9)$$

When nuclear motion is considered (Section 13.2), one finds that the equilibrium dissociation energy D_e differs from the molecular ground-vibrational-state dissociation energy D_0 . The lowest state of nuclear motion has zero rotational energy [as shown by Eq. (6.47)] but has a nonzero vibrational energy—the zero-point energy. If we use the harmonic-oscillator approximation for the vibration of a diatomic molecule (Section 4.3), then this zero-point energy is $\frac{1}{2}h\nu$. This zero-point energy raises the energy for the ground state of nuclear motion $\frac{1}{2}h\nu$ above the minimum in the $U(R)$ curve, so D_0 is less than D_e and $D_0 \approx D_e - \frac{1}{2}h\nu$. Different electronic states of the same molecule have different $U(R)$ curves (Figs. 13.5 and 13.19) and different values of R_e , D_e , D_0 , and ν .

Consider an ideal gas composed of diatomic molecules AB. In the limit of absolute zero temperature, all the AB molecules are in their ground states of electronic and nuclear motion, so D_0N_A (where N_A is the Avogadro constant and D_0 is for the ground electronic state of AB) is the change in the thermodynamic internal energy U and enthalpy H for dissociation of 1 mole of ideal-gas diatomic molecules: $N_AD_0 = \Delta U_0^\circ = \Delta H_0^\circ$ for $\text{AB(g)} \rightarrow \text{A(g)} + \text{B(g)}$.

For some diatomic-molecule electronic states, solution of the electronic Schrödinger equation gives a $U(R)$ curve with no minimum. Such states are not bound and the molecule will dissociate. Examples include some of the states in Fig. 13.5.

Assuming that we have solved the electronic Schrödinger equation, we next consider nuclear motions. According to our picture, the electrons move much faster than the nuclei. When the nuclei change their configuration slightly, say from q'_α to q''_α , the electrons immediately adjust to the change, with the electronic wave function changing from $\psi_{\text{el}}(q_i; q'_\alpha)$ to $\psi_{\text{el}}(q_i; q''_\alpha)$ and the electronic energy changing from $U(q'_\alpha)$ to $U(q''_\alpha)$. Thus, as the nuclei move, the electronic energy varies smoothly as a function of the parameters defining the nuclear configuration, and $U(q_\alpha)$ becomes, in effect, the potential energy for the nuclear motion. The electrons act like a spring connecting the nuclei. As the internuclear distance

changes, the energy stored in the spring changes. Hence the Schrödinger equation for nuclear motion is

$$\hat{H}_N \psi_N = E \psi_N \quad (13.10)$$

$$\hat{H}_N = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 + U(q_{\alpha}) \quad (13.11)$$

The variables in the nuclear Schrödinger equation are the nuclear coordinates, symbolized by q_{α} . The energy eigenvalue E in (13.10) is the *total* energy of the molecule, since the Hamiltonian (13.11) includes operators for both nuclear energy and electronic energy. E is simply a number and does not depend on any coordinates. Note that for each electronic state of a molecule we must solve a different nuclear Schrödinger equation, since U differs from state to state. In this chapter we shall concentrate on the electronic Schrödinger equation (13.4).

In Section 13.2, we shall show that the total energy E for an electronic state of a diatomic molecule is approximately the sum of electronic, vibrational, rotational, and translational energies, $E \approx E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{tr}}$, where the constant E_{elec} [not to be confused with E_{el} in (13.7)] is given by $E_{\text{elec}} = U(R_e)$.

The approximation of separating electronic and nuclear motions is called the **Born–Oppenheimer approximation** and is basic to quantum chemistry. [The American physicist J. Robert Oppenheimer (1904–1967) was a graduate student of Born in 1927. During World War II, Oppenheimer directed the Los Alamos laboratory that developed the atomic bomb.] Born and Oppenheimer’s mathematical treatment indicated that the true molecular wave function is adequately approximated as

$$\psi(q_i, q_{\alpha}) = \psi_{\text{el}}(q_i; q_{\alpha}) \psi_N(q_{\alpha}) \quad (13.12)$$

if $(m_e/m_{\alpha})^{1/4} \ll 1$. The Born–Oppenheimer approximation introduces little error for the ground electronic states of diatomic molecules. Corrections for excited electronic states are larger than for the ground state, but still are usually small as compared with the errors introduced by the approximations used to solve the electronic Schrödinger equation of a many-electron molecule. Hence we shall not worry about corrections to the Born–Oppenheimer approximation. For further discussion of the Born–Oppenheimer approximation, see J. Goodisman, *Diatomic Interaction Potential Theory*, Academic Press, 1973, Volume 1, Chapter 1.

Born and Oppenheimer’s 1927 paper justifying the Born–Oppenheimer approximation is seriously lacking in rigor. Subsequent work has better justified the Born–Oppenheimer approximation, but significant questions still remain; “the problem of the coupling of nuclear and electronic motions is, at the moment, without a sensible solution and . . . is an area where much future work can and must be done” [B. T. Sutcliffe, *J. Chem. Soc. Faraday Trans.*, **89**, 2321 (1993); see also B. T. Sutcliffe and R. G. Woolley, *Phys. Chem. Chem. Phys.*, **7**, 3664 (2005), and Sutcliffe and Woolley, arxiv.org/abs/1206.4239].

13.2 Nuclear Motion in Diatomic Molecules

Most of this chapter deals with the electronic Schrödinger equation for diatomic molecules, but this section examines nuclear motion in a bound electronic state of a diatomic molecule. From (13.10) and (13.11), the Schrödinger equation for nuclear motion in a diatomic-molecule bound electronic state is

$$\left[-\frac{\hbar^2}{2m_{\alpha}} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_{\beta}} \nabla_{\beta}^2 + U(R) \right] \psi_N = E \psi_N \quad (13.13)$$

where α and β are the nuclei, and the nuclear-motion wave function ψ_N is a function of the nuclear coordinates $x_\alpha, y_\alpha, z_\alpha, x_\beta, y_\beta, z_\beta$.

The potential energy $U(R)$ is a function of only the relative coordinates of the two nuclei, and the work of Section 6.3 shows that the two-particle Schrödinger equation (13.13) can be reduced to two separate one-particle Schrödinger equations—one for translational energy of the entire molecule and one for internal motion of the nuclei relative to each other. We have

$$\psi_N = \psi_{N,\text{tr}}\psi_{N,\text{int}} \quad \text{and} \quad E = E_{\text{tr}} + E_{\text{int}} \quad (13.14)$$

The translational energy levels can be taken as the energy levels (3.72) of a particle in a three-dimensional box whose dimensions are those of the container holding the gas of diatomic molecules.

The Schrödinger equation for $\psi_{N,\text{int}}$ is [Eq. (6.43)]

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + U(R) \right] \psi_{N,\text{int}} = E_{\text{int}} \psi_{N,\text{int}}, \quad \mu \equiv m_\alpha m_\beta / (m_\alpha + m_\beta) \quad (13.15)$$

where $\psi_{N,\text{int}}$ is a function of the coordinates of one nucleus relative to the other. The best coordinates to use are the spherical coordinates of one nucleus relative to the other (Fig. 6.5 with m_N and m_e replaced by m_α and m_β). The radius r in relative spherical coordinates is the internuclear distance R , and we shall denote the relative angular coordinates by θ_N and ϕ_N . Since the potential energy in (13.15) depends on R only, this is a central-force problem, and the work of Section 6.1 shows that

$$\psi_{N,\text{int}} = P(R) Y_J^M(\theta_N, \phi_N), \quad J = 0, 1, 2, \dots, \quad M = -J, \dots, J \quad (13.16)$$

where the Y_J^M functions are the spherical harmonic functions with quantum numbers J and M .

From (6.17), the radial function $P(R)$ is found by solving

$$-\frac{\hbar^2}{2\mu} \left[P''(R) + \frac{2}{R} P'(R) \right] + \frac{J(J+1)\hbar^2}{2\mu R^2} P(R) + U(R)P(R) = E_{\text{int}} P(R) \quad (13.17)$$

This differential equation is simplified by defining $F(R)$ as

$$F(R) \equiv RP(R) \quad (13.18)$$

Substitution of $P = F/R$ into (13.17) gives [Eq. (6.137)]

$$-\frac{\hbar^2}{2\mu} F''(R) + \left[U(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} \right] F(R) = E_{\text{int}} F(R) \quad (13.19)$$

which is a one-dimensional Schrödinger equation with the effective potential energy $U(R) + J(J+1)\hbar^2/2\mu R^2$.

The most fundamental way to solve (13.19) is as follows: (a) Solve the electronic Schrödinger equation (13.7) at several values of R to obtain E_{el} of the particular molecular electronic state you are interested in; (b) add $Z_\alpha Z_\beta e^2 / 4\pi\epsilon_0 R$ to each E_{el} value to obtain U at these R values; (c) devise a mathematical function $U(R)$ whose parameters are adjusted to give a good fit to the calculated U values; (d) insert the function $U(R)$ found in (c) into the nuclear-motion radial Schrödinger equation (13.19) and solve (13.19) by numerical methods.

A commonly used fitting procedure for step (c) is the method of *cubic splines*, for which computer programs exist (see *Press et al.*, Chapter 3; *Shoup*, Chapter 6).

As for step (d), numerical solution of the one-dimensional Schrödinger equation (13.19) is done using either the *Cooley–Numerov method* [see J. Tellinghuisen, *J. Chem. Educ.*, **66**,

51 (1989)], which is a modification of the Numerov method (Sections 4.4 and 6.9), or the *finite-element method* [see D. J. Searles and E. I. von Nagy-Felsobuki, *Am. J. Phys.*, **56**, 444 (1988)].

The solutions $F(R)$ of the radial equation (13.19) for a given J are characterized by a quantum number v , where v is the number of nodes in $F(R)$; $v = 0, 1, 2, \dots$. The energy levels E_{int} [which are found from the condition that $P(R) = F(R)/R$ be quadratically integrable] depend on the quantum number J , which occurs in (13.19), and depend on v , which characterizes $F(R)$; $E_{\text{int}} = E_{v,J}$. The angular factor $Y_J^M(\theta_N, \phi_N)$ in (13.16) is a function of the angular coordinates. Changes in θ_N and ϕ_N with R held fixed correspond to changes in the spatial orientation of the diatomic molecule, which is rotational motion. The quantum numbers J and M are rotational quantum numbers. Note that Y_J^M is the wave function of a rigid two-particle rotor [Eq. (6.46)]. A change in the R coordinate is a change in the internuclear distance, which is a vibrational motion, and the quantum number v , which characterizes $F(R)$, is a vibrational quantum number.

Since accurate solution of the electronic Schrödinger equation [step (a)] is hard, one often uses simpler, less accurate procedures than that of steps (a) to (d). The simplest approach is to expand $U(R)$ in a Taylor series about R_e (Prob. 4.1):

$$U(R) = U(R_e) + U'(R_e)(R - R_e) + \frac{1}{2}U''(R_e)(R - R_e)^2 + \frac{1}{6}U'''(R_e)(R - R_e)^3 + \dots \quad (13.20)$$

At the equilibrium internuclear distance R_e , the slope of the $U(R)$ curve is zero (Fig. 13.1), so $U'(R_e) = 0$. We can anticipate that the molecule will vibrate about the equilibrium distance R_e . For R close to R_e , $(R - R_e)^3$ and higher powers will be small, and we shall neglect these terms. Defining the **equilibrium force constant** k_e as $k_e \equiv U''(R_e)$, we have

$$U(R) \approx U(R_e) + \frac{1}{2}k_e(R - R_e)^2 = U(R_e) + \frac{1}{2}k_e x^2 \quad (13.21)$$

$$k_e \equiv U''(R_e) \quad \text{and} \quad x \equiv R - R_e$$

We have approximated $U(R)$ by a parabola [Fig. 4.6 with $V \equiv U(R) - U(R_e)$ and $x \equiv R - R_e$].

With the change of independent variable $x \equiv R - R_e$, (13.19) becomes

$$-\frac{\hbar^2}{2\mu}S''(x) + \left[U(R_e) + \frac{1}{2}k_e x^2 + \frac{J(J+1)\hbar^2}{2\mu(x + R_e)^2} \right] S(x) \approx E_{\text{int}} S(x) \quad (13.22)$$

$$\text{where } S(x) \equiv F(R) \quad (13.23)$$

Expanding $1/(x + R_e)^2$ in a Taylor series, we have (Prob. 13.7)

$$\frac{1}{(x + R_e)^2} = \frac{1}{R_e^2(1 + x/R_e)^2} = \frac{1}{R_e^2} \left(1 - 2\frac{x}{R_e} + 3\frac{x^2}{R_e^2} - \dots \right) \approx \frac{1}{R_e^2} \quad (13.24)$$

We are assuming that $R - R_e = x$ is small compared with R_e , so all terms after the 1 have been neglected in (13.24). Substitution of (13.24) into (13.22) and rearrangement gives

$$-\frac{\hbar^2}{2\mu}S''(x) + \frac{1}{2}k_e x^2 S(x) \approx \left[E_{\text{int}} - U(R_e) - \frac{J(J+1)\hbar^2}{2\mu R_e^2} \right] S(x) \quad (13.25)$$

Equation (13.25) is the same as the Schrödinger equation for a one-dimensional harmonic oscillator with coordinate x , mass μ , potential energy $\frac{1}{2}k_e x^2$, and energy eigenvalues $E_{\text{int}} - U(R_e) - J(J+1)\hbar^2/2\mu R_e^2$. [The boundary conditions for (13.25) and (4.32) are not the same, but this difference is unimportant and can be ignored (*Levine, Molecular*

Spectroscopy, p. 147).] We can therefore set the terms in brackets in (13.25) equal to the harmonic-oscillator eigenvalues, and we have

$$\begin{aligned} E_{\text{int}} - U(R_e) - J(J+1)\hbar^2/2\mu R_e^2 &\approx (v + \tfrac{1}{2})h\nu_e \\ E_{\text{int}} &\approx U(R_e) + (v + \tfrac{1}{2})h\nu_e + J(J+1)\hbar^2/2\mu R_e^2 \end{aligned} \quad (13.26)$$

$$\nu_e = (k_e/\mu)^{1/2}/2\pi, \quad v = 0, 1, 2, \dots \quad (13.27)$$

where (4.23) was used for ν_e , the **equilibrium** (or **harmonic**) **vibrational frequency**. The molecular internal energy E_{int} is approximately the sum of the electronic energy $U(R_e) \equiv E_{\text{elec}}$ (which differs for different electronic states of the same molecule), the vibrational energy $(v + \frac{1}{2})h\nu_e$, and the rotational energy $J(J+1)\hbar^2/2\mu R_e^2$. The approximations (13.21) and (13.24) correspond to a harmonic-oscillator, rigid-rotor approximation. From (13.26) and (13.14), the molecular energy $E = E_{\text{tr}} + E_{\text{int}}$ is approximately the sum of translational, rotational, vibrational, and electronic energies:

$$E \approx E_{\text{tr}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$$

From (13.14), (13.16), (13.18), and (13.23), the nuclear-motion wave function is

$$\psi_N \approx \psi_{N,\text{tr}} S_v(R - R_e) R^{-1} Y_J^M(\theta_N, \phi_N) \quad (13.28)$$

where $S_v(R - R_e)$ is a harmonic-oscillator eigenfunction with quantum number v .

The approximation (13.26) gives rather poor agreement with experimentally observed vibration–rotation energy levels of diatomic molecules. The accuracy can be improved by the addition of the first- and second-order perturbation-theory energy corrections due to the terms neglected in (13.21) and (13.24). When this is done (see *Levine, Molecular Spectroscopy*, Section 4.2), the energy contains additional terms corresponding to vibrational anharmonicity [Eq. (4.60)], vibration–rotation interaction, and rotational centrifugal distortion of the molecule (Section 6.4), where vibrational anharmonicity is the largest of these corrections and centrifugal distortion is the smallest.

EXAMPLE

An approximate representation of the potential-energy function of a diatomic molecule is the Morse function

$$U(R) = U(R_e) + D_e[1 - e^{-a(R-R_e)}]^2$$

Use of $U''(R_e) = k_e$ [Eq. (4.59)] and (13.27) gives (see Prob. 4.29; the Morse functions in Prob. 4.29 and in this example differ because of different choices for the zero of energy)

$$a = (k_e/2D_e)^{1/2} = 2\pi\nu_e(\mu/2D_e)^{1/2}$$

Use the Morse function and the Numerov method (Section 4.4) to (a) find the lowest six vibrational energy levels of the $^1\text{H}_2$ molecule in its ground electronic state, which has $D_e/hc = 38297 \text{ cm}^{-1}$, $\nu_e/c = 4403.2 \text{ cm}^{-1}$, and $R_e = 0.741 \text{ \AA}$, where h and c are Planck's constant and the speed of light; (b) find $\langle R \rangle$ for each of these vibrational states.

- (a) The vibrational energy levels correspond to states with the rotational quantum number $J = 0$. Making the change of variables $x \equiv R - R_e$ and $S(x) \equiv F(R)$ [Eq. (13.23)] and substituting the Morse function into the nuclear-motion Schrödinger equation (13.19), we get for $J = 0$

$$-(\hbar^2/2\mu)S''(x) + D_e(1 - e^{-ax})^2S(x) = [E_{\text{int}} - U(R_e)]S(x) = E_{\text{vib}}S(x)$$

since for $J = 0$, $E_{\text{int}} = E_{\text{elec}} + E_{\text{vib}} = U(R_e) + E_{\text{vib}}$ [Eq. (13.26)]. As usual in the Numerov method, we switch to the dimensionless reduced variables $E_{\text{vib},r} \equiv E_{\text{vib}}/A$ and $x_r \equiv x/B$, where A and B are products of powers of the constants $\hbar$, μ , and a . The procedure of Section 4.4 gives (Prob. 13.8a) $A = \hbar^2 a^2 / \mu$ and $B = a^{-1}$, so

$$x_r \equiv x/B = ax, \quad E_{\text{vib},r} \equiv E_{\text{vib}}/A = \mu E_{\text{vib}} / \hbar^2 a^2 = (2D_e / \hbar^2 \nu_e^2) E_{\text{vib}}$$

where we used $a = 2\pi\nu_e(\mu/2D_e)^{1/2}$. Substitution of

$$x = x_r/a, \quad E_{\text{vib}} = \hbar^2 a^2 E_{\text{vib},r} / \mu, \quad D_{e,r} = D_e / (\hbar^2 a^2 / \mu), \quad S(x) = S_r(x_r) B^{-1/2} \\ S'' = B^{-5/2} S_r'' = B^{-1/2} B^{-2} S_r'' = B^{-1/2} a^2 S_r''$$

[Eqs. (4.78) and (4.79)] into the differential equation for $S(x)$ gives

$$S_r''(x_r) = [2D_{e,r}(1 - e^{-x_r})^2 - 2E_{\text{vib},r}] S_r(x_r) \equiv G_r S_r(x_r)$$

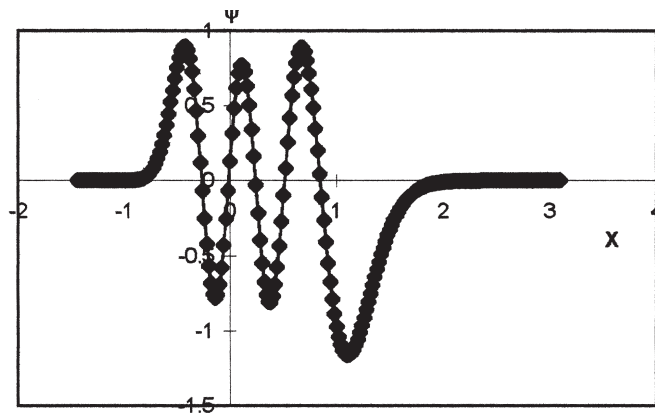
This last equation has the form of (4.82) with $G_r \equiv 2D_{e,r}(1 - e^{-x_r})^2 - 2E_{\text{vib},r}$, so we are now ready to apply the Numerov procedure of Section 4.4. For the H_2 ground electronic state, we find (Prob. 13.8b)

$$A = \hbar^2 \nu_e^2 / 2D_e = \hbar^2 c^2 (4403.2 \text{ cm}^{-1})^2 / 2hc(38297 \text{ cm}^{-1}) = (253.129 \text{ cm}^{-1}) hc \\ B = 0.51412 \text{ \AA}, \quad D_{e,r} = D_e / A = 151.29_4$$

We want to start and end the Numerov procedure in the classically forbidden regions. If we used the harmonic-oscillator approximation for the vibrational levels, the energies of the first six vibrational levels would be $(v + \frac{1}{2})\hbar\nu_e$, $v = 0, 1, \dots, 5$. The reduced energy of the sixth harmonic-oscillator vibrational level would be $5.5\hbar\nu_e/A = 5.5\hbar\nu_e/(253 \text{ cm}^{-1})hc = 5.5(4403 \text{ cm}^{-1})/(253 \text{ cm}^{-1}) = 95.7$. Because of anharmonicity (Section 4.3), the sixth vibrational level will actually occur below 95.7, so we are safe in using 95.7 to find the limits of the classically allowed region. We have $D_{e,r}(1 - e^{-x_r})^2 = 95.7$, and with $D_{e,r} = 151.29$, we find $x_r = -0.58$ and $x_r = 1.58$ as the limits of the classically allowed region for a reduced energy of 95.7. Extending the range by 1.2 at each end, we would start the Numerov procedure at $x_r = -1.8$ and end at $x_r = 2.8$. However, $x_r = (R - R_e)/B = (R - 0.741 \text{ \AA})/(0.514 \text{ \AA})$ and the minimum possible internuclear distance R is 0, so the minimum possible value of x_r is -1.44 . We therefore start at $x_r = -1.44$ and end at 2.8. If we take an interval of $s_r = 0.04$, we will have about 106 points, which is adequate, but we will try for higher accuracy by taking $s_r = 0.02$ to give about 212 points. With these choices, we set up the Numerov spreadsheet in the usual manner (or use Mathcad or the computer program of Table 4.1). We find (Prob. 13.9) the following lowest six $E_{\text{vib},r}$ values: 8.572525, 24.967566, 40.362582, 54.757570, 68.152531, 80.547472. Using $E_{\text{vib},r} \equiv E_{\text{vib}}/A$, we find the lowest levels to be $E_{\text{vib}}/hc = 2169.95, 6320.01, 10216.94, 13860.73, 17251.38, 20388.90 \text{ cm}^{-1}$. Note the reduced spacings between levels as the vibrational quantum number increases. (For comparison, the harmonic-oscillator approximation gives the following values: 2201.6, 6604.8, 11008.0, 15411.2, 19814.4, 24217.6 cm^{-1} .)

It happens that the Schrödinger equation for the Morse function can be analytically solved virtually exactly, and the analytic solution (Prob. 13.11) gives the following lowest eigenvalues: 2169.96, 6320.03, 10216.97, 13860.78, 17251.47, 20389.02 cm^{-1} . Agreement between the Numerov Morse-function values and the analytic Morse-function values is very good. The experimentally observed lowest vibrational levels of H_2 are 2170.08, 6331.22, 10257.19, 13952.43, 17420.44, 20662.00 cm^{-1} . The deviations of the Morse-function values from the experimental values indicate that the Morse function is not a very accurate representation of the ground-state H_2 $U(R)$ function.

FIGURE 13.2 The $v = 5$ Morse vibrational wave function for H_2 as found by the Numerov method.



- (b) We have $\langle x_r \rangle \approx \int_{-1.44}^{2.8} x_r |S_r|^2 dx_r \approx \sum_{x_r=-1.44}^{2.8} x_r |S_r|^2 s_r$, where $s_r = 0.02$ is the interval spacing (not to be confused with the vibrational wave function S_r), and where the vibrational wave function S_r must be normalized. (See also Prob. 13.12.) We normalize S_r as described in Section 4.4, and then create a column of $x_r |S_r|^2 s_r$ values. Next we sum these values to find the following results for the six lowest vibrational states (Prob. 13.9b) $\langle x_r \rangle = 0.0440, 0.1365, 0.2360, 0.3435, 0.4605, 0.5884$. Using $x_r = (R - R_e)/B$, we find the following values: $\langle R \rangle = 0.763, 0.811, 0.862, 0.918, 0.978, 1.044 \text{ \AA}$. (To get accurate $\langle x_r \rangle$ values, $E_{\text{vib},r}$ must be found to many more decimal places than given in (a)—enough places to make the wave function close to zero at 2.8. If the spreadsheet does not allow you to enter enough decimal places to do this for $v = 0$, you can take the right-hand limit as 2.5 instead of 2.8.) Because of vibrational anharmonicity, the molecule gets larger as the vibrational quantum number increases. This effect is rather large for light atoms such as hydrogen. The $v = 5$ Numerov–Morse vibrational wave function (Fig. 13.2) shows marked asymmetry about the origin ($x_r = 0$, which corresponds to $R = R_e$). For a spectacular example of the effect of anharmonicity on bond length, see the discussion of He_2 (the world’s largest diatomic molecule) near the end of Section 13.7.

13.3 Atomic Units

Most quantum chemists report the results of their calculations using **atomic units**.

The hydrogen-atom Hamiltonian operator (assuming infinite nuclear mass) in SI units is $-(\hbar^2/2m_e)\nabla^2 - e^2/4\pi\epsilon_0 r$. The system of atomic units is defined as follows. The units of mass, charge, and angular momentum are defined as the electron’s mass m_e , the proton’s charge e , and $\hbar$, respectively (rather than the kilogram, the coulomb, and the $\text{kg m}^2/\text{s}$); the unit of permittivity is $4\pi\epsilon_0$, rather than the $\text{C}^2 \text{N}^{-1} \text{m}^{-2}$. (The atomic unit of mass used in quantum chemistry should not be confused with the quantity 1 amu, which is one-twelfth the mass of a ^{12}C atom.) When we switch to atomic units, $\hbar$, m_e , e , and $4\pi\epsilon_0$ each have a numerical value of 1. Hence, to change a formula from SI units to atomic units, we simply set each of these quantities equal to 1. Thus, in SI atomic units, the H-atom Hamiltonian is $-\frac{1}{2}\nabla^2 - 1/r$, where r is now measured in atomic units of length rather than in meters. The ground-state energy of the hydrogen atom is given by (6.94) as $-\frac{1}{2}(e^2/4\pi\epsilon_0 a_0)$. Since [Eq. (6.106)] $a_0 = 4\pi\epsilon_0 \hbar^2/m_e e^2$, the numerical value of a_0 (the Bohr radius) in atomic units is 1, and the ground-state energy of the hydrogen atom has the numerical value (neglecting nuclear motion) $-\frac{1}{2}$ in atomic units.

The atomic unit of energy, $e^2/4\pi\epsilon_0 a_0$, is called the **hartree** (symbol E_h):

$$1 \text{ hartree} \equiv E_h \equiv \frac{e^2}{4\pi\epsilon_0 a_0} = \frac{m_e e^4}{(4\pi\epsilon_0)^2 \hbar^2} = 27.211385 \text{ eV} = 4.359744 \times 10^{-18} \text{ J} \quad (13.29)$$

The ground-state energy of the hydrogen atom is $-\frac{1}{2}$ hartree if nuclear motion is neglected. The atomic unit of length is called the **bohr**:

$$1 \text{ bohr} \equiv a_0 \equiv 4\pi\epsilon_0 \hbar^2 / m_e e^2 = 0.52917721 \text{ \AA} \quad (13.30)$$

To find the atomic unit of any other quantity (for example, time) one combines $\hbar$, m_e , e , and $4\pi\epsilon_0$ so as to produce a quantity having the desired dimensions. One finds (Prob. 13.14) the atomic unit of time to be $\hbar/E_h = 2.4188843 \times 10^{-17} \text{ s}$ and the atomic unit of electric dipole moment to be $ea_0 = 8.478353 \times 10^{-30} \text{ C m}$.

Atomic units will be used in Chapters 13 to 17.

A more rigorous way to define atomic units is as follows. Starting with the H-atom electronic Schrödinger equation in SI units, we define (as in Section 4.4) the dimensionless reduced variables $E_r \equiv E/A$ and $r_r \equiv r/B$, where A and B are products of powers of the Schrödinger-equation constants $\hbar$, m_e , e , and $4\pi\epsilon_0$ such that A and B have dimensions of energy and length, respectively. The procedure of Section 4.4 shows that (Prob. 13.13) $A = m_e e^4 / (4\pi\epsilon_0)^2 \hbar^2 = e^2 / 4\pi\epsilon_0 a_0 \equiv 1 \text{ hartree}$ and $B = \hbar^2 4\pi\epsilon_0 / m_e e^2 = a_0 \equiv 1 \text{ bohr}$. For this three-dimensional problem, the H-atom wave function has dimensions of $L^{-3/2}$, so the reduced dimensionless ψ_r is defined as $\psi_r \equiv \psi B^{3/2}$. Also,

$$\frac{\partial^2 \psi_r}{\partial r_r^2} = B^{3/2} \frac{\partial^2 \psi}{\partial r^2} \left(\frac{\partial r}{\partial r_r} \right)^2 = B^{3/2} \frac{\partial^2 \psi}{\partial r^2} B^2 = B^{3/2} \frac{\partial^2 \psi}{\partial r^2} a_0^2$$

Introducing the reduced quantities into the Schrödinger equation, we find (Prob. 13.13) that the reduced H-atom Schrödinger equation is $-\frac{1}{2} \nabla_r^2 \psi_r - (1/r_r) \psi_r = E_r \psi_r$, where ∇_r^2 is given by Eq. (6.6) with r replaced by r_r . In practice, people do not bother to include the r subscripts and instead write $-\frac{1}{2} \nabla^2 \psi - (1/r) \psi = E \psi$.

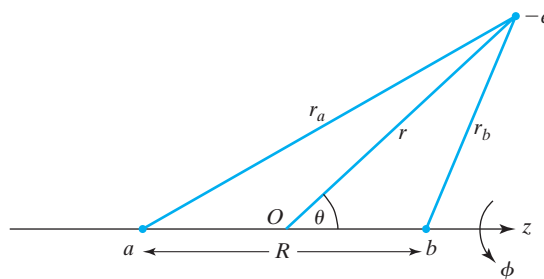
13.4 The Hydrogen Molecule Ion

We now begin the study of the electronic energies of molecules. We shall use the Born–Oppenheimer approximation, keeping the nuclei fixed while we solve, as best we can, the Schrödinger equation for the motion of the electrons. We shall usually be considering an isolated molecule, ignoring intermolecular interactions. Our results will be most applicable to molecules in the gas phase at low pressure. For inclusion of solvent effects, see Sections 15.17 and 17.6.

We start with diatomic molecules, the simplest of which is H_2^+ , the hydrogen molecule ion, consisting of two protons and one electron. Just as the one-electron H atom serves as a starting point in the discussion of many-electron atoms, the one-electron H_2^+ ion furnishes many ideas useful for discussing many-electron diatomic molecules. The electronic Schrödinger equation for H_2^+ is separable, and we can get exact solutions for the eigenfunctions and eigenvalues.

Figure 13.3 shows H_2^+ . The nuclei are at a and b ; R is the internuclear distance; r_a and r_b are the distances from the electron to nuclei a and b . Since the nuclei are fixed, we have a one-particle problem whose purely electronic Hamiltonian is [Eq. (13.5)]

$$\hat{H}_{\text{el}} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} \quad (13.31)$$

FIGURE 13.3 Interparticle distances in H_2^+ .

The first term is the electronic kinetic-energy operator; the second and third terms are the attractions between the electron and the nuclei. In atomic units the purely electronic Hamiltonian for H_2^+ is

$$\hat{H}_{\text{el}} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \quad (13.32)$$

In Fig. 13.3 the coordinate origin is on the internuclear axis, midway between the nuclei, with the z axis lying along the internuclear axis. The H_2^+ electronic Schrödinger equation is not separable in spherical coordinates. However, separation of variables is possible using *confocal elliptic coordinates* ξ , η , and ϕ . The coordinate ϕ is the angle of rotation of the electron about the internuclear (z) axis, the same as in spherical coordinates. The coordinates ξ (xi) and η (eta) are defined by

$$\xi \equiv \frac{r_a + r_b}{R}, \quad \eta \equiv \frac{r_a - r_b}{R} \quad (13.33)$$

The ranges of these coordinates are

$$0 \leq \phi \leq 2\pi, \quad 1 \leq \xi \leq \infty, \quad -1 \leq \eta \leq 1 \quad (13.34)$$

We must put the Hamiltonian (13.32) into these coordinates. We have

$$r_a = \frac{1}{2}R(\xi + \eta), \quad r_b = \frac{1}{2}R(\xi - \eta) \quad (13.35)$$

We also need the expression for the Laplacian in confocal elliptic coordinates. One way to find this is to express ξ , η , and ϕ in terms of x , y , and z , the Cartesian coordinates of the electron, and then use the chain rule to find $\partial/\partial x$, $\partial/\partial y$, and $\partial/\partial z$ in terms of $\partial/\partial \xi$, $\partial/\partial \eta$, and $\partial/\partial \phi$. We then form $\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. The derivation of ∇^2 is omitted. (For a discussion, see *Margenau and Murphy*, Chapter 5.) Substitution of ∇^2 and (13.35) into (13.32) gives $\hat{H}_{\text{el}}$ of H_2^+ in confocal elliptic coordinates. The result is omitted.

For the hydrogen atom, whose Hamiltonian has spherical symmetry, the electronic angular-momentum operators $\hat{L}^2$ and $\hat{L}_z$ both commute with $\hat{H}$. The H_2^+ ion does not have spherical symmetry, and one finds that $[\hat{L}^2, \hat{H}_{\text{el}}] \neq 0$ for H_2^+ . However, H_2^+ does have axial symmetry, and one can show that $\hat{L}_z$ commutes with $\hat{H}_{\text{el}}$ of H_2^+ . Therefore, the electronic wave functions can be chosen to be eigenfunctions of $\hat{L}_z$. The eigenfunctions of $\hat{L}_z$ are [Eq. (5.81)]

$$\text{constant} \cdot (2\pi)^{-1/2} e^{im\phi}, \quad \text{where } m = 0, \pm 1, \pm 2, \pm 3, \dots \quad (13.36)$$

The z component of electronic orbital angular momentum in H_2^+ is $m\hbar$ or m in atomic units. The total electronic orbital angular momentum is not a constant for H_2^+ .

The “constant” in (13.36) is a constant only as far as $\partial/\partial\phi$ is concerned, so the H_2^+ wave functions have the form $\psi_{\text{el}} = F(\xi, \eta)(2\pi)^{-1/2}e^{im\phi}$. One now tries a separation of variables:

$$\psi_{\text{el}} = L(\xi)M(\eta)(2\pi)^{-1/2}e^{im\phi} \quad (13.37)$$

Substitution of (13.37) into $\hat{H}_{\text{el}}\psi_{\text{el}} = E_{\text{el}}\psi_{\text{el}}$ gives an equation in which the variables are separable. One gets two ordinary differential equations, one for $L(\xi)$ and one for $M(\eta)$. Solving these equations, one finds that the condition that ψ_{el} be well-behaved requires that, for each fixed value of R , only certain values of E_{el} are allowed. This gives a set of different electronic states. There is no algebraic formula for E_{el} ; it must be calculated numerically for each desired value of R for each state. In addition to the quantum number m , the H_2^+ electronic wave functions are characterized by the quantum numbers n_ξ and n_η , which give the number of nodes in the $L(\xi)$ and $M(\eta)$ factors in ψ_{el} .

For the ground electronic state, the quantum number m is zero. At $R = \infty$, the H_2^+ ground state is dissociated into a proton and a ground-state hydrogen atom; hence $E_{\text{el}}(\infty) = -\frac{1}{2}$ hartree. At $R = 0$, the two protons have come together to form the He^+ ion with ground-state energy: $-\frac{1}{2}(2)^2$ hartrees $= -2$ hartrees. Addition of the internuclear repulsion $1/R$ (in atomic units) to $E_{\text{el}}(R)$ gives the $U(R)$ potential-energy curve for nuclear motion. Plots of the ground-state $E_{\text{el}}(R)$ and $U(R)$, as found from solution of the electronic Schrödinger equation, are shown in Fig. 13.4. At $R = \infty$ the internuclear repulsion is 0, and U is $-\frac{1}{2}$ hartree.

The $U(R)$ curve is found to have a minimum at $R_e = 1.9972$ bohrs $= 1.057$ Å, indicating that the H_2^+ ground electronic state is a stable bound state. The calculated value of E_{el} at 1.9972 bohrs is -1.1033 hartrees. Addition of the internuclear repulsion $1/R$ gives $U(R_e) = -0.6026$ hartree, compared with -0.5000 hartree at $R = \infty$. The ground-state binding energy is thus $D_e = 0.1026$ hartree $= 2.79$ eV. This corresponds to 64.4 kcal/mol $= 269$ kJ/mol. The binding energy is only 17% of the total energy at the equilibrium internuclear distance. Thus a small error in the total energy can correspond to a large error in the binding energy. For heavier molecules the situation is even worse, since chemical binding energies are of the same order of magnitude for most diatomic molecules, but the total electronic energy increases markedly for heavier molecules.

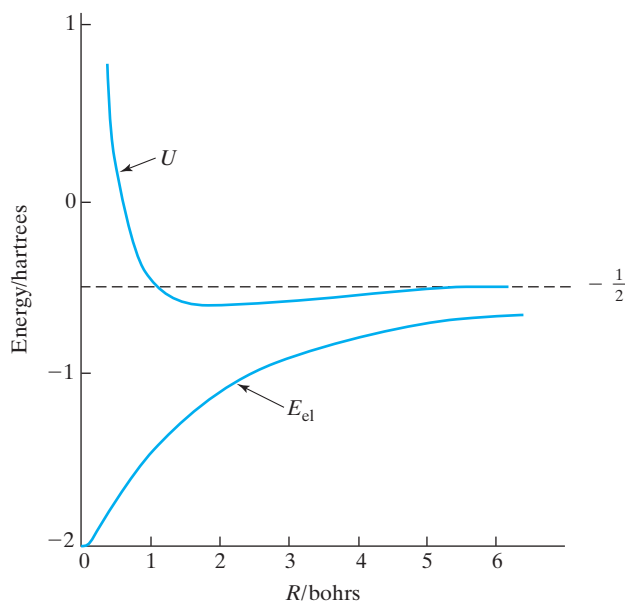
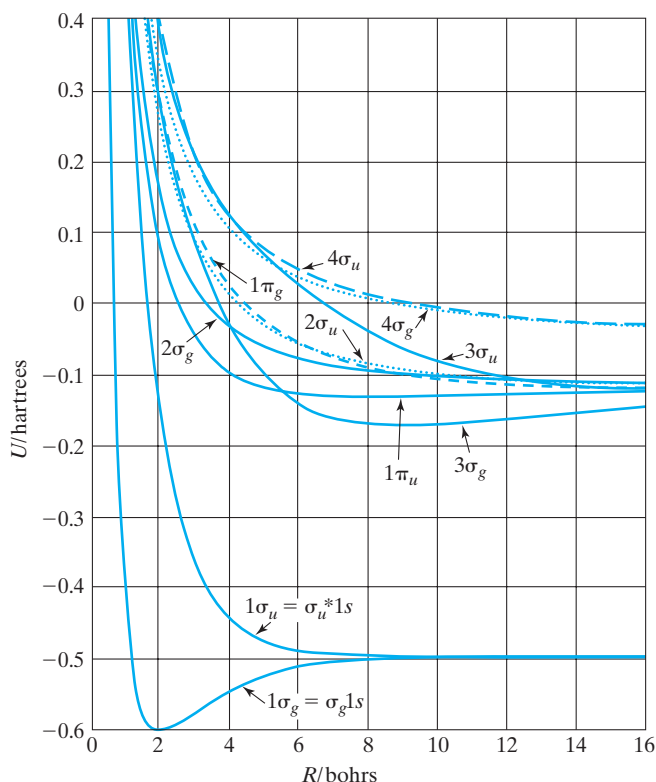


FIGURE 13.4 Electronic energy with (U) and without (E_{el}) internuclear repulsion for the H_2^+ ground electronic state.

FIGURE 13.5 $U(R)$ curves for several H_2^+ electronic states. Dashed lines are used to help distinguish closely spaced states. Not visible on the scale of this diagram is a slight minimum in the curve of the first excited electronic state at 12.5 bohrs with a well depth of 0.00006 hartrees.



Note that the single electron in H_2^+ is sufficient to give a stable bound state.

Figure 13.5 shows the $U(R)$ curves for the first several electronic energy levels of H_2^+ , as found by solving the electronic Schrödinger equation.

The angle ϕ occurs in $\hat{H}_{\text{el}}$ of H_2^+ only as $\partial^2/\partial\phi^2$. When ψ_{el} of (13.37) is substituted into $\hat{H}_{\text{el}}\psi_{\text{el}} = E_{\text{el}}\psi_{\text{el}}$, the $e^{im\phi}$ factor cancels, and we are led to differential equations for $L(\xi)$ and $M(\eta)$ in which the m quantum number occurs only as m^2 . Since E_{el} is found from the $L(\xi)$ and $M(\eta)$ differential equations, E_{el} depends on m^2 , and each electronic level with $m \neq 0$ is doubly degenerate, corresponding to states with quantum numbers $+|m|$ and $-|m|$. In the standard notation for diatomic molecules [F. A. Jenkins, *J. Opt. Soc. Am.*, **43**, 425 (1953)], the absolute value of m is called λ :

$$\lambda \equiv |m|$$

(Some texts define λ as identical to m .) Similar to the s, p, d, f, g notation for hydrogen-atom states, a letter code is used to specify λ , the absolute value (in atomic units) of the component along the molecular axis of the electron's orbital angular momentum:

λ	0	1	2	3	4
letter	σ	π	δ	ϕ	γ

(13.38)

Thus the lowest H_2^+ electronic state is a σ state.

Besides classifying the states of H_2^+ according to λ , we can also classify them according to their parity (Section 7.5). From Fig. 13.12, inversion of the electron's coordinates

through the origin O changes ϕ to $\phi + \pi$, r_a to r_b , and r_b to r_a . This leaves the potential-energy part of the electronic Hamiltonian (13.31) unchanged. We previously showed the kinetic-energy operator to be invariant under inversion. Hence the parity operator commutes with the Hamiltonian (13.31), and the H_2^+ electronic wave functions can be classified as either even or odd. For even electronic wave functions, we use the subscript g (from the German word *gerade*, meaning even); for odd wave functions, we use u (from *ungerade*).

The lowest σ_g energy level in Fig. 13.5 is labeled $1\sigma_g$, the next-lowest σ_g level at small R is labeled $2\sigma_g$, and so on. The lowest σ_u level is labeled $1\sigma_u$, and so on. The alternative notation $\sigma_g 1s$ indicates that this level dissociates to a $1s$ hydrogen atom. The meaning of the star in $\sigma_u^* 1s$ will be explained later.

For completeness, we must take spin into account by multiplying each spatial H_2^+ electronic wave function by α or β , depending on whether the component of electron spin along the internuclear axis is $+\frac{1}{2}$ or $-\frac{1}{2}$ (in atomic units). Inclusion of spin doubles the degeneracy of all levels.

The H_2^+ ground electronic state has $R_e = 2.00$ bohrs $= 2.00(4\pi\epsilon_0\hbar^2/m_e e^2)$. The negative muon (symbol μ^-) is a short-lived (half-life 2×10^{-6} s) elementary particle whose charge is the same as that of an electron but whose mass m_μ is 207 times m_e . When a beam of negative muons (produced when ions accelerated to high speed collide with ordinary matter) enters H_2 gas, muomolecular ions that consist of two protons and one muon are formed. This species, symbolized by $(p\mu p)^+$, is an H_2^+ ion in which the electron has been replaced by a muon. Its R_e is found by replacing m_e with m_μ in R_e :

$$2.00(4\pi\epsilon_0\hbar^2/m_\mu e^2) = 2.00(4\pi\epsilon_0\hbar^2/207m_e e^2) = (2.00/207) \text{ bohr} = 0.0051 \text{ \AA}$$

The two nuclei in this muon are 207 times closer than in H_2^+ . The magnitude of the vibrational-wave-function factor $S_v(R - R_e)$ in (13.28) is small but not entirely negligible for $R - R_e = -0.0051 \text{ \AA}$, so there is some probability for the nuclei in $(p\mu p)^+$ to come in contact, and nuclear fusion might occur. The isotopic nuclei ^2H (deuterium, D) and ^3H (tritium, T) undergo fusion much more readily than protons, so instead of H_2 gas, one uses a mixture of D_2 and T_2 gases. After fusion occurs, the muon is released and can then be recaptured to catalyze another fusion. Under the right conditions, one muon can catalyze 150 fusions on average before it decays. Unfortunately, at present, more energy is needed to produce the muon beam than is released by the fusion. (See en.wikipedia.org/wiki/Muon-catalyzed_fusion.)

In the rest of this chapter, the subscript el will be dropped from the electronic wave function, Hamiltonian, and energy. It will be understood in Chapters 13 to 17 that ψ means ψ_{el} .

13.5 Approximate Treatments of the H_2^+ Ground Electronic State

For a many-electron atom, the self-consistent-field (SCF) method is used to construct an approximate wave function as a Slater determinant of (one-electron) spin-orbitals. The one-electron spatial part of a spin-orbital is an atomic orbital (AO). We took each AO as a product of a spherical harmonic and a radial factor. As an initial approximation to the radial factors, we can use hydrogenlike radial functions with effective nuclear charges.

For many-electron molecules, which (unlike H_2^+) cannot be solved exactly, we want to use many of the ideas of the SCF treatment of atoms. We shall write an approximate molecular electronic wave function as a Slater determinant of (one-electron) spin-orbitals. The one-electron spatial part of a molecular spin-orbital is a **molecular orbital** (MO).

Because of the Pauli principle, each MO can hold no more than two electrons, just as for AOs. What kind of functions do we use for the MOs? Ideally, the analytic form of each MO is found by an SCF calculation (Section 14.3). In this section, we seek simple approximations for the MOs that will enable us to gain some qualitative understanding of chemical bonding. Just as we took the angular part of each AO to be the same kind of function (a spherical harmonic) as in the one-electron hydrogenlike atom, we shall take the angular part of each diatomic MO to be $(2\pi)^{-1/2}e^{im\phi}$, as in H_2^+ . However, the ξ and η factors in the H_2^+ wave functions are complicated functions not readily usable in MO calculations. We therefore seek simpler functions that will provide reasonably accurate approximations to the H_2^+ wave functions and that can be used to construct molecular orbitals for many-electron diatomic molecules. With this discussion as motivation for looking at approximate solutions in a case where the Schrödinger equation is exactly solvable, we consider approximate treatments of H_2^+ .

We shall use the variation method, writing down some function containing several parameters and varying them to minimize the variational integral. This will give an approximation to the ground-state wave function and an upper bound to the ground-state energy. By use of the factor $e^{im\phi}$ in the trial function, we can get an upper bound to the energy of the lowest H_2^+ level for any given value of m (see Section 8.2). By using linear variation functions, we can get approximations for excited states.

The H_2^+ ground state has $m = 0$, and the wave function depends only on ξ and η . We could try any well-behaved function of these coordinates as a trial variation function. We shall, however, use a more systematic approach based on the idea of a molecule as being formed from the interaction of atoms.

Consider what the H_2^+ wave function would look like for large values of the internuclear separation R . When the electron is near nucleus a , nucleus b is so far away that we essentially have a hydrogen atom with origin at a . Thus, when r_a is small, the ground-state H_2^+ electronic wave function should resemble the ground-state hydrogen-atom wave function of Eq. (6.104). We have $Z = 1$, and the Bohr radius a_0 has the numerical value 1 in atomic units; hence (6.104) becomes

$$\pi^{-1/2}e^{-r_a} \quad (13.39)$$

Similarly, we conclude that when the electron is near nucleus b , the H_2^+ ground-state wave function will be approximated by

$$\pi^{-1/2}e^{-r_b} \quad (13.40)$$

This suggests that we try as a variation function

$$c_1\pi^{-1/2}e^{-r_a} + c_2\pi^{-1/2}e^{-r_b} \quad (13.41)$$

where c_1 and c_2 are variational parameters. When the electron is near nucleus a , the variable r_a is small and r_b is large, and the first term in (13.41) predominates, giving a function resembling (13.39). The function (13.41) is a linear variation function, and we are led to solve a secular equation, which has the form (8.56), where the subscripts 1 and 2 refer to the functions (13.39) and (13.40).

We can also approach the problem using perturbation theory. We take the unperturbed system as the H_2^+ molecule with $R = \infty$. For $R = \infty$, the electron can be bound to nucleus a with wave function (13.39), or it can be bound to nucleus b with wave function (13.40). In either case the energy is $-\frac{1}{2}$ hartree, and we have a doubly degenerate unperturbed energy level. Bringing the nuclei in from infinity gives rise to a perturbation that splits the doubly degenerate unperturbed level into two levels. This is illustrated by the $U(R)$ curves for the two lowest H_2^+ electronic states, which both dissociate to a ground-state hydrogen atom (see Fig. 13.5). The correct zeroth-order wave functions for the perturbed levels are linear

combinations of the form (13.41), and we are led to a secular equation of the form (8.56), with W replaced by $E^{(0)} + E^{(1)}$ (see Prob. 9.20).

Before solving (8.56), let us improve the trial function (13.41). Consider the limiting behavior of the H_2^+ ground-state electronic wave function as R goes to zero. In this limit we get the He^+ ion, which has the ground-state wave function [put $Z = 2$ in (6.104)]

$$2^{3/2}\pi^{-1/2}e^{-2r} \quad (13.42)$$

From Fig. 13.3 we see that as R goes to zero, both r_a and r_b go to r . Hence as R goes to zero, the trial function (13.41) goes to $(c_1 + c_2)\pi^{-1/2}e^{-r}$. Comparing with (13.42), we see that our trial function has the wrong limiting behavior at $R = 0$; it should go to e^{-2r} , not e^{-r} . We can fix things by multiplying r_a and r_b in the exponentials by a variational parameter k , which will be some function of R ; $k = k(R)$. For the correct limiting behavior at $R = 0$ and at $R = \infty$, we have $k(0) = 2$ and $k(\infty) = 1$ for the H_2^+ ground electronic state. Physically, k is some sort of effective nuclear charge, which increases as the nuclei come together. We thus take the trial function as

$$\phi = c_a 1s_a + c_b 1s_b \quad (13.43)$$

where the c 's are variational parameters and

$$1s_a = k^{3/2}\pi^{-1/2}e^{-kr_a}, \quad 1s_b = k^{3/2}\pi^{-1/2}e^{-kr_b} \quad (13.44)$$

The factor $k^{3/2}$ normalizes $1s_a$ and $1s_b$ [see Eq. (6.104)]. The molecular-orbital function (13.43) is a **linear combination of atomic orbitals**, an LCAO-MO. The trial function (13.43) was first used by Finkelstein and Horowitz in 1928.

For the function (13.43), the secular equation (8.56) is

$$\begin{vmatrix} H_{aa} - WS_{aa} & H_{ab} - WS_{ab} \\ H_{ba} - WS_{ba} & H_{bb} - WS_{bb} \end{vmatrix} = 0 \quad (13.45)$$

The integrals H_{aa} and H_{bb} are

$$H_{aa} = \int 1s_a^* \hat{H} 1s_a dv, \quad H_{bb} = \int 1s_b^* \hat{H} 1s_b dv \quad (13.46)$$

where the H_2^+ electronic Hamiltonian operator $\hat{H}$ is given by (13.32). We can relabel the variables in a definite integral without affecting its value. Changing a to b and b to a changes $1s_a$ to $1s_b$ but leaves $\hat{H}$ unaffected (this would not be true for a heteronuclear diatomic molecule). Hence $H_{aa} = H_{bb}$. We have

$$H_{ab} = \int 1s_a^* \hat{H} 1s_b dv, \quad H_{ba} = \int 1s_b^* \hat{H} 1s_a dv \quad (13.47)$$

Since $\hat{H}$ is Hermitian and the functions in these integrals are real, we conclude that $H_{ab} = H_{ba}$. The integral H_{ab} is called a *resonance* (or *bond*) *integral*. Since $1s_a$ and $1s_b$ are normalized and real, we have

$$S_{aa} = \int 1s_a^* 1s_a dv = 1 = S_{bb}$$

$$S_{ab} = \int 1s_a^* 1s_b dv = S_{ba} \quad (13.48)$$

The **overlap integral** S_{ab} lies between 1 and 0, and decreases as the distance between the two nuclei increases.

The secular equation (13.45) becomes

$$\begin{vmatrix} H_{aa} - W & H_{ab} - S_{ab}W \\ H_{ab} - S_{ab}W & H_{aa} - W \end{vmatrix} = 0 \quad (13.49)$$

$$H_{aa} - W = \pm (H_{ab} - S_{ab}W) \quad (13.50)$$

$$W_1 = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}, \quad W_2 = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \quad (13.51)$$

These two roots are upper bounds to the energies of the ground and first excited electronic states of H_2^+ . We shall see that H_{ab} is negative, so W_1 is the lower-energy root.

We now find the coefficients in (13.43) for each of the roots of the secular equation. From Eq. (8.54), we have

$$(H_{aa} - W)c_a + (H_{ab} - S_{ab}W)c_b = 0 \quad (13.52)$$

Substituting in W_1 from (13.51) [or using (13.50)], we get

$$c_a/c_b = 1 \quad (13.53)$$

$$\phi_1 = c_a(1s_a + 1s_b) \quad (13.54)$$

We fix c_a by normalization:

$$|c_a|^2 \int (1s_a^2 + 1s_b^2 + 2 \cdot 1s_a 1s_b) dv = 1 \quad (13.55)$$

$$|c_a| = \frac{1}{(2 + 2S_{ab})^{1/2}} \quad (13.56)$$

The normalized trial function corresponding to the energy W_1 is therefore

$$\phi_1 = \frac{1s_a + 1s_b}{\sqrt{2}(1 + S_{ab})^{1/2}} \quad (13.57)$$

For the root W_2 , we find $c_b = -c_a$ and

$$\phi_2 = \frac{1s_a - 1s_b}{\sqrt{2}(1 - S_{ab})^{1/2}} \quad (13.58)$$

Equations (13.57) and (13.58) come as no surprise. Since the nuclei are identical, we expect $|\phi|^2$ to remain unchanged on interchanging a and b ; in other words, we expect no polarity in the bond.

We now consider evaluation of the integrals H_{aa} , H_{ab} , and S_{ab} . From (13.44) and (13.33), the integrand of S_{ab} is $1s_a 1s_b = k^3 \pi^{-1} e^{-k(r_a + r_b)} = k^3 \pi^{-1} e^{-kR\xi}$. The volume element in confocal elliptic coordinates is (Eyring, Walter, and Kimball, Appendix III)

$$dv = \frac{1}{8} R^3 (\xi^2 - \eta^2) d\xi d\eta d\phi \quad (13.59)$$

Substitution of these expressions for $1s_a 1s_b$ and dv into S_{ab} and use of the Appendix integral (A.11) to do the ξ integral gives (Prob. 13.16)

$$S_{ab} = e^{-kR} (1 + kR + \frac{1}{3} k^2 R^2) \quad (13.60)$$

The evaluation of H_{aa} and H_{ab} is considered in Prob. 13.17. The results are

$$H_{aa} = \frac{1}{2} k^2 - k - R^{-1} + e^{-2kR} (k + R^{-1}) \quad (13.61)$$

$$H_{ab} = -\frac{1}{2}k^2 S_{ab} - k(2 - k)(1 + kR)e^{-kR} \quad (13.62)$$

where $\hat{H}$ is given by (13.32) and so omits the internuclear repulsion.

Substituting the values for the integrals into (13.51), we get

$$W_{1,2} = -\frac{1}{2}k^2 + \frac{k^2 - k - R^{-1} + R^{-1}(1 + kR)e^{-2kR} \pm k(k - 2)(1 + kR)e^{-kR}}{1 \pm e^{-kR}(1 + kR + k^2 R^2/3)} \quad (13.63)$$

where the upper signs are for W_1 . Since $\hat{H}$ in (13.32) omits the internuclear repulsion $1/R$, W_1 and W_2 are approximations to the purely electronic energy E_{el} , and $1/R$ must be added to $W_{1,2}$ to get $U_{1,2}(R)$ [Eq. (13.8)].

The final task is to vary the parameter k at many fixed values of R so as to minimize first $U_1(R)$ and then $U_2(R)$. This can be done numerically using a computer (Prob. 13.19) or analytically. The results are that, for the $1s_a + 1s_b$ function (13.57), k increases almost monotonically from 1 to 2 as R decreases from ∞ to 0; for the $1s_a - 1s_b$ function (13.58), k decreases almost monotonically from 1 to 0.4 as R decreases from ∞ to 0. Since $0 < k \leq 2$ and $S_{ab} > 0$, Eq. (13.62) shows that the integral H_{ab} is always negative. Therefore, W_1 in (13.51) corresponds to the ground electronic state $\sigma_g 1s$ of H_2^+ . For the ground state, one finds $k(R_e) = 1.24$.

We might ask why the variational parameter k for the $\sigma_u^* 1s$ state goes to 0.4, rather than to 2, as R goes to zero. The answer is that this state of H_2^+ does not go to the ground state ($1s$) of He^+ as R goes to zero. The $\sigma_u^* 1s$ state has odd parity and must correlate with an odd state of He^+ . The lowest odd states of He^+ are the $2p$ states (Section 11.5); since the $\sigma_u^* 1s$ state has zero electronic orbital angular momentum along the internuclear (z) axis, this state must go to an atomic $2p$ state with $m = 0$, that is, to the $2p_0 = 2p_z$ state.

Having found $k(R)$ for each root, one calculates W_1 and W_2 from (13.63) and adds $1/R$ to get the $U(R)$ curves. The calculated ground-state $U(R)$ curve has a minimum at 2.00 bohrs (Prob. 13.20), in agreement with the true R_e value 2.00 bohrs, and has $U(R_e) = -15.96$ eV, giving a predicted D_e of 2.36 eV, as compared with the true value 2.79 eV. (If we omit varying k but simply set it equal to 1, we get $R_e = 2.49$ bohrs and $D_e = 1.76$ eV.)

Now consider the appearance of the trial functions for the $\sigma_g 1s$ and $\sigma_u^* 1s$ states at intermediate values of R . Figure 13.6 shows the values of the functions $(1s_a)^2$ and $(1s_b)^2$ at points on the internuclear axis (see also Fig. 6.7). For the $\sigma_g 1s$ function $1s_a + 1s_b$, we get a buildup of electronic probability density between the nuclei, as shown in Fig. 13.7. It is especially significant that the buildup of charge between the nuclei is greater than that obtained by simply taking the sum of the separate atomic charge densities. The probability

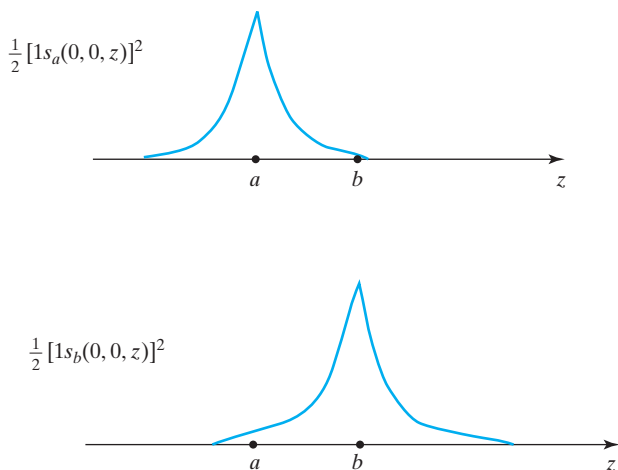
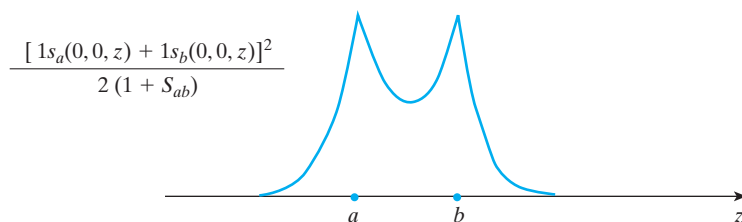


FIGURE 13.6 Atomic probability densities for H_2^+ . Note the cusps at the nuclei.

FIGURE 13.7 Probability density along the internuclear axis for the LCAO-MO function $N(1s_a + 1s_b)$.



density for an electron in a $1s_a$ atomic orbital is $(1s_a)^2$. If we add the probability density for half an electron in a $1s_a$ AO and half an electron in a $1s_b$ AO, we get

$$\frac{1}{2}(1s_a^2 + 1s_b^2) \quad (13.64)$$

However, in quantum mechanics, we do not add the separate atomic probability densities. Instead, we add the wave functions, as in (13.57). The H_2^+ ground-state probability density is then

$$\phi_1^2 = \frac{1}{2(1 + S_{ab})} [1s_a^2 + 1s_b^2 + 2(1s_a 1s_b)] \quad (13.65)$$

The difference between (13.65) and (13.64) is

$$\phi_1^2 - \frac{1}{2}(1s_a^2 + 1s_b^2) = \frac{1}{2(1 + S_{ab})} [2(1s_a 1s_b) - S_{ab}(1s_a^2 + 1s_b^2)] \quad (13.66)$$

Putting $R = 2.00$ and $k = 1.24$ in Eq. (13.60), we find that $S_{ab} = 0.46$ at R_e . (It might be thought that because of the orthogonality of different AOs, the overlap integral S_{ab} should be zero. However, the AOs $1s_a$ and $1s_b$ are eigenfunctions of *different* Hamiltonian operators—one for a hydrogen atom at a and one for a hydrogen atom at b . Hence the orthogonality theorem does not apply.)

Consider now the relative magnitudes of the two terms in brackets in (13.66) for points on the molecular axis. To the left of nucleus a , the function $1s_b$ is very small; to the right of nucleus b , the function $1s_a$ is very small. Hence outside the region between the nuclei, the product $1s_a 1s_b$ is small, and the second term in brackets in (13.66) is dominant. This gives a subtraction of electronic charge density outside the internuclear region, as compared with the sum of the densities of the individual atoms. Now consider the region between the nuclei. At the midpoint of the internuclear axis (and anywhere on the plane perpendicular to the axis and bisecting it), we have $1s_a = 1s_b$, and the bracketed terms in (13.66) become $2(1s_a)^2 - 0.92(1s_a)^2 \approx 1s_a^2$, which is positive. We thus get a buildup of charge probability density between the nuclei in the molecule, as compared with the sum of the densities of the individual atoms. This buildup of electronic charge between the nuclei allows the electron to feel the attractions of both nuclei at the same time, which lowers its potential energy. The greater the overlap in the internuclear region between the atomic orbitals forming the bond, the greater the charge buildup in this region.

The preceding discussion seems to attribute the bonding in H_2^+ mainly to the lowering in the average electronic potential energy that results from having the shared electron interact with two nuclei instead of one. This, however, is an incomplete picture. Calculations on H_2^+ by Feinberg and Ruedenberg show that the decrease in electronic potential energy due to the sharing is of the same order of magnitude as the nuclear repulsion energy $1/R$ and hence is insufficient by itself to give binding. Two other effects also contribute to the bonding. The increase in atomic orbital exponent ($k = 1.24$ at R_e versus 1.0 at ∞) causes charge to accumulate near the nuclei (as well as in the internuclear region), and this further lowers the electronic potential energy. Moreover, the buildup of charge in the internuclear region makes $\partial\psi/\partial z$ zero at the midpoint of the molecular axis and small in the

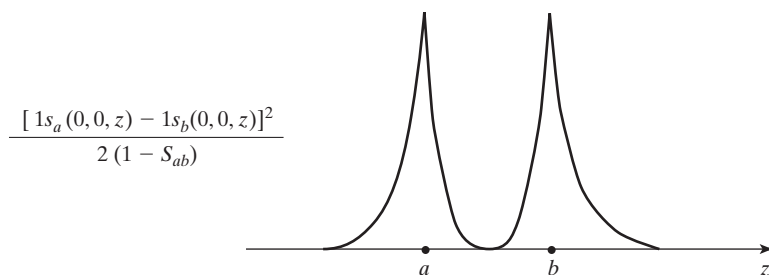


FIGURE 13.8 Probability density along the internuclear axis for the LCAO-MO function $N'(1s_a - 1s_b)$.

region close to this point. Hence the z component of the average electronic kinetic energy [which can be expressed as $\frac{1}{2} \int |\partial\psi/\partial z|^2 d\tau$; Prob. 7.7b] is lowered as compared with the atomic $\langle T_z \rangle$. (However, the *total* average electronic kinetic energy is raised; see Section 14.5.) For details, see M. J. Feinberg and K. Ruedenberg, *J. Chem. Phys.*, **54**, 1495 (1971); M. P. Melrose et al., *Theor. Chim. Acta*, **88**, 311 (1994); see also K. Ruedenberg and M. W. Schmidt, *J. Phys. Chem. A*, **113**, 1954 (2009); *J. Comput. Chem.*, **28**, 391 (2007).

Bader, however, has criticized the views of Feinberg and Ruedenberg. Bader states (among other points) that H_2^+ and H_2 are atypical and that, in contrast to the increase of charge density in the immediate vicinity of the nuclei in H_2 and H_2^+ , molecule formation that involves atoms other than H is usually accompanied by a substantial reduction in charge density in the immediate vicinity of the nuclei. See R. F. W. Bader in *The Force Concept in Chemistry*, B. M. Deb, ed., Van Nostrand Reinhold, 1981, pp. 65–67, 71, 95–100, 113–115. Further study is needed before the origin of the covalent bond can be considered a settled question.

The σ_u^*1s trial function $1s_a - 1s_b$ is proportional to $e^{-kr_a} - e^{-kr_b}$. On the plane perpendicular to the internuclear axis and midway between the nuclei, we have $r_a = r_b$, so this plane is a nodal plane for the σ_u^*1s function. We do not get a buildup of charge between the nuclei for this state, and the $U(R)$ curve has no minimum. We say that the σ_g1s orbital is **bonding** and the σ_u^*1s orbital is **antibonding**. (See Fig. 13.8.)

Reflection of the electron's coordinates in the σ_h symmetry plane perpendicular to the molecular axis and midway between the nuclei converts r_a to r_b and r_b to r_a and leaves ϕ unchanged [Eq. (13.79)]. The operator $\hat{O}_{\sigma_h}$ (Section 12.1) commutes with the electronic Hamiltonian (13.32) and with the parity (inversion) operator. Hence we can choose the H_2^+ wave functions to be eigenfunctions of this reflection operator as well as of the parity operator. Since the square of this reflection operator is the unit operator, its eigenvalues must be +1 and -1 (Section 7.5). States of H_2^+ for which the wave function changes sign upon reflection in this plane (eigenvalue -1) are indicated by a star as a superscript to the letter that specifies λ . States whose wave functions are unchanged on reflection in this plane are left unstarred. Since orbitals with eigenvalue -1 for this reflection have a nodal plane between the nuclei, starred orbitals are antibonding.

Instead of using graphs, we can make contour diagrams of the orbitals (Section 6.7); see Fig. 13.9.

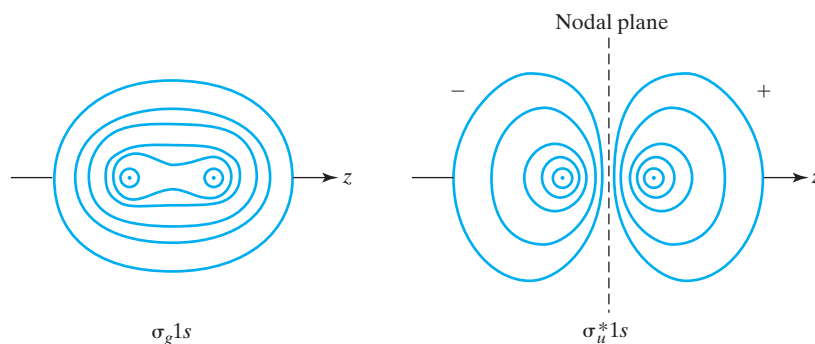


FIGURE 13.9 Contours of constant $|\psi|$ for the σ_g1s and σ_u^*1s MOs. The three-dimensional contour surfaces are generated by rotating these figures about the z axis. Note the resemblance of the antibonding-MO contours to those of a $2p_z$ AO.

Sometimes the binding in H_2^+ is attributed to the resonance integral H_{ab} , since in the approximate treatment we have given, it provides most of the binding energy. This viewpoint is misleading. In the exact treatment of Section 13.4, there arose no such resonance integral. The resonance integral simply arises out of the nature of the LCAO approximation we used.

In summary, we have formed the two H_2^+ MOs (13.57) and (13.58), one bonding and one antibonding, from the AOs $1s_a$ and $1s_b$. The MO energies are given by Eq. (13.51) as

$$W_{1,2} = H_{aa} \pm \frac{H_{ab} - H_{aa}S_{ab}}{1 \pm S_{ab}} \quad (13.67)$$

where $H_{aa} = \langle 1s_a | \hat{H} | 1s_a \rangle$, with $\hat{H}$ being the purely electronic Hamiltonian of H_2^+ . The integral H_{aa} would be the molecule's purely electronic energy if the electron's wave function in the molecule were $1s_a$. In a sense, H_{aa} is the energy of the $1s_a$ orbital in the molecule. In the limit $R = \infty$, H_{aa} becomes the $1s$ AO energy in the H atom. In the molecule, H_{aa} is substantially lower than the electronic energy of an H atom because the electron is attracted to both nuclei. A diagram of MO formation from AOs is given in Fig. 13.22. To get $U(R)$, the electronic energy including nuclear repulsion, we must add $1/R$ to (13.67).

Problem 13.21 outlines the use of Mathcad to create an animation showing how contour plots of the H_2^+ LCAO MOs ϕ_1 and ϕ_2 change as R changes.

We have described the lowest two H_2^+ electronic states according to the state of the hydrogen atom obtained on dissociation. This is a **separated-atoms description**. Alternatively, we can use the state of the atom formed as the internuclear distance goes to zero. This is a **united-atom description**. We saw that for the two lowest electronic states of H_2^+ the united-atom states are the $1s$ and $2p_0$ states of He^+ . The united-atom designation is put on the left of the symbol for λ . The $\sigma_g 1s$ state thus has the united-atom designation $1s\sigma_g$. The $\sigma_u^* 1s$ state has the united-atom designation $2p\sigma_u^*$. It is not necessary to write this state as $2p_0\sigma_u^*$, because the fact that it is a σ state tells us that it correlates with the united-atom $2p_0$ state. For the united-atom description, the subscripts g and u are not needed, since molecular states correlating with $s, d, g, \dots$ atomic states must be g , while states correlating with $p, f, h, \dots$ atomic states must be u . From the separated-atoms states, we cannot tell whether the molecular wave function is g or u . Thus from the $1s$ separated-atoms state we formed both a g and a u function for H_2^+ .

Before constructing approximate molecular orbitals for other H_2^+ states, we consider how the trial function (13.57) can be improved. From the viewpoint of perturbation theory, (13.57) is the correct zeroth-order wave function. We know that the perturbation of molecule formation will mix in other hydrogen-atom states besides $1s$. Dickinson in 1933 used a trial function with some $2p_0$ character mixed in (since the ground state of H_2^+ is a σ state, it would be wrong to mix in $2p_{\pm 1}$ functions); he took

$$\phi = [1s_a + c(2p_0)_a] + [1s_b + c(2p_0)_b] \quad (13.68)$$

where c is a variational parameter and where (Table 6.2)

$$1s_a = k^{3/2} \pi^{-1/2} e^{-kr_a}, \quad (2p_0)_a = (2p_z)_a = \frac{\beta^{5/2}}{4(2\pi)^{1/2}} r_a e^{-\beta r_a/2} \cos \theta_a$$

with k and β being two other variational parameters. We have similar expressions for $1s_b$ and $(2p_0)_b$. The angles θ_a and θ_b refer to two sets of spherical coordinates, one set at each nucleus; see Fig. 13.10. The definitions of θ_a and θ_b correspond to using a right-handed coordinate system on atom a and a left-handed system on atom b . The coefficient c goes to zero as R goes to either zero or infinity.

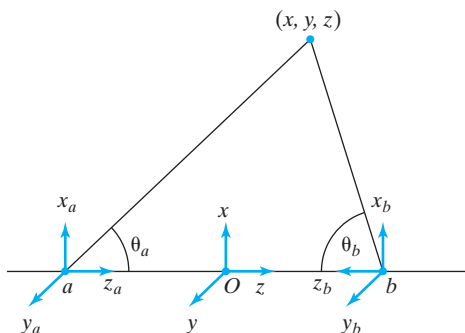


FIGURE 13.10 Coordinate systems for a homonuclear diatomic molecule.

The mixing together of two or more AOs on the same atom is called **hybridization**. The function $1s + c2p_0$ is a hybridized atomic orbital. Since the $2p_0$ function is positive in one lobe and negative in the other, the inclusion of $2p_0$ produces additional charge buildup between the nuclei, giving a greater binding energy. The hybridization allows for the polarization of the $1s_a$ and $1s_b$ atomic orbitals that occurs on molecule formation. The function (13.68) gives a $U(R)$ curve with a minimum at 2.01 bohrs. At this distance, the parameters have the values $k = 1.246$, $\beta = 2.965$, and $c = 0.138$ [F. Weinhold, *J. Chem. Phys.*, **54**, 530 (1971)]. The calculated D_e is 2.73 eV, close to the true value 2.79 eV.

The quantum mechanics and spectroscopy of H_2^+ are reviewed in C. A. Leach and R. E. Moss, *Annu. Rev. Phys. Chem.*, **46**, 55 (1995).

One final point. The approximate wave functions in this chapter are written in atomic units. When rewriting these functions in ordinary units, we must remember that wave functions are not dimensionless. A one-particle wave function ψ has units of $\text{length}^{-3/2}$ (Section 3.5). The AOs $1s_a$ and $1s_b$ that occur in the functions (13.57) and (13.58) are given by (13.44) in atomic units. In ordinary units, $1s_a = (k/a_0)^{3/2} \pi^{-1/2} e^{-kr_a/a_0}$.

13.6 Molecular Orbitals for H_2^+ Excited States

In the preceding section, we used the approximate functions (13.57) and (13.58) for the two lowest H_2^+ electronic states. Now we construct approximate functions for further excited states so as to build up a supply of H_2^+ -like molecular orbitals. We shall then use these MOs to discuss many-electron diatomic molecules qualitatively, just as we used hydrogenlike AOs to discuss many-electron atoms.

To get approximations to higher H_2^+ MOs, we can use the linear-variation-function method. We saw that it was natural to take variation functions for H_2^+ as linear combinations of hydrogenlike atomic-orbital functions, giving LCAO-MOs. To get approximate MOs for higher states, we add in more AOs to the linear combination. Thus, to get approximate wave functions for the six lowest H_2^+ σ states, we use a linear combination of the three lowest $m = 0$ hydrogenlike functions on each atom:

$$\phi = c_1 1s_a + c_2 2s_a + c_3 (2p_0)_a + c_4 1s_b + c_5 2s_b + c_6 (2p_0)_b$$

As found in the preceding section for the function (13.43), the symmetry of the homonuclear diatomic molecule makes the coefficients of the atom- b orbitals equal to ± 1 times the corresponding atom- a orbital coefficients:

$$\phi = [c_1 1s_a + c_2 2s_a + c_3 (2p_0)_a] \pm [c_1 1s_b + c_2 2s_b + c_3 (2p_0)_b] \quad (13.69)$$

where the upper sign goes with the even (g) states.

Consider the relative magnitudes of the coefficients in (13.69). For the two electronic states that dissociate into a $1s$ hydrogen atom, we expect that c_1 will be considerably greater than c_2 or c_3 , since c_2 and c_3 vanish in the limit of R going to infinity. Thus the Dickinson function (13.68) has the $2p_0$ coefficient equal to one-seventh the $1s$ coefficient at R_e . (This function does not include a $2s$ term, but if it did, we would find its coefficient to be small compared with the $1s$ coefficient.) As a first approximation, we therefore set c_2 and c_3 equal to zero, taking

$$\phi = c_1(1s_a \pm 1s_b) \quad (13.70)$$

as an approximation for the wave functions of these two states (as we already have done). From the viewpoint of perturbation theory, if we take the separated atoms as the unperturbed problem, the functions (13.70) are the correct zeroth-order wave functions.

The same argument for the two states that dissociate to a $2s$ hydrogen atom gives us approximate wave functions for them

$$\phi = c_2(2s_a \pm 2s_b) \quad (13.71)$$

since c_1 and c_3 will be small for these states. The functions (13.71) are only an approximation to what we would find if we carried out the linear variation treatment. To find rigorous upper bounds to the energies of these two H_2^+ states, we must use the trial function (13.69) and solve the appropriate secular equation (8.58) (or use matrix algebra—Section 8.6).

In general, we have two H_2^+ states correlating with each separated-atoms state, and rough approximations to the wave functions of these two states will be the LCAO functions $f_a + f_b$ and $f_a - f_b$, where f is a hydrogenlike wave function. The functions (13.70) give the $\sigma_g 1s$ and $\sigma_u^* 1s$ states. Similarly, the functions (13.71) give the $\sigma_g 2s$ and $\sigma_u^* 2s$ molecular orbitals. The outer contour lines for these orbitals are like those for the corresponding MOs made from $1s$ AOs. However, since the $2s$ AO has a nodal sphere while the $1s$ AO does not, each of these MOs has one more nodal surface than the corresponding $\sigma_g 1s$ or $\sigma_u^* 1s$ MO.

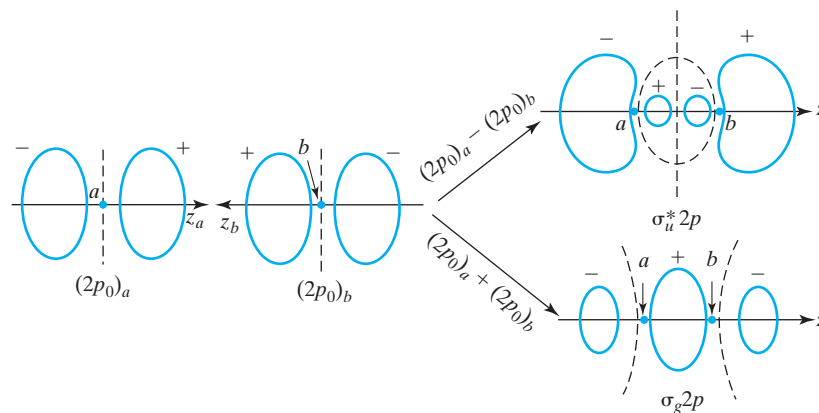
Next we have the combinations

$$(2p_0)_a \pm (2p_0)_b = (2p_z)_a \pm (2p_z)_b \quad (13.72)$$

giving the $\sigma_g 2p$ and $\sigma_u^* 2p$ MOs (Fig. 13.11). These are σ MOs even though they correlate with $2p$ separated AOs, since they have $m = 0$.

The preceding discussion is oversimplified. For the hydrogen atom, the $2s$ and $2p$ AOs are degenerate, and so we can expect the correct zeroth-order functions for the $\sigma_g 2s$, $\sigma_u^* 2s$, $\sigma_g 2p$, and $\sigma_u^* 2p$ MOs of H_2^+ to each be mixtures of $2s$ and $2p$ AOs rather than containing only $2s$ or $2p$ character. [In the $R \rightarrow \infty$ limit, H_2^+ consists of an H atom perturbed by the essentially uniform electric field of a far-distant proton. Problem 9.23

FIGURE 13.11 Formation of $\sigma_g 2p$ and $\sigma_u^* 2p$ MOs from $2p_z$ AOs. The dashed lines indicate nodal surfaces. The signs on the contours give the sign of the wave function. The contours are symmetric about the z axis. (Because of substantial $2s$ – $2p$ hybridization, these contours are not accurate representations of true MO shapes. For accurate contours, see the reference for Fig. 13.20.)



showed that the correct zeroth-order functions for the $n = 2$ levels of an H atom in a uniform electric field in the z direction are $2^{-1/2}(2s + 2p_0)$, $2^{-1/2}(2s - 2p_0)$, $2p_1$, and $2p_{-1}$. Thus, for H_2^+ , $2s$ and $2p_0$ in Eqs. (13.71) and (13.72) should be replaced by $2s + 2p_0$ and $2s - 2p_0$.] For molecules that dissociate into many-electron atoms, the separated-atoms $2s$ and $2p$ AOs are not degenerate but do lie close together in energy. Hence the first-order corrections to the wave functions will mix substantial $2s$ character into the $\sigma 2p$ MOs and substantial $2p$ character into the $\sigma 2s$ MOs. Thus the designation of an MO as $\sigma 2s$ or $\sigma 2p$ should not be taken too literally. For H_2^+ and H_2 , the united-atom designations of the MOs are preferable to the separated-atoms designations, but we shall use mostly the latter.

For the other two $2p$ atomic orbitals, we can use either the $2p_{+1}$ and $2p_{-1}$ complex functions or the $2p_x$ and $2p_y$ real functions. If we want MOs that are eigenfunctions of $\hat{L}_z$, we will choose the complex p orbitals, giving the MOs

$$(2p_{+1})_a + (2p_{+1})_b \quad (13.73)$$

$$(2p_{+1})_a - (2p_{+1})_b \quad (13.74)$$

$$(2p_{-1})_a + (2p_{-1})_b \quad (13.75)$$

$$(2p_{-1})_a - (2p_{-1})_b \quad (13.76)$$

From Eq. (6.114) we have, since $\phi_a = \phi_b = \phi$,

$$(2p_{+1})_a + (2p_{+1})_b = \frac{1}{8}\pi^{-1/2}(r_a e^{-r_a/2} \sin \theta_a + r_b e^{-r_b/2} \sin \theta_b) e^{i\phi} \quad (13.77)$$

Since $\lambda = |m| = 1$, this is a π orbital. The inversion operation amounts to the coordinate transformation (Fig. 13.12)

$$r_a \rightarrow r_b, \quad r_b \rightarrow r_a, \quad \phi \rightarrow \phi + \pi \quad (13.78)$$

We have $e^{i(\phi+\pi)} = (\cos \pi + i \sin \pi) e^{i\phi} = -e^{i\phi}$. From Fig. 13.12 we see that inversion converts θ_a to θ_b and vice versa. Thus inversion converts (13.77) to its negative, meaning it is a u orbital. Reflection in the plane perpendicular to the axis and midway between the nuclei causes the following transformations (Prob. 13.24):

$$r_a \rightarrow r_b, \quad r_b \rightarrow r_a, \quad \phi \rightarrow \phi, \quad \theta_a \rightarrow \theta_b, \quad \theta_b \rightarrow \theta_a \quad (13.79)$$

This leaves (13.77) unchanged, so we have an unstarred (bonding) orbital. The designation of (13.77) is then $\pi_u 2p_{+1}$.

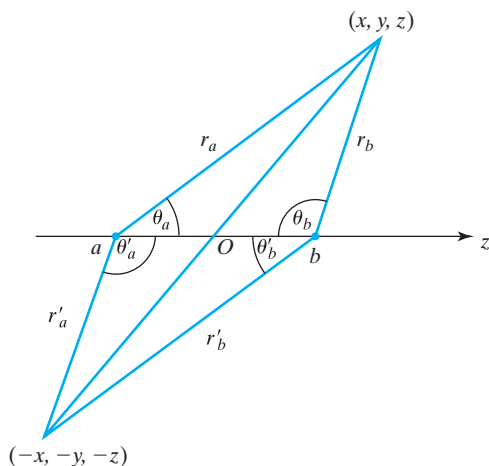
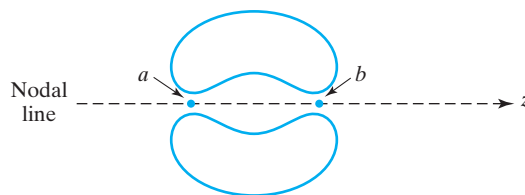


FIGURE 13.12 The effect of inversion of the electron's coordinates in H_2^+ . We have $r'_a = r_b$, $r'_b = r_a$, and $\phi' = \phi + \pi$.

FIGURE 13.13 Cross section of the $\pi_u 2p_{+1}$ (or $\pi_u 2p_{-1}$) molecular orbital. To obtain the three-dimensional contour surface, rotate the figure about the z axis. The z axis is a nodal line for this MO (as it is for the $2p_{+1}$ AO.)



The function (13.77) is complex. Taking its absolute value, we can plot the orbital contours of constant probability density (Section 6.7). Since $|e^{i\phi}| = 1$, the probability density is independent of ϕ , giving a density that is symmetric about the z (internuclear) axis. **Figure 13.13** shows a cross section of this orbital in a plane containing the nuclei. The three-dimensional shape is found by rotating this figure about the z axis, creating a sort of fat doughnut.

The MO (13.75) differs from (13.77) only in having $e^{i\phi}$ replaced by $e^{-i\phi}$ and is designated $\pi_u 2p_{-1}$. The coordinate ϕ enters the H_2^+ Hamiltonian as $\partial^2/\partial\phi^2$. Since $\partial^2 e^{i\phi}/\partial\phi^2 = \partial^2 e^{-i\phi}/\partial\phi^2$, the states (13.73) and (13.75) have the same energy. Recall (Section 13.4) that the $\lambda = 1$ energy levels are doubly degenerate, corresponding to $m = \pm 1$. Since $|e^{i\phi}| = |e^{-i\phi}|$, the $\pi_u 2p_{+1}$ and $\pi_u 2p_{-1}$ MOs have the same shapes, just as the $2p_{+1}$ and $2p_{-1}$ AOs have the same shapes.

The functions (13.74) and (13.76) give the $\pi_g^* 2p_{+1}$ and $\pi_g^* 2p_{-1}$ MOs. These functions do not give charge buildup between the nuclei; see **Fig. 13.14**.

Now consider the more familiar alternative of using the $2p_x$ and $2p_y$ AOs to make the MOs. The linear combination

$$(2p_x)_a + (2p_x)_b \quad (13.80)$$

gives the $\pi_u 2p_x$ MO (**Fig. 13.15**). This MO is not symmetrical about the internuclear axis but builds up probability density in two lobes, one above and one below the yz plane, which is a nodal plane for this function. The wave function has opposite signs on each side of this plane. The linear combination

$$(2p_x)_a - (2p_x)_b \quad (13.81)$$

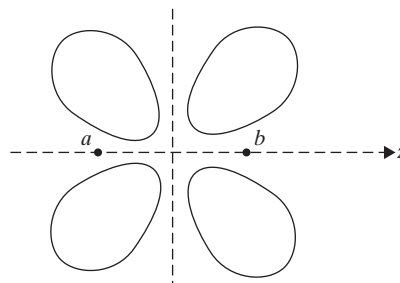
gives the $\pi_g^* 2p_x$ MO (**Fig. 13.15**). Since the $2p_y$ functions differ from the $2p_x$ functions solely by a rotation of 90° about the internuclear axis, they give MOs differing from those of **Fig. 13.15** by a 90° rotation about the z axis. The linear combinations

$$(2p_y)_a + (2p_y)_b \quad (13.82)$$

$$(2p_y)_a - (2p_y)_b \quad (13.83)$$

give the $\pi_u 2p_y$ and $\pi_g^* 2p_y$ molecular orbitals. The MOs (13.80) and (13.82) have the same energy. The MOs (13.81) and (13.83) have the same energy. (Note that the g $\pi 2p$ MOs are antibonding, while the u $\pi 2p$ MOs are bonding.)

FIGURE 13.14 Cross section of the $\pi_g^* 2p_{+1}$ (or $\pi_g^* 2p_{-1}$) MO. To obtain the three-dimensional contour surface, rotate the figure about the z axis. The z axis and the xy plane are nodes.



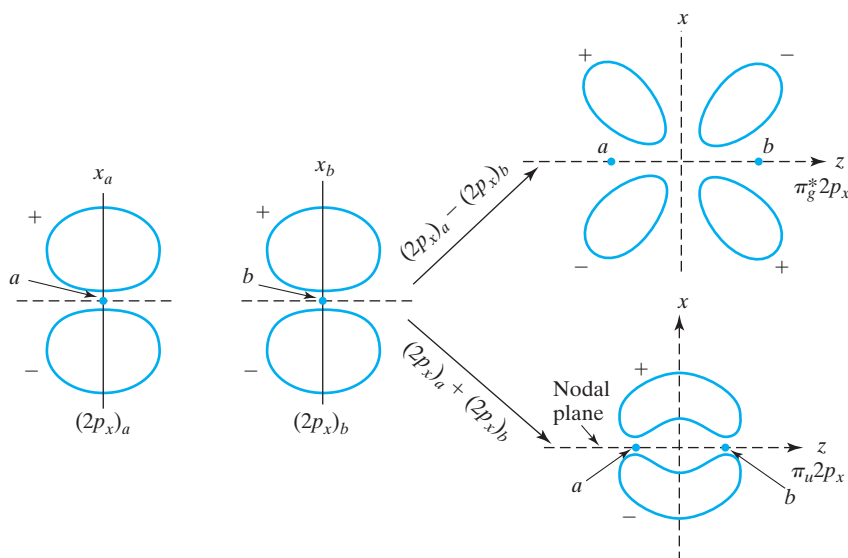


FIGURE 13.15 Formation of the $\pi_u 2p_x$ and $\pi_g^* 2p_x$ MOs. Since $\phi = 0$ in the xz plane, the cross sections of these MOs in the xz plane are the same as for the corresponding $\pi_u 2p_{+1}$ and $\pi_g^* 2p_{-1}$ MOs. However, the $\pi 2p_x$ MOs are not symmetrical about the z axis. Rather, they consist of blobs of probability density above and below the nodal yz plane.

Just as the $2p_x$ and $2p_y$ AOs are linear combinations of the $2p_{+1}$ and $2p_{-1}$ AOs [Eqs. (6.118) and (6.120)], the $\pi_u 2p_x$ and $\pi_u 2p_y$ MOs are linear combinations of the $\pi_u 2p_{+1}$ and $\pi_u 2p_{-1}$ MOs. We can use any linear combination of the eigenfunctions of a degenerate energy level and still have an energy eigenfunction. Just as the $2p_{+1}$ and $2p_{-1}$ AOs are eigenfunctions of $\hat{L}_z$ and the $2p_x$ and $2p_y$ AOs are not, the $\pi_u 2p_{+1}$ and $\pi_u 2p_{-1}$ MOs are eigenfunctions of $\hat{L}_z$ and the $\pi_u 2p_x$ and $\pi_u 2p_y$ MOs are not. For the H_2^+ $\pi_u 2p$ energy level, we can use the pair of real MOs (13.80) and (13.82), or the pair of complex MOs (13.73) and (13.75), or any two linearly independent linear combinations of these functions.

We have shown the correlation of the H_2^+ MOs with the separated-atoms AOs. We can also show how they correlate with the united-atom AOs. As R goes to zero, the $\sigma_u^* 1s$ MO (Fig. 13.9) increasingly resembles the $2p_z$ AO, with which it correlates. Similarly, the $\pi_u 2p$ MOs correlate with p united-atom states, while the $\pi_g^* 2p$ MOs correlate with d united-atom states.

An online simulation of H_2^+ MOs is at www.falstad.com/qmimo; you can vary the internuclear distance.

13.7 MO Configurations of Homonuclear Diatomic Molecules

We now use the H_2^+ MOs developed in the last section to discuss many-electron homonuclear diatomic molecules. (**Homonuclear** means the two nuclei are the same; **heteronuclear** means they are different.) If we ignore the interelectronic repulsions, the zeroth-order wave function is a Slater determinant of H_2^+ -like one-electron spin-orbitals. We approximate the spatial part of the H_2^+ spin-orbitals by the LCAO-MOs of the last section. Treatments that go beyond this crude first approximation will be discussed later.

The sizes and energies of the MOs vary with varying internuclear distance for each molecule and vary as we go from one molecule to another. Thus we saw how the orbital exponent k in the H_2^+ trial function (13.54) varied with R . As we go to molecules with higher nuclear charge, the parameter k for the $\sigma_g 1s$ MO will increase, giving a more compact MO. We want to consider the order of the MO energies. Because of the variation of these energies with R and variations from molecule to molecule, numerous crossings occur, just

TABLE 13.1 Molecular-Orbital Nomenclature for Homonuclear Diatomic Molecules

Separated-Atoms Description	United-Atom Description	Numbering by Symmetry
$\sigma_g 1s$	$1s\sigma_g$	$1\sigma_g$
$\sigma_u^* 1s$	$2p\sigma_u^*$	$1\sigma_u$
$\sigma_g 2s$	$2s\sigma_g$	$2\sigma_g$
$\sigma_u^* 2s$	$3p\sigma_u^*$	$2\sigma_u$
$\pi_u 2p$	$2p\pi_u$	$1\pi_u$
$\sigma_g 2p$	$3s\sigma_g$	$3\sigma_g$
$\pi_g^* 2p$	$3d\pi_g^*$	$1\pi_g$
$\sigma_u^* 2p$	$4p\sigma_u^*$	$3\sigma_u$

as for atomic-orbital energies (Fig. 11.2). Hence we cannot give a definitive order. However, the following is the order in which the MOs fill as we go across the periodic table:

$$\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \pi_u 2p_x = \pi_u 2p_y < \sigma_g 2p < \pi_g^* 2p_x = \pi_g^* 2p_y < \sigma_u^* 2p$$

Each bonding orbital fills before the corresponding antibonding orbital. The $\pi_u 2p$ orbitals are close in energy to the $\sigma_g 2p$ orbital, and it was formerly believed that the $\sigma_g 2p$ MO filled first.

Besides the separated-atoms designation, there are other ways of referring to these MOs; see [Table 13.1](#). The second column of this table gives the united-atom designations. The nomenclature of the third column uses $1\sigma_g$ for the lowest σ_g MO, $2\sigma_g$ for the second lowest σ_g MO, and so on.

Figure 13.16 shows how these MOs correlate with the separated-atoms and united-atom AOs. Because of the variation of MO energies from molecule to molecule, this

FIGURE 13.16 Correlation diagram for homonuclear diatomic MOs. (This diagram does not hold for H_2^+ .) The dashed vertical line corresponds to the order in which the MOs fill.

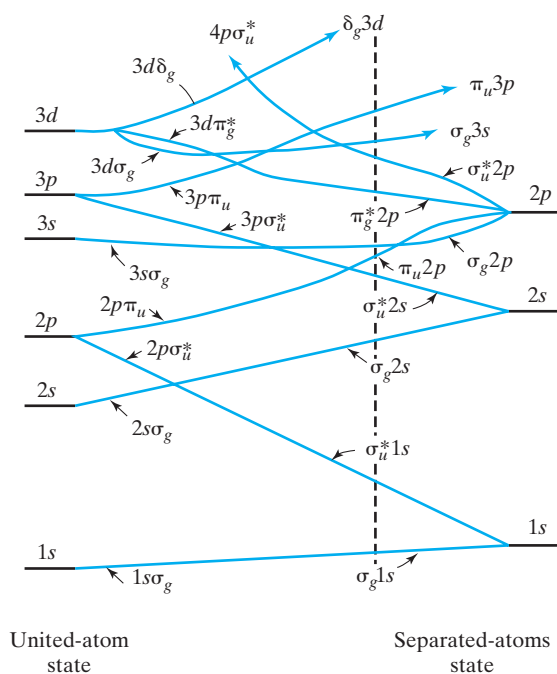


diagram is not quantitative. (The word *correlation* is being used here to mean a correspondence; this is a different meaning than in the term *electron correlation*.)

Recall (Prob. 7.29 and Fig. 6.13) that $s, d, g, \dots$ united-atom AOs are even functions and therefore correlate with *gerade* (g) MOs, whereas $p, f, h, \dots$ AOs are odd functions and correlate with *ungerade* (u) MOs.

A useful principle in drawing orbital correlation diagrams is the *noncrossing rule*, which states that for MO correlation diagrams of many-electron diatomic molecules, the energies of MOs with the same symmetry cannot cross. For diatomic MOs the word *symmetry* refers to whether the orbital is g or u and whether it is $\sigma, \pi, \delta, \dots$. For example, two σ_g MOs cannot cross on a correlation diagram. From the noncrossing rule, we conclude that the lowest MO of a given symmetry type must correlate with the lowest united-atom AO of that symmetry, and similarly for higher orbitals. [A similar noncrossing rule holds for potential-energy curves $U(R)$ for different electronic states of a many-electron diatomic molecule.] The proof of the noncrossing rule is a bit subtle; see C. A. Mead, *J. Chem. Phys.*, **70**, 2276 (1979) for a thorough discussion.

Just as we discussed atoms by filling in the AOs, giving rise to atomic configurations such as $1s^2 2s^2$, we shall discuss homonuclear diatomic molecules by filling in the MOs, giving rise to molecular electronic configurations such as $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2$. (Recall that with a single atomic configuration there is associated a hierarchy of terms, levels, and states; the same is true for a molecular configuration; see Section 13.8.)

Figure 13.17 shows the homonuclear diatomic MOs formed from the $1s, 2s$, and $2p$ AOs.

For H_2^+ we have the ground-state configuration $\sigma_g 1s$, which gives a one-electron bond. For excited states the electron is in one of the higher MOs.

For H_2 we put the two electrons in the $\sigma_g 1s$ MO with opposite spins, giving the ground-state configuration $(\sigma_g 1s)^2$. The two bonding electrons give a single bond. The ground-state dissociation energy D_e is 4.75 eV.

Now consider He_2 . Two electrons go in the $\sigma_g 1s$ MO, thereby filling it. The other two go in the next MO, $\sigma_u^* 1s$. The ground-state configuration is $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2$. With

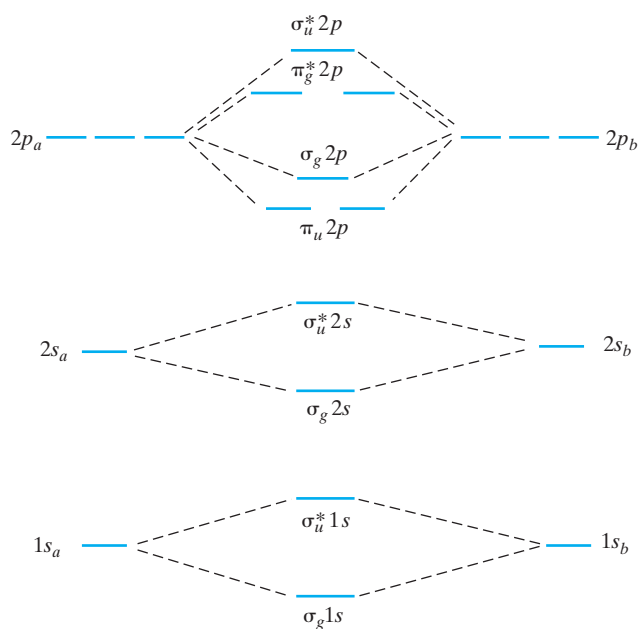


FIGURE 13.17 Homonuclear diatomic MOs formed from $1s, 2s$, and $2p$ AOs.

two bonding and two antibonding electrons, we expect no net bonding, in agreement with the fact that the ground electronic state of He_2 shows no substantial minimum in the potential-energy curve. However, if an electron is excited from the antibonding σ_u^*1s MO to a higher MO that is bonding, the molecule will have three bonding electrons and only one antibonding electron. We therefore expect that He_2 has bound excited electronic states, with a significant minimum in the $U(R)$ curve of each such state. Indeed, about two dozen such bound excited states of He_2 have been spectroscopically observed in gas discharge tubes. Of course, such excited states decay to the ground electronic state, and then the molecule dissociates.

The repulsion of two $1s^2$ helium atoms can be ascribed mainly to the Pauli repulsion between electrons with parallel spins (Section 10.3). Each helium atom has a pair of electrons with opposite spin, and each pair tends to exclude the other pair from occupying the same region of space.

Removal of an antibonding electron from He_2 gives the He_2^+ ion, with ground-state configuration $(\sigma_g1s)^2(\sigma_u^*1s)$ and one net bonding electron. Ground-state properties of this molecule are quite close to those for H_2^+ ; see Table 13.2 later in this section.

Li_2 has the ground-state configuration $(\sigma_g1s)^2(\sigma_u^*1s)^2(\sigma_g2s)^2$ with two net bonding electrons, leading to the description of the molecule as containing an Li–Li single bond. Experimentally, Li_2 is a stable species. In Li_2 the orbital exponent of the $1s$ AOs is considerably greater than in H_2^+ or H_2 , because of the increase in the nuclear charges from 1 to 3. This shrinks the $1s_a$ and $1s_b$ AOs in closer to the corresponding nuclei. There is thus only very slight overlap between these two AOs, and the integrals S_{ab} and H_{ab} are very small for these AOs. As a result, the energies of the σ_g1s and σ_u^*1s MOs in Li_2 are nearly equal to each other and to the energy of a $1s$ Li AO. (For very small R , the $1s_a$ and $1s_b$ AOs do overlap appreciably and their energies then differ considerably.) The Li_2 ground-state configuration is often written as $KK(\sigma_g2s)^2$ to indicate the negligible change in inner-shell orbital energies on molecule formation, which is in accord with the chemist's usual idea of bonding involving only the valence electrons. The orbital exponent of the $2s$ AOs in Li_2 is not much greater than 1, because these electrons are screened from the nucleus by the $1s$ electrons.

The Be_2 ground-state configuration $KK(\sigma_g2s)^2(\sigma_u^*2s)^2$ has no net bonding electrons.

The B_2 ground-state configuration $KK(\sigma_g2s)^2(\sigma_u^*2s)^2(\pi_u2p)^2$ has two net bonding electrons, indicating a stable ground state, as is found experimentally. The bonding electrons are π electrons, which is at variance with the notion that single bonds are always σ bonds. We have two degenerate π_u2p MOs. Recall that when we had an atomic configuration such as $1s^22s^22p^2$ we obtained several terms, which because of interelectronic repulsions had different energies. We saw that the term with the highest total spin was generally the lowest (Hund's rule). With the molecular configuration of B_2 given above, we also have a number of terms. Since the lower (σ) MOs are all filled, their electrons must be paired and contribute nothing to the total spin. If the two π_u2p electrons are both in the same MO (for example, both in π_u2p_{+1}), their spins must be paired (antiparallel), giving a total molecular electronic spin of zero. If, however, we have one electron in the π_u2p_{+1} MO and the other in the π_u2p_{-1} MO, their spins can be parallel, giving a net spin of 1; by Hund's rule, this term will be lowest, and the ground term of B_2 will have spin multiplicity $2S + 1 = 3$. Investigation of the electron-spin-resonance spectrum of B_2 trapped in solid neon at low temperature showed that the B_2 ground term is a triplet with $S = 1$ [L. B. Knight et al., *J. Am. Chem. Soc.*, **109**, 3521 (1987)].

The C_2 ground-state configuration $KK(\sigma_g2s)^2(\sigma_u^*2s)^2(\pi_u2p)^4$ with four net bonding electrons gives a stable ground state with a double bond. As mentioned, the π_u2p and σ_g2p MOs have nearly the same energy in many molecules. The triplet term of the

C_2 $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^3(\sigma_g 2p)$ configuration lies only 0.09 eV above the ground $(\pi_u 2p)^4$ singlet term.

The N_2 ground-state configuration $KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$ with six net bonding electrons gives a triple bond, in accord with the Lewis structure $:N \equiv N:$.

The O_2 ground-state configuration is

$$KK(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^2$$

Spectroscopic evidence shows that in O_2 (and in F_2) the $\sigma_g 2p$ MO is lower in energy than the $\pi_u 2p$ MO. The four net bonding electrons give a double bond. The $\pi_g^* 2p_x$ and $\pi_g^* 2p_y$ MOs have the same energy, and by putting one electron in each with parallel spins, we get a triplet term. By Hund's rule this is the ground term. This explanation of the paramagnetism of O_2 was one of the early triumphs of MO theory.

For F_2 the $\dots(\pi_g^* 2p)^4$ ground-state configuration gives a single bond.

For Ne_2 the $\dots(\pi_g^* 2p)^4(\sigma_u^* 2p)^2$ configuration gives no net bonding electrons and no chemical bond.

We can go on to describe homonuclear diatomic molecules formed from atoms of the next period. Thus the lowest electron configuration of Na_2 is $KKLL(\sigma_g 3s)^2$. However, there are some differences as compared with the corresponding molecules of the preceding period. For Al_2 , the ground term is the triplet term of the $\dots(\sigma_g 3p)(\pi_u 3p)$ configuration, which lies a mere 0.02 eV below the triplet term of the $\dots(\pi_u 3p)^2$ configuration [C. W. Bauschlicher et al., *J. Chem. Phys.*, **86**, 7007 (1987)]. For Si_2 , the ground term is the triplet term of the $\dots(\sigma_g 3p)^2(\pi_u 3p)^2$ configuration, which lies 0.08 eV below the triplet term of the $\dots(\sigma_g 3p)(\pi_u 3p)^3$ configuration [T. N. Kitsopolous et al., *J. Chem. Phys.*, **95**, 1441 (1991)].

Table 13.2 lists D_e , R_e , and $\tilde{\nu}_e \equiv \nu_e/c$ for the ground electronic states of some homonuclear diatomic molecules, where ν_e is the harmonic vibrational frequency (13.27). (In

TABLE 13.2 Properties of Homonuclear Diatomic Molecules in Their Ground Electronic States

Molecule	Ground Term	Bond Order	D_e/eV	$R_e/\text{\AA}$	$\tilde{\nu}_e/\text{cm}^{-1}$
H_2^+	$2\Sigma_g^+$	$\frac{1}{2}$	2.79	1.06	2322
H_2	$1\Sigma_g^+$	1	4.75	0.741	4403
He_2^+	$2\Sigma_u^+$	$\frac{1}{2}$	2.5	1.08	1698
He_2	$1\Sigma_g^+$	0	0.0009	2.97	33
Li_2	$1\Sigma_g^+$	1	1.07	2.67	351
Be_2	$1\Sigma_g^+$	0	0.115	2.45	276
B_2	$3\Sigma_g^-$	1	3.1	1.59	1051
C_2	$1\Sigma_g^+$	2	6.3	1.24	1855
N_2^+	$2\Sigma_g^+$	$2\frac{1}{2}$	8.85	1.12	2207
N_2	$1\Sigma_g^+$	3	9.91	1.10	2358
O_2^+	$2\Pi_g$	$2\frac{1}{2}$	6.78	1.12	1905
O_2	$3\Sigma_g^-$	2	5.21	1.21	1580
F_2	$1\Sigma_g^+$	1	1.66	1.41	917
Ne_2	$1\Sigma_g^+$	0	0.0036	3.1	14

the research literature, $\tilde{\nu}_e$ is written as ω_e .) The table also lists the *bond order*, which is one-half the difference between the number of bonding and antibonding electrons. [For a survey of various methods to calculate bond orders, see J. J. Jules and J. R. Lombardi, *THEOCHEM*, **664–665**, 255 (2003); see also J. F. Gonthier et al., *Chem. Soc. Rev.*, **41**, 4671 (2012).] As the bond order increases, D_e and ν_e tend to increase and R_e decreases. (The high ν_e of H_2 is due to its small reduced mass μ .) The term symbols in this table are explained in the next section.

Bonding MOs produce charge buildup between the nuclei, whereas antibonding MOs produce charge depletion between the nuclei. Hence removal of an electron from a bonding MO usually decreases D_e , whereas removal of an electron from an antibonding MO increases D_e . (Note that as R decreases in Fig. 13.16, the energies of bonding MOs decrease, while the energies of antibonding MOs increase.) For example, the highest filled MO in N_2 is bonding, and Table 13.2 shows that in going from the ground state of N_2 to that of N_2^+ the dissociation energy decreases (and the bond length increases). In contrast, the highest filled MO of O_2 is antibonding, and in going from O_2 to O_2^+ the dissociation energy increases (and R_e decreases). The designation of bonding or antibonding is not relevant to the effect of the electrons on the total energy of the molecule. Energy is always required to ionize a stable molecule, no matter which electron is removed. Hence both bonding and antibonding electrons in a stable molecule decrease the total molecular energy.

If the interaction between two ground-state He atoms were strictly repulsive (as predicted by MO theory), the atoms in He gas would not attract one another at all and the gas would never liquefy. Of course, helium gas can be liquefied. Configuration-interaction calculations and direct experimental evidence from scattering experiments show that as two He atoms approach each other there is an initial weak attraction, with the potential energy reaching a minimum at 2.97 Å of 0.00095 eV below the separated-atoms energy. At distances less than 2.97 Å, the force becomes increasingly repulsive because of overlap of the electron probability densities. The initial attraction (called a **London or dispersion force**) results from instantaneous correlation between the motions of the electrons in one atom and the motions of the electrons in the second atom. Therefore, a calculation that includes electron correlation is needed to deal with dispersion attractions.

The general term for all kinds of intermolecular forces is **van der Waals forces**. Except for highly polar molecules, the dispersion force is the largest contributor to intermolecular attractions. The dispersion force increases as the molecular size increases, so boiling points tend to increase as the molecular weight increases.

The slight minimum in the $U(R)$ curve at relatively large intermolecular separation produced by the dispersion force can be deep enough to allow the existence at low temperatures of molecules bound by the dispersion interaction. Such species are called **van der Waals molecules**. For example, argon gas at 100 K has a small concentration of Ar_2 van der Waals molecules. Ar_2 has $D_e = 0.012$ eV, $R_e = 3.77$ Å, and has seven bound vibrational levels ($v = 0, \dots, 6$).

For the ground electronic state of He_2 [corresponding to the electron configuration $(\sigma_g 1s)^2(\sigma_u^* 1s)^2$], the zero-point vibrational energy is very slightly less than the dissociation energy D_e associated with the dispersion attraction, so the $v = 0, J = 0$ level is the only bound level. Because of the extremely weak binding, He_2 exists in significant amounts only at very low temperatures. He_2 was detected mass spectrometrically in a beam of helium gas cooled to 10^{-3} K by expansion [F. Luo et al., *J. Chem. Phys.*, **98**, 3564 (1993); **100**, 4023 (1994)]. Accurate theoretical calculations on He_2 give $D_e = 0.000948$ eV, $D_0 = 0.00000014$ eV, $R_e = 2.97$ Å and give the average internuclear distance in He_2 as $\langle R \rangle \approx 47$ Å [M. Przybytek et al., *Phys. Rev. Lett.*, **104**, 183003 (2010); M. Jeziorska et al., *J. Chem. Phys.*, **127**, 124303 (2007)]. $\langle R \rangle$ is huge because the $v = 0$ level lies so close to the dissociation limit.

Examples of diatomic van der Waals molecules and their R_e and D_e values include Ne_2 , 3.1 Å, 0.0036 eV; HeNe , 3.2 Å, 0.0012 eV; Ca_2 , 4.28 Å, 0.13 eV; Mg_2 , 3.89 Å, 0.053 eV. Observed polyatomic van der Waals molecules include $(\text{O}_2)_2$, $\text{H}_2\text{--N}_2$, Ar--HCl , and $(\text{Cl}_2)_2$. For van der Waals bonding, R_e is significantly greater and D_e is very substantially less than the values for chemically bound molecules. The Be_2 bond length of 2.45 Å is much shorter than is typical for van der Waals molecules; the closeness of the $2p$ orbitals to $2s$ orbitals in Be allows substantial $2s\text{--}2p$ hybridization in Be_2 and perhaps gives some amount of covalent character in addition to the dispersion attraction. For more on van der Waals molecules, see *Chem. Rev.*, **88**, 813–988 (1988); **94**, 1721–2160 (1994); **100**, 3861–4264 (2000).

13.8 Electronic Terms of Diatomic Molecules

We now consider the terms arising from a given diatomic molecule electron configuration.

For atoms, each set of degenerate atomic orbitals constitutes an atomic subshell. For example, the $2p_{+1}$, $2p_0$, and $2p_{-1}$ AOs constitute the $2p$ subshell. An atomic electronic configuration is defined by giving the number of electrons in each subshell; for example, $1s^2 2s^2 2p^4$. For molecules, each set of degenerate molecular orbitals constitutes a molecular **shell**. For example, the $\pi_u 2p_{+1}$ and $\pi_u 2p_{-1}$ MOs constitute the $\pi_u 2p$ shell. Each diatomic σ shell consists of one MO, while each π , δ , ϕ , . . . shell consists of two MOs; diatomic σ shells are filled with two electrons, while non- σ shells hold up to four electrons. We define a molecular electronic **configuration** by giving the number of electrons in each shell, for example, $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^3$.

For H_2^+ , the operator $\hat{L}_z$ commutes with $\hat{H}$. For a many-electron diatomic molecule, one finds that the operator for the axial component of the total electronic orbital angular momentum commutes with $\hat{H}$. The component of electronic orbital angular momentum along the molecular axis has the possible values $M_L \hbar$, where $M_L = 0, \pm 1, \pm 2, \pm \dots$. To calculate M_L , we simply add algebraically the m 's of the individual electrons. Analogous to the symbol λ for a one-electron molecule, Λ is defined as

$$\Lambda \equiv |M_L| \quad (13.84)$$

(Some people define Λ as equal to M_L .) The following code specifies the value of Λ :

Λ	0	1	2	3	4
letter	Σ	Π	Δ	Φ	Γ

For $\Lambda \neq 0$, there are two possible values of M_L , namely, $+\Lambda$ and $-\Lambda$. As in H_2^+ , the electronic energy depends on M_L^2 , so there is a double degeneracy associated with the two values of M_L . Note that lowercase letters refer to individual electrons, while capital letters refer to the whole molecule.

Just as in atoms, the individual electron spins add vectorially to give a total electronic spin $\mathbf{S}$, whose magnitude has the possible values $[S(S+1)]^{1/2} \hbar$, with $S = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$. The component of $\mathbf{S}$ along an axis has the possible values $M_S \hbar$, where $M_S = S, S-1, \dots, -S$. As in atoms, the quantity $2S+1$ is called the **spin multiplicity** and is written as a left superscript to the code letter for Λ . Diatomic electronic states that arise from the same electron configuration and that have the same value for Λ and the same value for S are said to belong to the same electronic **term**. We now consider how the terms belonging to a given electron configuration are derived. (We are assuming Russell–Saunders coupling, which holds for molecules composed of atoms of not-too-high atomic number.)

A filled diatomic molecule shell consists of one or two filled molecular orbitals. The Pauli principle requires that, for two electrons in the same molecular orbital, one have $m_s = +\frac{1}{2}$ and the other have $m_s = -\frac{1}{2}$. Hence the quantum number M_S , which is the algebraic sum of the individual m_s values, must be zero for a filled-shell molecular

configuration. Therefore, we must have $S = 0$ for a configuration containing only filled molecular shells. A filled σ shell has two electrons with $m = 0$, so M_L is zero. A filled π shell has two electrons with $m = +1$ and two electrons with $m = -1$, so M_L (which is the algebraic sum of the m 's) is zero. The same situation holds for filled $\delta, \phi, \dots$ shells. Thus a closed-shell molecular configuration has both S and Λ equal to zero and gives rise to only a $^1\Sigma$ term. An example is the ground electronic configuration of H_2 . (Recall that a filled-subshell atomic configuration gives only a ^1S term.) In deriving molecular terms, we need consider only electrons outside filled shells.

A single σ electron has $s = \frac{1}{2}$, so S must be $\frac{1}{2}$, and we get a $^2\Sigma$ term. An example is the ground electronic configuration of H_2^+ . A single π electron gives a $^2\Pi$ term, and so on.

Now consider more than one electron. Electrons that are in different molecular shells are called *nonequivalent*. For such electrons we do not have to worry about giving two of them the same set of quantum numbers, and the terms are easily derived. Consider two nonequivalent σ electrons, a $\sigma\sigma$ configuration. Since both m 's are zero, we have $M_L = 0$. Each s is $\frac{1}{2}$, so S can be 1 or 0. We thus have the terms $^1\Sigma$ and $^3\Sigma$. Similarly, a $\sigma\pi$ configuration gives $^1\Pi$ and $^3\Pi$ terms.

For a $\pi\delta$ configuration, we have singlet and triplet terms. The π electron can have $m = \pm 1$, and the δ electron can have $m = \pm 2$. The possible values for M_L are thus $+3, -3, +1$, and -1 . This gives $\Lambda = 3$ or 1, and we have the terms $^1\Pi, ^3\Pi, ^1\Phi, ^3\Phi$. (In atoms we add the *vectors* $\mathbf{L}_i$ to get the total $\mathbf{L}$; hence a pd atomic configuration gives P, D , and F terms. In diatomic molecules, however, we add the z *components* of the orbital angular momenta. This is an algebraic rather than a vectorial addition, so a $\pi\delta$ molecular configuration gives Π and Φ terms and no Δ terms.)

For a $\pi\pi$ configuration of two nonequivalent electrons, each electron has $m = \pm 1$, and we have the M_L values 2, $-2, 0, 0$. The values of Λ are 2, 0, and 0; the terms are $^1\Delta, ^3\Delta, ^1\Sigma, ^3\Sigma, ^1\Sigma$, and $^3\Sigma$. The values $+2$ and -2 correspond to the two degenerate states of the same Δ term. However, Σ terms are nondegenerate (apart from spin degeneracy), and the two values of M_L that are zero indicate two different Σ terms (which become four Σ terms when we consider spin).

Consider the forms of the wave functions for the $\pi\pi$ terms. We shall call the two π subshells π and π' and shall use a subscript to indicate the m value. For the Δ terms, both electrons have $m = +1$ or both have $m = -1$. For $M_L = +2$, we might write as the spatial factor in the wave function $\pi_{+1}(1)\pi'_{+1}(2)$ or $\pi_{+1}(2)\pi'_{+1}(1)$. However, these functions are neither symmetric nor antisymmetric with respect to exchange of the indistinguishable electrons and are unacceptable. Instead, we must take the linear combinations (we shall not bother with normalization constants)

$$^1\Delta: \pi_{+1}(1)\pi'_{+1}(2) + \pi_{+1}(2)\pi'_{+1}(1) \quad (13.85)$$

$$^3\Delta: \pi_{+1}(1)\pi'_{+1}(2) - \pi_{+1}(2)\pi'_{+1}(1) \quad (13.86)$$

Similarly, with both electrons having $m = -1$, we have the spatial factors

$$^1\Delta: \pi_{-1}(1)\pi'_{-1}(2) + \pi_{-1}(2)\pi'_{-1}(1) \quad (13.87)$$

$$^3\Delta: \pi_{-1}(1)\pi'_{-1}(2) - \pi_{-1}(2)\pi'_{-1}(1) \quad (13.88)$$

The functions (13.85) and (13.87) are symmetric with respect to exchange. They therefore go with the antisymmetric two-electron spin factor (11.60), which has $S = 0$. Thus (13.85) and (13.87) are the spatial factors in the wave functions for the two states of the doubly degenerate $^1\Delta$ term. The antisymmetric functions (13.86) and (13.88) must go with the symmetric two-electron spin functions (11.57), (11.58), and (11.59), giving the six states of the $^3\Delta$ term. These states all have the same energy (if we neglect spin-orbit interaction).

Now consider the wave functions of the Σ terms. These have one electron with $m = +1$ and one electron with $m = -1$. We start with the four functions

$$\pi_{+1}(1)\pi'_{-1}(2), \quad \pi_{+1}(2)\pi'_{-1}(1), \quad \pi_{-1}(1)\pi'_{+1}(2), \quad \pi_{-1}(2)\pi'_{+1}(1)$$

Combining them to get symmetric and antisymmetric functions, we have

$$\begin{aligned} {}^1\Sigma^+: & \pi_{+1}(1)\pi'_{-1}(2) + \pi_{+1}(2)\pi'_{-1}(1) + \pi_{-1}(1)\pi'_{+1}(2) + \pi_{-1}(2)\pi'_{+1}(1) \\ {}^1\Sigma^-: & \pi_{+1}(1)\pi'_{-1}(2) + \pi_{+1}(2)\pi'_{-1}(1) - \pi_{-1}(1)\pi'_{+1}(2) - \pi_{-1}(2)\pi'_{+1}(1) \\ {}^3\Sigma^+: & \pi_{+1}(1)\pi'_{-1}(2) - \pi_{+1}(2)\pi'_{-1}(1) + \pi_{-1}(1)\pi'_{+1}(2) - \pi_{-1}(2)\pi'_{+1}(1) \\ {}^3\Sigma^-: & \pi_{+1}(1)\pi'_{-1}(2) - \pi_{+1}(2)\pi'_{-1}(1) - \pi_{-1}(1)\pi'_{+1}(2) + \pi_{-1}(2)\pi'_{+1}(1) \end{aligned} \quad (13.89)$$

The first two functions in (13.89) are symmetric. They therefore go with the antisymmetric singlet spin function (11.60). Clearly, these two spatial functions have different energies. The last two functions in (13.89) are antisymmetric and hence are the spatial factors in the wave functions of the two ${}^3\Sigma$ terms. The four functions in (13.89) are found to have eigenvalue $+1$ or -1 with respect to reflection of electronic coordinates in the xz σ_v symmetry plane containing the molecular (z) axis (Prob. 13.30). The superscripts $+$ and $-$ refer to this eigenvalue.

Examination of the Δ terms (13.85) to (13.88) shows that they are not eigenfunctions of the symmetry operator $\hat{O}_{\sigma_v}$ (Section 12.1). Since a twofold degeneracy (apart from spin degeneracy) is associated with these terms, there is no necessity that their wave functions be eigenfunctions of this operator. However, since $\hat{O}_{\sigma_v}$ commutes with the Hamiltonian, we can *choose* the eigenfunctions to be eigenfunctions of $\hat{O}_{\sigma_v}$. Thus we can combine the functions (13.85) and (13.87), which belong to a degenerate energy level, as follows:

$$(13.85) + (13.87) \quad \text{and} \quad (13.85) - (13.87)$$

These two linear combinations are eigenfunctions of $\hat{O}_{\sigma_v}$ with eigenvalues $+1$ and -1 , and we could refer to them as ${}^1\Delta^+$ and ${}^1\Delta^-$ states. Since they have the same energy, there is no point in using the $+$ and $-$ superscripts. Thus the $+$ and $-$ designations are used only for Σ terms. However, when one considers the interaction between the molecular rotational angular momentum and the electronic orbital angular momentum, there is a very slight splitting (called *Λ -type doubling*) of the two states of a ${}^1\Delta$ term. It turns out that the correct zeroth-order wave functions for this perturbation are the linear combinations that are eigenfunctions of $\hat{O}_{\sigma_v}$, so in this case there is a point to distinguishing between Δ^+ and Δ^- states. The linear combinations $(13.85) \pm (13.87)$, which are eigenfunctions of $\hat{O}_{\sigma_v}$, are not eigenfunctions of $\hat{L}_z$ but are superpositions of $\hat{L}_z$ eigenfunctions with eigenvalues $+2$ and -2 .

We can distinguish $+$ and $-$ terms for one-electron configurations. The wave function of a single σ electron has no ϕ factor and hence must correspond to a Σ^+ term. For a π electron, the MOs that are eigenfunctions of $\hat{L}_z$ are the π_{+1} and π_{-1} functions (whose probability densities are each symmetric about the z axis; Fig. 13.14). The π_{+1} and π_{-1} functions are not eigenfunctions of $\hat{O}_{\sigma_v}$, but the linear combinations $\pi_{+1} + \pi_{-1} = \pi_x$ and $\pi_{+1} - \pi_{-1} = \pi_y$ are. The π_x and π_y MOs (whose probability densities are not symmetric about the z axis; Fig. 13.15) are the correct zeroth-order functions if the perturbation of the electronic wave functions due to molecular rotation is considered. The π_x and π_y MOs have eigenvalues $+1$ and -1 , respectively, for reflection in the xz plane, and eigenvalues -1 and $+1$, respectively, for reflection in the yz plane. (The operators $\hat{L}_z$ and $\hat{O}_{\sigma_v}$ do not commute; Prob. 13.31. Hence we cannot have all the eigenfunctions of $\hat{H}$ being eigenfunctions of both these operators as well. However, since each of these operators commutes with the electronic Hamiltonian and since there is no element of choice in the wave function of a nondegenerate level, all the σ MOs must be eigenfunctions of both $\hat{L}_z$ and $\hat{O}_{\sigma_v}$.)

Electrons in the same molecular shell are called *equivalent*. There are fewer terms for equivalent electrons than for the corresponding nonequivalent electron configuration, because of the Pauli principle. Thus, for a π^2 configuration of two equivalent π electrons, four of the eight functions (13.85) to (13.89) vanish; the remaining functions give a $^1\Delta$ term, a $^1\Sigma^+$ term, and a $^3\Sigma^-$ term. Alternatively, we can make a table similar to Table 11.1 and use it to derive the terms for equivalent electrons.

Table 13.3 lists terms arising from various electron configurations. A filled shell always gives the single term $^1\Sigma^+$. A π^3 configuration gives the same result as a π configuration.

For homonuclear diatomic molecules, a *g* or *u* right subscript is added to the term symbol to show the parity of the electronic states belonging to the term. Terms arising from an electron configuration that has an odd number of electrons in molecular orbitals of odd parity are odd (*u*); all other terms are even (*g*). This is the same rule as for atoms.

The term symbols given in Table 13.2 are readily derived from the MO configurations. For example, O_2 has a π^2 configuration, which gives the three terms $^1\Sigma_g^+$, $^3\Sigma_g^-$, and $^1\Delta_g$. Hund's rule tells us that $^3\Sigma_g^-$ is the lowest term, as listed. The $v = 0$ levels of the $^1\Delta_g$ and $^1\Sigma_g^+$ O_2 terms lie 0.98 eV and 1.6 eV, respectively, above the $v = 0$ level of the ground $^3\Sigma_g^-$ term. Singlet O_2 is a reaction intermediate in many organic, biochemical, and inorganic reactions. [See C. S. Foote et al., eds., *Active Oxygen in Chemistry*, Springer, 1995; J. S. Valentine et al., eds., *Active Oxygen in Biochemistry*, Springer, 1995; C. Schweitzer and R. Schmidt, *Chem. Rev.*, **103**, 1685 (2003).]

Most stable diatomic molecules have a $^1\Sigma^+$ ground term ($^1\Sigma_g^+$ for homonuclear diatomics). Exceptions include B_2 , Al_2 , Si_2 , O_2 , and NO , which has a $^2\Pi$ ground term.

Spectroscopists prefix the ground term of a molecule by the symbol *X*. Excited terms of the same spin multiplicity as the ground term are designated as *A*, *B*, *C*, . . . , while excited terms of different spin multiplicity from the ground term are designated as *a*, *b*, *c*, ... Exceptions are C_2 and N_2 , where the ground terms are $^1\Sigma_g^+$ but the letters *A*, *B*, *C*, . . . are used for excited triplet terms.

Just as for atoms, spin-orbit interaction can split a molecular term into closely spaced energy levels, giving a multiplet structure to the term. The projection of the total electronic

TABLE 13.3 Electronic Terms of Diatomic Molecules

Configuration	Terms
$\sigma\sigma$	$^1\Sigma^+, ^3\Sigma^+$
$\sigma\pi; \sigma\pi^3$	$^1\Pi, ^3\Pi$
$\pi\pi; \pi\pi^3$	$^1\Sigma^+, ^3\Sigma^+, ^1\Sigma^-, ^3\Sigma^-, ^1\Delta, ^3\Delta$
$\pi\delta; \pi^3\delta; \pi\delta^3$	$^1\Pi, ^3\Pi, ^1\Phi, ^3\Phi$
σ	$^2\Sigma^+$
$\sigma^2; \pi^4; \delta^4$	$^1\Sigma^+$
$\pi; \pi^3$	$^2\Pi$
π^2	$^1\Sigma^+, ^3\Sigma^-, ^1\Delta$
$\delta; \delta^3$	$^2\Delta$
δ^2	$^1\Sigma^+, ^3\Sigma^-, ^1\Gamma$

spin S on the molecular axis is $M_S\hbar$. In molecules the quantum number M_S is called Σ (not to be confused with the symbol meaning $\Lambda = 0$):

$$\Sigma = S, S - 1, \dots, -S$$

The axial components of electronic orbital and spin angular momenta add, giving as the total axial component of electronic angular momentum $(\Lambda + \Sigma)\hbar$. (Recall that Λ is the absolute value of M_L . We consider Σ to be positive when it has the same direction as Λ , and negative when it has the opposite direction as Λ .) The possible values of $\Lambda + \Sigma$ are

$$\Lambda + S, \Lambda + S - 1, \dots, \Lambda - S$$

The value of $\Lambda + \Sigma$ is written as a right subscript to the term symbol to distinguish the energy levels of the term. Thus a ${}^3\Delta$ term has $\Lambda = 2$ and $S = 1$ and gives rise to the levels ${}^3\Delta_3$, ${}^3\Delta_2$, and ${}^3\Delta_1$. In a sense, $\Lambda + \Sigma$ is the analog in molecules of the quantum number J in atoms. However, $\Lambda + \Sigma$ is the quantum number of the z component of total electronic angular momentum and therefore can take on negative values. Thus a ${}^4\Pi$ term has the four levels ${}^4\Pi_{5/2}$, ${}^4\Pi_{3/2}$, ${}^4\Pi_{1/2}$, and ${}^4\Pi_{-1/2}$. The absolute value of $\Lambda + \Sigma$ is called Ω :

$$\Omega \equiv |\Lambda + \Sigma| \quad (13.90)$$

The spin-orbit interaction energy in diatomic molecules can be shown to be well approximated by $A\Lambda\Sigma$, where A depends on Λ and on the internuclear distance R but not on Σ . The spacing between levels of the multiplet is thus constant. When A is positive, the level with the lowest value of $\Lambda + \Sigma$ lies lowest, and the multiplet is *regular*. When A is negative, the multiplet is *inverted*. Note that for $\Lambda \neq 0$ the spin multiplicity $2S + 1$ always equals the number of multiplet components. This is not always true for atoms.

Each energy level of a multiplet with $\Lambda \neq 0$ is doubly degenerate, corresponding to the two values for M_L . Thus a ${}^3\Delta$ term has six different wave functions [Eqs. (13.86), (13.88), (11.57) to (11.59)] and therefore six different molecular electronic states. Spin-orbit interaction splits the ${}^3\Delta$ term into three levels, each doubly degenerate. The double degeneracy of the levels is removed by the Λ -type doubling mentioned previously.

For Σ terms ($\Lambda = 0$), the spin-orbit interaction is very small (zero in the first approximation), and the quantum numbers Σ and Ω are not defined.

A ${}^1\Sigma$ term always corresponds to a single nondegenerate energy level.

13.9 The Hydrogen Molecule

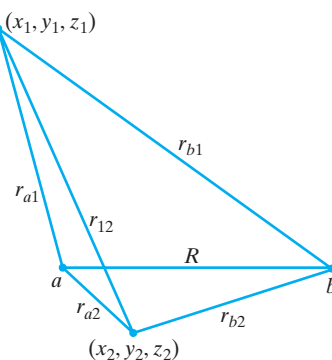
The hydrogen molecule is the simplest molecule containing an electron-pair bond. The purely electronic Hamiltonian (13.5) for H_2 is in atomic units

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} \quad (13.91)$$

where 1 and 2 are the electrons and a and b are the nuclei (Fig. 13.18). Just as in the helium atom, the $1/r_{12}$ interelectronic-repulsion term prevents the Schrödinger equation from being separable. We therefore use approximation methods.

We start with the molecular-orbital approach. The ground-state electron configuration of H_2 is $(\sigma_g 1s)^2$, and we can write an approximate wave function as the Slater determinant

$$\begin{aligned} \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g 1s(1)\alpha(1) & \sigma_g 1s(1)\beta(1) \\ \sigma_g 1s(2)\alpha(2) & \sigma_g 1s(2)\beta(2) \end{vmatrix} &= \sigma_g 1s(1)\sigma_g 1s(2) \cdot 2^{-1/2} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ &= f(1)f(2) \cdot 2^{-1/2} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (13.92) \end{aligned}$$

FIGURE 13.18 Interparticle distances in H_2 .

which is similar to (10.26) for the helium atom. To save time, we write f instead of $\sigma_g 1s$. As we saw in Section 10.4, omission of the spin factor does not affect the variational integral for a two-electron problem. Hence we want to choose f so as to minimize

$$\frac{\iint f^*(1)f^*(2)\hat{H}f(1)f(2) dv_1 dv_2}{\iint |f(1)|^2|f(2)|^2 dv_1 dv_2}$$

where the integration is over the spatial coordinates of the two electrons. Ideally, f should be found by an SCF calculation. For simplicity we can use an H_2^+ -like MO. (The H_2 Hamiltonian becomes the sum of two H_2^+ Hamiltonians if we omit the $1/r_{12}$ term.) We saw in Section 13.5 that the function [Eq. (13.57)]

$$\frac{k^{3/2}}{(2\pi)^{1/2}(1 + S_{ab})^{1/2}} (e^{-kr_a} + e^{-kr_b})$$

gives a good approximation to the ground-state H_2^+ wave function. Hence we try as a variation function ϕ for H_2 the product of two such LCAO functions, one for each electron:

$$\phi = \frac{\zeta^3}{2\pi(1 + S_{ab})} (e^{-\zeta r_{a1}} + e^{-\zeta r_{b1}})(e^{-\zeta r_{a2}} + e^{-\zeta r_{b2}}) \quad (13.93)$$

$$\phi = \frac{1}{2(1 + S_{ab})} [1s_a(1) + 1s_b(1)][1s_a(2) + 1s_b(2)] \quad (13.94)$$

where the effective nuclear charge ζ will differ from k for H_2^+ . Since

$$\hat{H} = \hat{H}_1^0 + \hat{H}_2^0 + 1/r_{12}$$

where $\hat{H}_1^0$ and $\hat{H}_2^0$ are H_2^+ Hamiltonians for each electron, we have

$$\iint \phi^* \hat{H} \phi dv_1 dv_2 = 2W_1 + \iint \frac{\phi^2}{r_{12}} dv_1 dv_2$$

where W_1 is given by (13.63) with k replaced by ζ . The evaluation of the $1/r_{12}$ integral is complicated and is omitted [see Slater, *Quantum Theory of Molecules and Solids*, Volume 1, page 65, and Appendix 6]. Coulson performed the variational calculation in 1937, using (13.93). [For the literature references of the H_2 calculations mentioned in this and later sections, see the bibliography in A. D. McLean et al., *Rev. Mod. Phys.*, **32**, 211 (1960).] Coulson found $R_e = 0.732 \text{ \AA}$, which is close to the true value $0.741 \text{ \AA}$; the minimum in the calculated $U(R)$ curve gave $D_e = 3.49 \text{ eV}$, as compared with the true value

4.75 eV (Table 13.2). (Of course, the percent error in the total electronic energy is much less than the percent error in D_e , but D_e is the quantity of chemical interest.) The value of ζ at 0.732 Å is 1.197, which is less than k for H_2^+ . We attribute this to the screening of the nuclei from each electron by the other electron.

How can we improve on the above simple MO result? We can look for the best possible MO function f in (13.92) to get the Hartree–Fock wave function for H_2 . This was done by Kolos and Roothaan [W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 219 (1960)]. They expanded f in elliptic coordinates [Eq. (13.34)]. Since $m = 0$ for the ground state, the $e^{im\phi}$ factor in the SCF MO is equal to 1 and f is a function of ξ and η only. The expansion used is

$$f = e^{-\alpha\xi} \sum_{p,q} a_{pq} \xi^p \eta^q$$

where p and q are integers and α and a_{pq} are variational parameters. The Hartree–Fock results are $R_e = 0.732$ Å and $D_e = 3.64$ eV, which is not much improvement over the value 3.49 eV given by the simple LCAO molecular orbital. The correlation energy for H_2 is thus -1.11 eV, close to the value -1.14 eV for the two-electron helium atom (Section 11.3). To get a truly accurate binding energy, we must go beyond the SCF approximation of writing the wave function in the form $f(1)f(2)$. We can use the same methods we used for atoms: configuration interaction and introduction of r_{12} into the trial function.

First, consider configuration interaction (CI). To reach the exact ground-state wave function, we include contributions from SCF (or other) functions for all the excited states with the same symmetry as the ground state. In the first approximation, only contributions from the lowest-lying excited states are included. The first excited configuration of H_2 is $(\sigma_g 1s)(\sigma_u^* 1s)$, which gives the terms $^1\Sigma_u^+$ and $^3\Sigma_u^+$. (We have one g and one u electron, so the terms are of odd parity.) The ground-state configuration $(\sigma_g 1s)^2$ is a $^1\Sigma_g^+$ state. Hence we do not get any contribution from the $(\sigma_g 1s)(\sigma_u^* 1s)$ states, since they have different parity from the ground state. Next consider the configuration $(\sigma_u^* 1s)^2$. This is a closed-shell configuration having the single state $^1\Sigma_g^+$. This is of the right symmetry to contribute to the ground-state wave function. As a simple CI trial function, we can take a linear combination of the MO wave functions for the $(\sigma_g 1s)^2$ and $(\sigma_u^* 1s)^2$ configurations. To simplify things, we will use the LCAO-MOs as approximations to the MOs. Thus we take

$$\phi = \sigma_g 1s(1)\sigma_g 1s(2) + c\sigma_u^* 1s(1)\sigma_u^* 1s(2) \quad (13.95)$$

where $\sigma_g 1s$ and $\sigma_u^* 1s$ are given by (13.57) and (13.58) with a variable orbital exponent and c is a variational parameter. This calculation was performed by Weinbaum in 1933. The result is a bond length of 0.757 Å and a dissociation energy of 4.03 eV, which is a considerable improvement over the Hartree–Fock result $D_e = 3.64$ eV. The orbital exponent has the optimum value 1.19. We can improve on this result by using a better form for the MOs of each configuration and by including more configuration functions. Hagstrom did a CI calculation in which the MOs were represented by expansions in elliptic coordinates. With 33 configuration functions, he found $D_e = 4.71$ eV, close to the true value 4.75 eV [S. Hagstrom and H. Shull, *Rev. Mod. Phys.*, **35**, 624 (1963)].

Now consider the use of r_{12} in H_2 trial functions. The first really accurate calculation of the hydrogen-molecule ground state was done by James and Coolidge in 1933. They used the trial function

$$\exp[-\delta(\xi_1 + \xi_2)] \sum c_{mnjkp} [\xi_1^m \xi_2^n \eta_1^j \eta_2^k + \xi_1^n \xi_2^m \eta_1^k \eta_2^j] r_{12}^p$$

where the summation is over integral values of m, n, j, k , and p . The variational parameters are δ and the c_{mnjkp} coefficients. The James and Coolidge function is symmetric with

respect to interchange of electrons 1 and 2, as it should be, since we have an antisymmetric ground-state spin function. With 13 terms in the sum, James and Coolidge found $D_e = 4.72$ eV, only 0.03 eV in error. Their work has been extended by Kolos, Wolniewicz, and co-workers, who used as many as 279 terms in the sum. Since it is D_0 that is determined from the observed electronic spectrum, they used the Cooley–Numerov method (Section 13.2) to calculate the vibrational levels from their theoretical $U(R)$ curve and then calculated D_0 . Including relativistic corrections and corrections to the Born–Oppenheimer approximation, they found $D_0/hc = 36118.1$ cm⁻¹, in agreement with the spectroscopically determined value 36118.1 cm⁻¹ [W. Kolos et al., *J. Chem. Phys.*, **84**, 3278 (1986); L. Wolniewicz, *J. Chem. Phys.*, **99**, 1851 (1993)]. An even more precise D_0 was calculated by workers who did high-precision calculations of relativistic corrections, corrections to the Born–Oppenheimer approximation, and quantum-electrodynamics corrections using a Born–Oppenheimer $U(R)$ found from wave functions having as many as 7000 terms to get $D_0/hc = 36118.0695(10)$ cm⁻¹, where the number in parentheses is the estimate of the uncertainty of the last digits [K. Piszczatowski et al., *J. Chem. Theory Comput.*, **5**, 3039 (2009); www.fuw.edu.pl/~krp/papers/D0.pdf]. The experimental value is 36118.0696(4) cm⁻¹. (Quantum electrodynamics is the relativistic quantum-mechanical theory of the interaction of radiation and matter formulated by Feynman, Schwinger, and Tomonaga in the late 1940s and is an improvement on the quantum field theory of Dirac.)

13.10 The Valence-Bond Treatment of H₂

The first quantum-mechanical treatment of the hydrogen molecule was by Heitler and London in 1927. Their ideas have been extended to give a general theory of chemical bonding, known as the **valence-bond** (VB) theory. The valence-bond method is more closely related to the chemist's idea of molecules as consisting of atoms held together by localized bonds than is the molecular-orbital method. The VB method views molecules as composed of atomic cores (nuclei plus inner-shell electrons) and bonding valence electrons. For H₂, both electrons are valence electrons.

The first step in the Heitler–London treatment of the H₂ ground state is to approximate the molecule as two ground-state hydrogen atoms. The wave function for two such noninteracting atoms is

$$f_1 = 1s_a(1)1s_b(2)$$

where a and b refer to the nuclei and 1 and 2 refer to the electrons. Of course, the function

$$f_2 = 1s_a(2)1s_b(1)$$

is also a valid wave function. This then suggests the trial variation function

$$c_1 f_1 + c_2 f_2 = c_1 1s_a(1)1s_b(2) + c_2 1s_a(2)1s_b(1) \quad (13.96)$$

This linear variation function leads to the determinantal secular equation $\det(H_{ij} - S_{ij}W) = 0$ [Eq. (8.57)], where $H_{11} = \langle f_1 | \hat{H} | f_1 \rangle$, $S_{11} = \langle f_1 | f_1 \rangle$, ...

We can also consider the problem using perturbation theory (as Heitler and London did). A ground-state hydrogen molecule dissociates to two neutral ground-state hydrogen atoms. We therefore take as the unperturbed problem two ground-state hydrogen atoms at infinite separation. One possible zeroth-order (unperturbed) wave function is $1s_a(1)1s_b(2)$. However, electron 2 could just as well be bound to nucleus a , giving the unperturbed wave function $1s_a(2)1s_b(1)$. These two unperturbed wave functions belong to a doubly degenerate energy level (exchange degeneracy). Under the perturbation of molecule formation, the

doubly degenerate level is split into two levels, and the *correct* zeroth-order wave functions are linear combinations of the two unperturbed wave functions:

$$c_1 1s_a(1)1s_b(2) + c_2 1s_a(2)1s_b(1)$$

This leads to a 2×2 secular determinant that is the same as (8.56), except that W is replaced by $E^{(0)} + E^{(1)}$; see Prob. 9.20.

We now solve the secular equation. The Hamiltonian is Hermitian, all functions are real, and f_1 and f_2 are normalized. Therefore

$$H_{12} = H_{21}, \quad S_{12} = S_{21}, \quad S_{11} = S_{22} = 1$$

Consider H_{11} and H_{22} :

$$H_{11} = \langle 1s_a(1)1s_b(2) | \hat{H} | 1s_a(1)1s_b(2) \rangle$$

$$H_{22} = \langle 1s_a(2)1s_b(1) | \hat{H} | 1s_a(2)1s_b(1) \rangle$$

Interchange of the coordinate labels 1 and 2 in H_{22} converts H_{22} to H_{11} , since this relabeling leaves $\hat{H}$ unchanged. Hence $H_{11} = H_{22}$. The secular equation $\det(H_{ij} - S_{ij}W) = 0$ becomes

$$\begin{vmatrix} H_{11} - W & H_{12} - WS_{12} \\ H_{12} - WS_{12} & H_{11} - W \end{vmatrix} = 0 \quad (13.97)$$

This equation has the same form as Eq. (13.49), and by analogy to Eqs. (13.51), (13.57), and (13.58) the approximate energies and wave functions are

$$W_1 = \frac{H_{11} + H_{12}}{1 + S_{12}}, \quad W_2 = \frac{H_{11} - H_{12}}{1 - S_{12}} \quad (13.98)$$

$$\phi_1 = \frac{f_1 + f_2}{\sqrt{2}(1 + S_{12})^{1/2}}, \quad \phi_2 = \frac{f_1 - f_2}{\sqrt{2}(1 - S_{12})^{1/2}} \quad (13.99)$$

The numerators of (13.99) are

$$f_1 \pm f_2 = 1s_a(1)1s_b(2) \pm 1s_a(2)1s_b(1)$$

From our previous discussion, we know that the ground state of H₂ is a $^1\Sigma$ state with the antisymmetric spin factor (11.60) and a symmetric spatial factor. Hence ϕ_1 must be the ground state. The Heitler–London ground-state wave function is

$$\frac{1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)}{\sqrt{2}(1 + S_{12})^{1/2}} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (13.100)$$

The Heitler–London wave functions for the three states of the lowest $^3\Sigma$ term are

$$\frac{1s_a(1)1s_b(2) - 1s_a(2)1s_b(1)}{\sqrt{2}(1 - S_{12})^{1/2}} \begin{cases} \alpha(1)\alpha(2) \\ 2^{-1/2} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \beta(1)\beta(2) \end{cases} \quad (13.101)$$

where S_{12} is given in Prob. 13.33.

Now consider the ground-state energy expression. We write the molecular electronic Hamiltonian as the sum of two H-atom Hamiltonians plus perturbing terms:

$$\hat{H} = \hat{H}_a(1) + \hat{H}_b(2) + \hat{H}' \quad (13.102)$$

$$\hat{H}_a(1) = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a1}}, \quad \hat{H}_b(1) = -\frac{1}{2}\nabla_2^2 - \frac{1}{r_{b2}}, \quad \hat{H}' = -\frac{1}{r_{b1}} - \frac{1}{r_{a2}} + \frac{1}{r_{12}}$$

The Heitler–London calculation does not introduce an effective nuclear charge into the $1s$ function. Hence $1s_a(1)$ is an eigenfunction of $\hat{H}_a(1)$ with eigenvalue $-\frac{1}{2}$ hartree, the hydrogen-atom ground-state energy. Using this result, one finds the following expressions for the VB energies (Prob. 13.33):

$$W_1 = -1 + \frac{Q + A}{1 + S_{ab}^2}, \quad W_2 = -1 + \frac{Q - A}{1 - S_{ab}^2} \quad (13.103)$$

where the *Coulomb integral* Q and the *exchange integral* A are defined by:

$$Q \equiv \langle 1s_a(1)1s_b(2) | \hat{H}' | 1s_a(1)1s_b(2) \rangle \quad (13.104)$$

$$A \equiv \langle 1s_a(2)1s_b(1) | \hat{H}' | 1s_a(1)1s_b(2) \rangle \quad (13.105)$$

and the overlap integral S_{ab} is defined by (13.48). The quantity -1 hartree in these expressions is the energy of two ground-state hydrogen atoms. To obtain the $U(R)$ potential-energy curves, we add the internuclear repulsion $1/R$ to these expressions.

Many of the integrals needed to evaluate W_1 and W_2 have been evaluated in the treatment of H_2^+ in Section 13.5. The only new integrals are those involving $1/r_{12}$. The hardest one is the two-center, two-electron exchange integral:

$$\iint 1s_a(1)1s_b(2) \frac{1}{r_{12}} 1s_a(2)1s_b(1) dv_1 dv_2$$

Two-center means that the integrand contains functions centered on two different nuclei, a and b ; *two-electron* means that the coordinates of two electrons occur in the integrand. This can be evaluated using an expansion for $1/r_{12}$ in confocal elliptic coordinates, similar to the expansion in Prob. 9.14 in spherical coordinates. Details of the integral evaluations are given in Slater, *Quantum Theory of Molecules and Solids*, Volume 1, Appendix 6. The results of the Heitler–London treatment are $D_e = 3.15$ eV, $R_e = 0.87$ Å. The agreement with the experimental values $D_e = 4.75$ eV, $R_e = 0.741$ Å is only fair. In this treatment, most of the binding energy is provided by the exchange integral A .

Consider some improvements on the Heitler–London function (13.100). One obvious step is the introduction of an orbital exponent ζ in the $1s$ function. This was done by Wang in 1928. The optimum value of ζ is 1.166 at R_e , and D_e and R_e are improved to 3.78 eV and 0.744 Å. Recall that Dickinson in 1933 improved the Finkelstein–Horowitz H_2^+ trial function by mixing in some $2p_z$ character into the atomic orbitals (hybridization). In 1931 Rosen used this idea to improve the Heitler–London–Wang function. He took the trial function

$$\phi = \phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)$$

where the atomic orbital ϕ_a is given by $\phi_a = e^{-\zeta r_a}(1 + cz_a)$, with a similar expression for ϕ_b . This allows for the polarization of the AOs on molecule formation. The result is a binding energy of 4.04 eV. Another improvement, the use of ionic structures, will be considered in the next section.

13.11 Comparison of the MO and VB Theories

Let us compare the molecular-orbital and valence-bond treatments of the H_2 ground state.

If ϕ_a symbolizes an atomic orbital centered on nucleus a , the spatial factor of the unnormalized LCAO-MO wave function for the H_2 ground state is

$$[\phi_a(1) + \phi_b(1)][\phi_a(2) + \phi_b(2)] \quad (13.106)$$

In the simplest treatment, ϕ is a $1s$ AO. The function (13.106) equals

$$\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2) + \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) \quad (13.107)$$

What is the physical significance of the terms? The last two terms have each electron in an atomic orbital centered on a different nucleus. These are covalent terms, corresponding to equal sharing of the electrons between the atoms. The first two terms have both electrons in AOs centered on the same nucleus. These are ionic terms, corresponding to the chemical structures



The covalent and ionic terms occur with equal weight, so this simple MO function gives a 50–50 chance as to whether the H_2 ground state dissociates to two neutral hydrogen atoms or to a proton and a hydride ion. Actually, the H_2 ground state dissociates to two neutral H atoms. Thus the simple MO function gives the wrong limiting value of the energy as R goes to infinity.

How can we remedy this? Since H_2 is nonpolar, chemical intuition tells us that ionic terms should contribute substantially less to the wave function than covalent terms. The simplest procedure is to omit the ionic terms of the MO function (13.107). This gives

$$\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) \quad (13.108)$$

We recognize (13.108) as the Heitler–London function (13.100).

Although interelectronic repulsion causes the electrons to avoid each other, there is some probability of finding both electrons near the same nucleus, corresponding to an ionic structure. Therefore, instead of simply dropping the ionic terms from (13.107), we might try

$$\phi_{\text{VB,imp}} = \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) + \delta[\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)] \quad (13.109)$$

where $\delta(R)$ is a variational parameter and the subscript imp indicates an improved VB function. In the language of valence-bond theory, this trial function represents **ionic-covalent resonance**. Of course, the ground-state wave function of H_2 does not undergo a time-dependent change back and forth from a covalent function corresponding to the structure $\text{H}—\text{H}$ to ionic functions. Rather (in the approximation we are considering), the wave function is a time-independent mixture of covalent and ionic functions. Since H_2 dissociates to neutral atoms, we know that $\delta(\infty) = 0$. A variational calculation done by Weinbaum in 1933 using $1s$ AOs with an orbital exponent gave the result that at R_e the parameter δ has the value 0.26; the orbital exponent was found to be 1.19, and the dissociation energy was calculated as 4.03 eV, a modest improvement over the Heitler–London–Wang value of 3.78 eV. With δ equal to zero in (13.109), we get the VB function (13.108). With δ equal to 1, we get the LCAO-MO function (13.107). The optimum value of δ turns out to be closer to zero than to 1, and, in fact, the Heitler–London–Wang VB function gives a better dissociation energy than the LCAO-MO function.

Let us compare the improved valence-bond trial function (13.109) with the simple LCAO-MO function improved by configuration interaction. The LCAO-MO CI trial function (13.95) has the (unnormalized) form

$$\phi_{\text{MO,imp}} = [\phi_a(1) + \phi_b(1)][\phi_a(2) + \phi_b(2)] + \gamma[\phi_a(1) - \phi_b(1)][\phi_a(2) - \phi_b(2)]$$

Since we have not yet normalized this function, there is no harm in multiplying it by the constant $1/(1 - \gamma)$. Doing so and rearranging terms, we get

$$\phi_{\text{MO,imp}} = \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) + \frac{1 + \gamma}{1 - \gamma}[\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)]$$

There is also no harm done if we define a new constant δ as $\delta = (1 + \gamma)/(1 - \gamma)$. We see then that this improved MO function and the improved VB function (13.109) are *identical*. Weinbaum viewed his H_2 calculation as a valence-bond calculation with inclusion of ionic terms. We have shown that we can just as well view the Weinbaum calculation as an MO calculation with configuration interaction. (This was the viewpoint adopted in Section 13.9.)

The MO function (13.107) underestimates electron correlation, in that it says that structures with both electrons on the same atom are just as likely as structures with each electron on a different atom. The VB function (13.108) overestimates electron correlation, in that it has no contribution from structures with both electrons on the same atom. In MO theory, electron correlation can be introduced by configuration interaction. In VB theory, electron correlation is reduced by ionic-covalent resonance. The simple VB method is more reliable at large R than the simple MO method, since the latter predicts the wrong dissociation products.

To further fix the differences between the MO and VB approaches, consider how each method divides the H_2 electronic Hamiltonian into unperturbed and perturbation Hamiltonians. For the MO method, we write

$$\hat{H} = \left[\left(-\frac{1}{2} \nabla_1^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} \right) + \left(-\frac{1}{2} \nabla_2^2 - \frac{1}{r_{a2}} - \frac{1}{r_{b2}} \right) \right] + \frac{1}{r_{12}}$$

where the unperturbed Hamiltonian consists of the bracketed terms. In MO theory the unperturbed Hamiltonian for H_2 is the sum of two H_2^+ Hamiltonians, one for each electron. Accordingly, the zeroth-order MO wave function is a product of two H_2^+ -like wave functions, one for each electron. Since the H_2^+ functions are complicated, we approximate the H_2^+ -like MOs as LCAOs. The effect of the $1/r_{12}$ perturbation is taken into account in an average way through use of self-consistent-field molecular orbitals. To take instantaneous electron correlation into account, we can use configuration interaction.

For the valence-bond method, the terms in the Hamiltonian are grouped in either of two ways:

$$\begin{aligned} \hat{H} &= \left[\left(-\frac{1}{2} \nabla_1^2 - \frac{1}{r_{a1}} \right) + \left(-\frac{1}{2} \nabla_2^2 - \frac{1}{r_{b2}} \right) \right] - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}} \\ \hat{H} &= \left[\left(-\frac{1}{2} \nabla_1^2 - \frac{1}{r_{b1}} \right) + \left(-\frac{1}{2} \nabla_2^2 - \frac{1}{r_{a2}} \right) \right] - \frac{1}{r_{a1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}} \end{aligned}$$

The unperturbed system is two hydrogen atoms. We have two zeroth-order functions consisting of products of hydrogen-atom wave functions, and these belong to a degenerate level. The correct ground-state zeroth-order function is the linear combination (13.100).

The MO method is used far more often than the VB method, because it is computationally much simpler than the VB method. The MO method was developed by Hund, Mulliken, and Lennard-Jones in the late 1920s. Originally, it was used largely for qualitative descriptions of molecules, but the electronic digital computer has made possible the calculation of accurate MO functions (Section 13.14). For a discussion of the relative merits of the MO and VB methods, see R. Hoffman et al., *Acc. Chem. Res.*, **36**, 750 (2003).

13.12 MO and VB Wave Functions for Homonuclear Diatomic Molecules

The MO approximation puts the electrons of a molecule in molecular orbitals, which extend over the whole molecule. As an approximation to the molecular orbitals, we usually use linear combinations of atomic orbitals. The VB method puts the electrons of a molecule in

atomic orbitals and constructs the molecular wave function by allowing for “exchange” of the valence electron pairs between the atomic orbitals of the bonding atoms. We compared the two methods for H_2 . We now consider other homonuclear diatomic molecules.

We begin with the ground state of He_2 . Each separated helium atom has the ground-state configuration $1s^2$. This closed-subshell configuration does not have any unpaired electrons to form valence bonds, and the VB wave function is simply the antisymmetrized product of the atomic-orbital functions. In the notation of Eq. (10.47), the He VB ground state wave function is the Slater determinant

$$|1s_a \overline{1s_a} 1s_b \overline{1s_b}| \quad (13.110)$$

The subscripts a and b refer to the two atoms, and the bar indicates spin function β . The $1s$ function in this wave function is a helium-atom $1s$ function, which ideally is an SCF atomic function but can be approximated by a hydrogenlike function with an effective nuclear charge. The VB wave function for He_2 has each electron paired with another electron in an orbital on the *same* atom and so predicts no bonding.

In the MO approach, He_2 has the ground-state configuration $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2$. With no net bonding electrons, no bonding is predicted, in agreement with the VB method. The MO approximation to the wave function is

$$|\sigma_g 1s \overline{\sigma_g 1s} \sigma_u^* 1s \overline{\sigma_u^* 1s}| \quad (13.111)$$

The simplest way to approximate the (unnormalized) MOs is to take them as linear combinations of the helium-atom AOs: $\sigma_g 1s = 1s_a + 1s_b$ and $\sigma_u^* 1s = 1s_a - 1s_b$. With this approximation, (13.111) becomes

$$|(1s_a + 1s_b) \overline{(1s_a + 1s_b)} (1s_a - 1s_b) \overline{(1s_a - 1s_b)}| \quad (13.112)$$

Using theorems about determinants, we can show (Prob. 13.34) that (13.112) is equal to

$$4|1s_a \overline{1s_a} 1s_b \overline{1s_b}| \quad (13.113)$$

which is identical (after normalization) to the VB function (13.110). This result is easily generalized to the statement that the simple VB and simple LCAO-MO methods give the same approximate wave functions for diatomic molecules formed from separated atoms with completely filled atomic subshells. We could now substitute the trial function (13.110) into the variational integral and calculate the repulsive curve for the interaction of two ground-state He atoms.

Before going on to Li_2 , let us express the Heitler–London valence-bond functions for H_2 as Slater determinants. The ground-state Heitler–London function (13.100) and Prob. 13.33a can be written as

$$\begin{aligned} \frac{1}{2}(1 + S_{ab}^2)^{-1/2} & \left\{ \begin{vmatrix} 1s_a(1)\alpha(1) & 1s_b(1)\beta(1) \\ 1s_a(2)\alpha(2) & 1s_b(2)\beta(2) \end{vmatrix} - \begin{vmatrix} 1s_a(1)\beta(1) & 1s_b(1)\alpha(1) \\ 1s_a(2)\beta(2) & 1s_b(2)\alpha(2) \end{vmatrix} \right\} \\ & = (2 + 2S_{ab}^2)^{-1/2} \{ |1s_a \overline{1s_b}| - |\overline{1s_a} 1s_b| \} \end{aligned} \quad (13.114)$$

In each Slater determinant, the electron on atom a is paired with an electron of opposite spin on atom b , corresponding to the Lewis structure $\text{H}—\text{H}$. The Heitler–London functions (13.101) for the lowest H_2 triplet state can also be written as Slater determinants. Omitting normalization constants, we write the Heitler–London H_2 functions as

$$\text{Singlet: } |1s_a \overline{1s_b}| - |\overline{1s_a} 1s_b| \quad (13.115)$$

$$\text{Triplet: } \begin{cases} |1s_a 1s_b| \\ |1s_a \overline{1s_b}| + |\overline{1s_a} 1s_b| \\ |\overline{1s_a} \overline{1s_b}| \end{cases} \quad (13.116)$$

Now consider Li_2 . The ground-state configuration of Li is $1s^2 2s$, and the Lewis structure of Li_2 is $\text{Li}—\text{Li}$, with the two $2s$ Li electrons paired and the $1s$ electrons remaining in the inner shell of each atom. The part of the valence-bond wave function involving the $1s$ electrons will be like the He_2 function (13.110), while the part of the VB wave function involving the $2s$ electrons (which form the bond) will be like the Heitler–London H_2 function (13.115). Of course, because of the indistinguishability of the electrons, there is complete electronic democracy, and we must allow every electron to be in every orbital. Hence we write the ground-state VB function for Li_2 using 6×6 Slater determinants:

$$|1s_a \overline{1s_a} 1s_b \overline{1s_b} 2s_a \overline{2s_b}| - |1s_a \overline{1s_a} 1s_b \overline{1s_b} \overline{2s_a} 2s_b| \quad (13.117)$$

We have written down (13.117) simply by analogy to (13.110) and (13.115). For a fuller justification of it, we should show that it is an eigenfunction of the spin operators $\hat{S}^2$ and $\hat{S}_z$ with eigenvalue zero for each operator, which corresponds to a singlet state. This can be shown, but we omit doing so. To save space, (13.117) is sometimes written as

$$|1s_a \overline{1s_a} 1s_b \overline{1s_b} \widehat{2s_a 2s_b}| \quad (13.118)$$

where the curved line indicates the pairing (bonding) of the $2s_a$ and $2s_b$ AOs.

The MO wave function for the Li_2 ground state is

$$|\sigma_g 1s \overline{\sigma_g 1s} \sigma_u^* 1s \overline{\sigma_u^* 1s} \sigma_g 2s \overline{\sigma_g 2s}| \quad (13.119)$$

If we approximate the two lowest MOs by $1s_a \pm 1s_b$ then the same procedure used in Prob. 13.34 to show that (13.111) is the same wave function as (13.110) shows that (13.119) is the same as

$$|1s_a \overline{1s_a} 1s_b \overline{1s_b} \sigma_g 2s \overline{\sigma_g 2s}|$$

Recall the notation $KK(\sigma_g 2s)^2$ for the Li_2 ground-state configuration.

Now consider the VB treatment of the N_2 ground state. The lowest configuration of N is $1s^2 2s^2 2p^3$. Hund's rule gives the ground level as $^4S_{3/2}$, with one electron in each of the three $2p$ AOs. We can thus pair the two $2p_x$ electrons, the two $2p_y$ electrons, and the two $2p_z$ electrons to form a triple bond. The Lewis structure is $:\text{N} \equiv \text{N}:$. How is this Lewis structure translated into the VB wave function? In the VB method, opposite spins are given to orbitals bonded together. We have three such pairs of orbitals and two ways to give opposite spins to the electrons of each bonding pair of AOs. Hence there are $2^3 = 8$ possible Slater determinants that we can write. We begin with

$$D_1 = |1s_a \overline{1s_a} 2s_a \overline{2s_a} 1s_b \overline{1s_b} 2s_b \overline{2s_b} 2p_{xa} \overline{2p_{xb}} 2p_{ya} \overline{2p_{yb}} 2p_{za} \overline{2p_{zb}}|$$

In all eight determinants, the first eight columns will remain unchanged, and to save space we write D_1 as

$$D_1 = |\cdots 2p_{xa} \overline{2p_{xb}} 2p_{ya} \overline{2p_{yb}} 2p_{za} \overline{2p_{zb}}| \quad (13.120)$$

Reversing the spins of the electrons in $2p_{xa}$ and $2p_{xb}$, we get

$$D_2 = |\cdots \overline{2p_{xa}} 2p_{xb} 2p_{ya} \overline{2p_{yb}} 2p_{za} \overline{2p_{zb}}| \quad (13.121)$$

There are six other determinants formed by interchanges of spins within the three pairs of bonding orbitals, and the VB wave function is a linear combination of eight determinants (Prob. 13.35). The following rule (see *Kauzmann*, pages 421–422) gives a VB wave function that is an eigenfunction of $\hat{S}^2$ with eigenvalue 0 (as is desired for the ground state): The coefficient of each determinant is +1 or –1 according to whether the number of spin interchanges required to generate the determinant from D_1 is even or odd, respectively. Thus D_2 has coefficient –1. [Compare also (13.115).] Clearly, the single-determinant ground-state N_2 MO function is easier to handle than the eight-determinant VB function.

13.13 Excited States of H₂

We have concentrated mostly on the ground electronic states of diatomic molecules. In this section we consider some of the excited states of H₂. **Figure 13.19** gives the potential-energy curves for some of the H₂ electronic energy levels.

The lowest MO configuration is $(1\sigma_g)^2$, where the notation of the third column of Table 13.1 is used. This closed-shell configuration gives only a nondegenerate $^1\Sigma_g^+$ level, designated $X^1\Sigma_g^+$. The LCAO-MO function is (13.93).

The next-lowest MO configuration is $(1\sigma_g)(1\sigma_u)$, which gives rise to the terms $^1\Sigma_u^+$ and $^3\Sigma_u^+$ (Table 13.3). Since there is no axial electronic orbital angular momentum, each of these terms corresponds to one level. Spectroscopists have named these electronic levels $B^1\Sigma_u^+$ and $b^3\Sigma_u^+$. By Hund's rule, the b level lies below the B level. The LCAO-MO functions for these levels are [see Eqs. (10.27)–(10.30)]

$$b^3\Sigma_u^+: 2^{-1/2}[1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)] \begin{cases} \alpha(1)\alpha(2) \\ 2^{-1/2}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \\ \beta(1)\beta(2) \end{cases}$$

$$B^1\Sigma_u^+: 2^{-1/2}[1\sigma_g(1)1\sigma_u(2) + 1\sigma_g(2)1\sigma_u(1)]2^{-1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

where $1\sigma_g \approx N(1s_a + 1s_b)$ and $1\sigma_u \approx N'(1s_a - 1s_b)$. The $b^3\Sigma_u^+$ level is triply degenerate. The $B^1\Sigma_u^+$ level is nondegenerate. The Heitler–London wave functions for the b level are given by (13.101). Both these levels have one bonding and one antibonding electron, and we would expect the potential-energy curves for both levels to be repulsive. Actually,

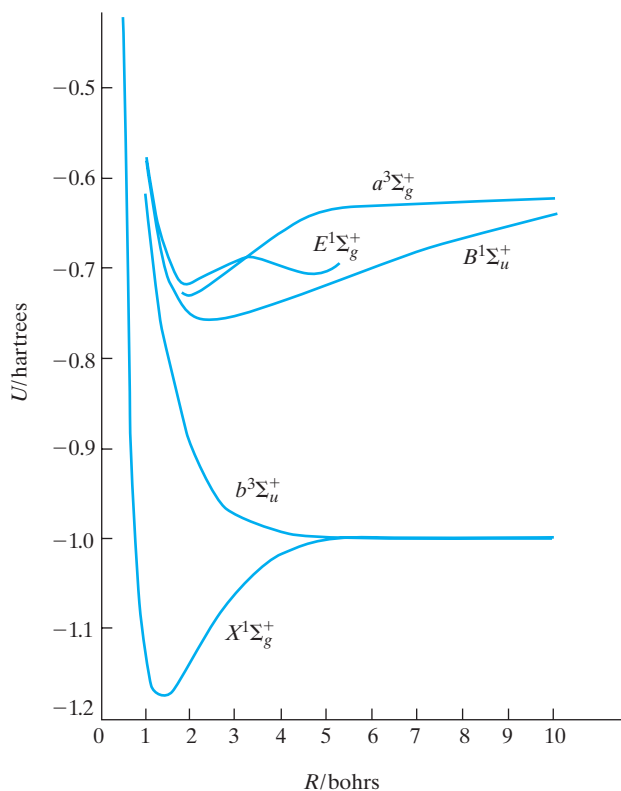


FIGURE 13.19 $U(R)$ curves for some electronic states of H₂. [See W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, **43**, 2429 (1965); **45**, 509 (1966); J. Gerhauser and H. S. Taylor, *J. Chem. Phys.*, **42**, 3621 (1965); W. Kolos, *J. Mol. Spectry*, **143**, 237 (1990).]

the B level has a minimum in its $U(R)$ curve. The stability of this state should caution us against drawing too hasty conclusions from very approximate wave functions.

We expect the next-lowest configuration to be $(1\sigma_g)(2\sigma_g)$, giving rise to $^1\Sigma_g^+$ and $^3\Sigma_g^+$ levels. These levels of H_2 are designated $E^1\Sigma_g^+$ and $a^3\Sigma_g^+$. By Hund's rule, the triplet lies lower. The E state has two substantial minima in its $U(R)$ curve, and is often called the EF state because of the two minima.

Although the $2\sigma_u$ MO fills before the two $1\pi_u$ MOs in going across the periodic table, the $1\pi_u$ MOs lie below the $2\sigma_u$ MO in H_2 . The configuration $(1\sigma_g)(1\pi_u)$ gives rise to the terms $^1\Pi_u$ and $^3\Pi_u$, the triplet lying lower. These terms are designated $C^1\Pi_u$ and $c^3\Pi_u$. The c term gives rise to the levels $c^3\Pi_{2u}$, $c^3\Pi_{1u}$, and $c^3\Pi_{0u}$. These levels lie so close together that they are usually not resolved in spectroscopic work. The C level shows a slight hump in its potential-energy curve at large R . Each level is twofold degenerate, which gives a total of eight electronic states arising from the $(1\sigma_g)(1\pi_u)$ configuration.

13.14 SCF Wave Functions for Diatomic Molecules

This section presents some examples of SCF MO wave functions for diatomic molecules.

The spatial orbitals ϕ_i in an MO wave function are each expressed as a linear combination of a set of one-electron **basis functions** χ_s :

$$\phi_i = \sum_s c_{si} \chi_s \quad (13.122)$$

For SCF calculations on diatomic molecules, one can use Slater-type orbitals [Eq. (11.14)] centered on the various atoms of the molecule as the basis functions. (For an alternative choice, see Section 15.4.) The procedure used to find the coefficients c_{si} of the basis functions in each SCF MO is discussed in Section 14.3. To have a complete set of AO basis functions, an infinite number of Slater orbitals are needed, but the true molecular Hartree–Fock wave function can be closely approximated with a reasonably small number of carefully chosen Slater orbitals. A **minimal basis set** for a molecular SCF calculation consists of a single basis function for each inner-shell AO and each valence-shell AO of each atom. An **extended** basis set is a set that is larger than a minimal set. Minimal-basis-set SCF calculations are easier than extended-basis-set calculations, but the latter are much more accurate.

SCF wave functions using a minimal basis set were calculated by Ransil for several light diatomic molecules [B. J. Ransil, *Rev. Mod. Phys.*, **32**, 245 (1960)]. As an example, the SCF MOs for the ground state of Li_2 [MO configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2$] at $R = R_e$ are

$$\begin{aligned} 1\sigma_g &= 0.706(1s_a + 1s_b) + 0.009(2s_{\perp a} + 2s_{\perp b}) + 0.0003(2p\sigma_a + 2p\sigma_b) \\ 1\sigma_u &= 0.709(1s_a - 1s_b) + 0.021(2s_{\perp a} - 2s_{\perp b}) + 0.003(2p\sigma_a - 2p\sigma_b) \\ 2\sigma_g &= -0.059(1s_a + 1s_b) + 0.523(2s_{\perp a} + 2s_{\perp b}) + 0.114(2p\sigma_a + 2p\sigma_b) \end{aligned} \quad (13.123)$$

The AO functions in these equations are STOs, except for $2s_{\perp}$. A Slater-type $2s$ AO has no radial nodes and is not orthogonal to a $1s$ STO. The Hartree–Fock $2s$ AO has one radial node ($n - l - 1 = 1$) and is orthogonal to the $1s$ AO. We can form an orthogonalized $2s$ orbital with the proper number of nodes by taking the following normalized linear combination of $1s$ and $2s$ STOs of the same atom (Schmidt orthogonalization):

$$2s_{\perp} = (1 - S^2)^{-1/2}(2s - S \cdot 1s) \quad (13.124)$$

where S is the overlap integral $\langle 1s|2s \rangle$. Ransil expressed the Li_2 orbitals using the (nonorthogonal) $2s$ STO, but since the orthogonalized $2s_\perp$ function gives a better representation of the $2s$ AO, the orbitals have been rewritten using $2s_\perp$. This changes the $1s$ and $2s$ coefficients, but the actual orbital is, of course, unchanged; see Prob. 13.37. The notation $2p\sigma$ for an AO indicates that the p orbital points along the molecular (z) axis; that is, a $2p\sigma$ AO is a $2p_z$ AO. (The $2p_x$ and $2p_y$ AOs are called $2p\pi$ AOs.) The optimum orbital exponents for the orbitals in (13.123) are $\zeta_{1s} = 2.689$, $\zeta_{2s} = 0.634$, $\zeta_{2p\sigma} = 0.761$.

Our previous simple expressions for these MOs were

$$1\sigma_g = \sigma_g 1s = 2^{-1/2}(1s_a + 1s_b)$$

$$1\sigma_u = \sigma_u^* 1s = 2^{-1/2}(1s_a - 1s_b)$$

$$2\sigma_g = \sigma_g 2s = 2^{-1/2}(2s_a + 2s_b)$$

Comparison of these with (13.123) shows the simple LCAO functions to be reasonable first approximations to the minimal-basis-set SCF MOs. The approximation is best for the $1\sigma_g$ and $1\sigma_u$ MOs, whereas the $2\sigma_g$ MO has substantial $2p\sigma$ AO contributions in addition to the $2s$ AO contributions. For this reason the notation of the third column of Table 13.1 (Section 13.7) is preferable to the separated-atoms MO notation. The substantial amount of $2s-2p\sigma$ hybridization is to be expected, since the $2s$ and $2p$ AOs are close in energy [see Eq. (9.27)]. The hybridization allows for the polarization of the $2s$ AOs in forming the molecule.

Let us compare the $3\sigma_g$ MO of the F_2 ground state at R_e as calculated by Ransil using a minimal basis set with that calculated by Wahl using an extended basis set [A. C. Wahl, *J. Chem. Phys.*, **41**, 2600 (1964)]:

$$3\sigma_{g,\text{min}} = 0.038(1s_a + 1s_b) - 0.184(2s_a + 2s_b) + 0.648(2p\sigma_a + 2p\sigma_b)$$

$$\zeta_{1s} = 8.65, \quad \zeta_{2s} = 2.58, \quad \zeta_{2p\sigma} = 2.49$$

$$3\sigma_{g,\text{ext}} = 0.048(1s_a + 1s_b) + 0.003(1s'_a + 1s'_b) - 0.257(2s_a + 2s_b)$$

$$+ 0.582(2p\sigma_a + 2p\sigma_b) + 0.307(2p\sigma'_a + 2p\sigma'_b) + 0.085(2p\sigma''_a + 2p\sigma''_b)$$

$$- 0.056(3s_a + 3s_b) + 0.046(3d\sigma_a + 3d\sigma_b) + 0.014(4f\sigma_a + 4f\sigma_b)$$

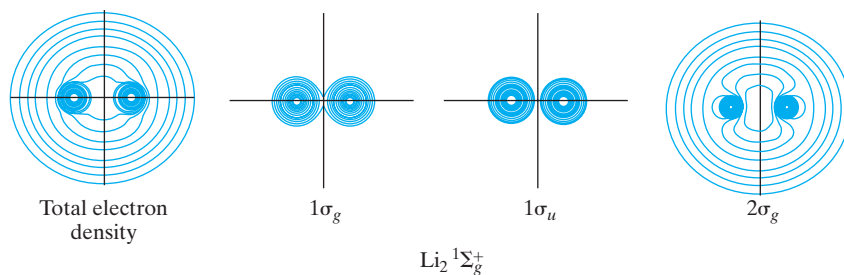
$$\zeta_{1s} = 8.27, \quad \zeta_{1s'} = 13.17, \quad \zeta_{2s} = 2.26$$

$$\zeta_{2p\sigma} = 1.85, \quad \zeta_{2p\sigma'} = 3.27, \quad \zeta_{2p\sigma''} = 5.86$$

$$\zeta_{3s} = 4.91, \quad \zeta_{3d\sigma} = 2.44, \quad \zeta_{4f\sigma} = 2.83$$

Just as several STOs are needed to give an accurate representation of Hartree–Fock AOs (Section 11.1), one needs more than one STO of a given n and l in the linear combination of STOs that is to accurately represent the Hartree–Fock MO. The primed and double-primed AOs in the extended-basis-set function are STOs with different orbital exponents. The $3d\sigma$ and $4f\sigma$ AOs are AOs with quantum number $m = 0$, that is, the $3d_0$ and $4f_0$ AOs. The total energies found are $-197.877E_h$ and $-198.768E_h$ for the minimal and extended calculations, respectively (where E_h is the hartree). Extrapolation of calculations using much larger basis sets than Wahl used gives the Hartree–Fock F_2 energy at R_e as $-198.773E_h$ [L. Bytautas et al., *J. Chem. Phys.*, **127**, 164317 (2007)]. The experimental energy of F_2 at R_e is $U(R_e) = -199.672E_h$. The correlation-energy definition (11.16) uses the nonrelativistic energy of the molecule. The relativistic contribution to the F_2 energy has been calculated to be $-0.142E_h$, so the exact nonrelativistic F_2 energy at R_e is $-199.672E_h + 0.142E_h = -199.530E_h$. Therefore, the correlation energy in F_2 is $-199.530E_h + 198.773E_h = -0.757E_h = -20.6 \text{ eV}$.

FIGURE 13.20 Hartree–Fock MO electron-density contours for the ground electronic state of Li_2 as calculated by Wahl. [A. C. Wahl, *Science*, **151**, 961 (1966); *Scientific American*, April 1970, p. 54; *Atomic and Molecular Structure: 4 Wall Charts*, McGraw-Hill, 1970.]



In discussing H_2^+ and H_2 , we saw how hybridization (the mixing of different AOs of the same atom) improves molecular wave functions. There is a tendency to think of hybridization as occurring only for certain molecular geometries. The SCF calculations make clear that all MOs are hybridized to some extent. Thus any diatomic-molecule σ MO is a linear combination of $1s, 2s, 2p_0, 3s, 3p_0, 3d_0, \dots$ AOs of the separated atoms.

To aid in deciding which AOs contribute to a given diatomic MO, we use two rules. First, only σ -type AOs ($s, p\sigma, d\sigma, \dots$) can contribute to a σ MO; only π -type AOs ($p\pi, d\pi, \dots$) can contribute to a π MO; and so on. Second, only AOs of reasonably similar energy contribute substantially to a given MO. (For examples, see the minimal- and extended-basis-set MOs quoted above.)

Wahl plotted the contours of the near Hartree–Fock molecular orbitals of homonuclear diatomic molecules from H_2 through F_2 . **Figure 13.20** shows these plots for Li_2 .

Of course, Hartree–Fock wave functions are only approximations to the true wave functions. It is possible to prove that a Hartree–Fock wave function gives a very good approximation to the electron probability density $\rho(x, y, z)$ for nuclear configurations in the region of the equilibrium configuration. A molecular property that involves only one-electron operators can be expressed as an integral involving ρ ; see Eq. (14.8). Consequently, such properties are accurately calculated using Hartree–Fock wave functions. An example is the molecular dipole moment [Eq. (14.21)]. For example, the LiH dipole moment calculated with a near Hartree–Fock ψ is 6.00 D (debyes) [S. Green, *J. Chem. Phys.*, **54**, 827 (1971)], compared with the experimental value 5.83 D. (One debye = 3.33564×10^{-30} C m.) For NaCl, the calculated and experimental dipole moments are 9.18 D and 9.02 D [R. L. Matcha, *J. Chem. Phys.*, **48**, 335 (1968)]. An error of about 0.2 D is typical in such calculations, but where the dipole moment is small, the percent error can be large. An extreme example is CO, for which the experimental moment is 0.11 D with the polarity C^-O^+ , but the near-Hartree–Fock moment is 0.27 D with the wrong polarity C^+O^- . However, a configuration-interaction wave function gives 0.12 D with the correct polarity [S. Green, *J. Chem. Phys.*, **54**, 827 (1971)].

A major weakness of the Hartree–Fock method is its failure to give accurate molecular dissociation energies. For example, an extended-basis-set calculation [P. E. Cade et al., *J. Chem. Phys.*, **44**, 1973 (1966)] gives $D_e = 5.3$ eV for N_2 , as compared with the true value 9.9 eV. (To calculate the Hartree–Fock D_e , the molecular energy at the minimum in the $U(R)$ Hartree–Fock curve is subtracted from the sum of the Hartree–Fock energies of the separated atoms.) A related defect of Hartree–Fock molecular wave functions is that the energy approaches the wrong limit as $R \rightarrow \infty$. Recall the MO discussion of H_2 .

13.15 MO Treatment of Heteronuclear Diatomic Molecules

The treatment of heteronuclear diatomic molecules is similar to that for homonuclear diatomic molecules. We first consider the MO description.

Suppose the two atoms have atomic numbers that differ only slightly; an example is CO. We could consider CO as being formed from the isoelectronic molecule N_2 by a gradual transfer of charge from one nucleus to the other. During this hypothetical transfer, the original N_2 MOs would slowly vary to give finally the CO MOs. We therefore expect the CO molecular orbitals to resemble somewhat those of N_2 . For a heteronuclear diatomic molecule such as CO, the symbols used for the MOs are similar to those for homonuclear diatomics. However, for a heteronuclear diatomic, the electronic Hamiltonian (13.5) is not invariant with respect to inversion of the electronic coordinates (that is, $\hat{H}_{el}$ does not commute with $\hat{\Pi}$), and the g, u property of the MOs disappears. The correlation between the N_2 and CO shell designations is

N_2	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$	$3\sigma_u$
CO	1σ	2σ	3σ	4σ	1π	5σ	2π	6σ

MOs of the same symmetry are numbered in order of increasing energy. Because of the absence of the g, u property, the numbers of corresponding homonuclear and heteronuclear MOs differ. **Figure 13.21** is a sketch of a contour of the CO $1\pi_{\pm 1}$ MOs as determined by an extended-basis-set SCF calculation [W. M. Huo, *J. Chem. Phys.*, **43**, 624 (1965)]. Note its resemblance to the contour of Fig. 13.13, which is for the $1\pi_{u,\pm 1}$ MOs of a homonuclear diatomic molecule.

The ground-state configuration of CO is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$, as compared with the N_2 configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$.

As in homonuclear diatomics, the heteronuclear diatomic MOs are approximated as linear combinations of atomic orbitals. The coefficients are found by the procedure of Section 14.3. For example, a minimal-basis-set SCF calculation using Slater AOs (with nonoptimized exponents given by Slater's rules) gives for the CO 5σ , 1π , and 2π MOs at $R = R_e$ [B. J. Ransil, *Rev. Mod. Phys.*, **32**, 245 (1960)]:

$$5\sigma = 0.027(1s_C) + 0.011(1s_O) + 0.739(2s_{\perp C}) + 0.036(2s_{\perp O}) \\ - 0.566(2p\sigma_C) - 0.438(2p\sigma_O)$$

$$1\pi = 0.469(2p\pi_C) + 0.771(2p\pi_O), \quad 2\pi = 0.922(2p\pi_C) - 0.690(2p\pi_O)$$

The expressions for the π MOs are simpler than those for the σ MOs because s and $p\sigma$ AOs cannot contribute to π MOs. For comparison, the corresponding MOs in N_2 at $R = R_e$ are (Ransil, op. cit.):

$$3\sigma_g = 0.030(1s_a + 1s_b) + 0.395(2s_{\perp a} + 2s_{\perp b}) - 0.603(2p\sigma_a + 2p\sigma_b)$$

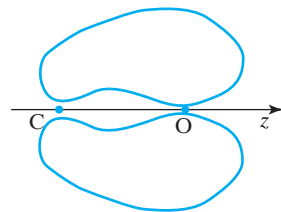
$$1\pi_u = 0.624(2p\pi_a + 2p\pi_b), \quad 1\pi_g = 0.835(2p\pi_a - 2p\pi_b)$$

The resemblance of CO and N_2 MOs is apparent. The 1σ MO in CO is found to be nearly the same as a $1s$ oxygen-atom AO; the 2σ MO in CO is essentially a carbon-atom $1s$ AO.

In general, for a heteronuclear diatomic molecule AB where the valence AOs of each atom are of s and p type and where the valence AOs of A do not differ greatly in energy from the valence AOs of B, we can expect the Fig. 13.17 pattern of

$$\sigma s < \sigma^* s < \pi p < \sigma p < \pi^* p < \sigma^* p$$

FIGURE 13.21 Cross section of a contour of the $1\pi_{\pm 1}$ MOs in CO.



valence-shell MOs formed from s and p valence-shell AOs to hold reasonably well. Figure 13.17 would be modified in that each valence AO of the more electronegative atom would lie below the corresponding valence AO of the other atom.

When the valence-shell AO energies of B lie very substantially below those of A, the s and $p\sigma$ valence AOs of B lie below the s valence-shell AO of A, and this affects which AOs contribute to each MO. Consider the molecule BF, for example. A minimal-basis-set calculation [Ransil, *Rev. Mod. Phys.*, **32**, 245 (1960)] gives the 1σ MO as essentially $1s_F$ and the 2σ MO as essentially $1s_B$. The 3σ MO is predominantly $2s_F$, with small amounts of $2s_B$, $2p\sigma_B$, and $2p\sigma_F$. The 4σ MO is predominantly $2p\sigma_F$, with significant amounts of $2s_B$ and $2s_F$ and a small amount of $2p\sigma_B$. This is quite different from N_2 , where the corresponding MO is formed predominantly from the $2s$ AOs on each N. The 1π MO is a bonding combination of $2p\pi_B$ and $2p\pi_F$. The 5σ MO is predominantly $2s_B$, with a substantial contribution from $2p\sigma_B$ and a significant contribution from $2p\sigma_F$. This is unlike the corresponding MO in N_2 , where the largest contributions are from $2p\sigma$ MOs on each atom. The 2π MO is an antibonding combination of $2p\pi_B$ and $2p\pi_F$. The 6σ MO has important contributions from $2p\sigma_B$, $2s_B$, $2s_F$, and $2p\sigma_F$.

We see from Fig. 11.2 that the $2p_F$ AO lies well below the $2s_B$ AO. This causes the $2p\sigma_F$ AO to contribute substantially to lower-lying MOs and the $2s_B$ AO to contribute substantially to higher-lying MOs, as compared with what happens in N_2 . (This effect occurs in CO, although to a lesser extent. Note the very substantial contribution of $2s_C$ to the 5σ MO. Also, the 4σ MO in CO has a very substantial contribution from $2p\sigma_O$.)

For a diatomic molecule AB where each atom has s and p valence-shell AOs (this excludes H and transition elements) and where the A and B valence AOs differ widely in energy, we may expect the pattern of valence MOs to be $\sigma < \sigma < \pi < \sigma < \pi < \sigma$, but it is not so easy to guess which AOs contribute to the various MOs or the bonding or antibonding character of the MOs. By feeding the valence electrons into these MOs, we can make a plausible guess as to the number of unpaired electrons and the ground term of the AB molecule (Prob. 13.38).

Diatomic hydrides are a special case, since H has only a $1s$ valence AO. Consider HF as an example. The ground-state configurations of the atoms are $1s$ for H and $1s^2 2s^2 2p^5$ for F. We expect the filled $1s$ and $2s$ F subshells to take little part in the bonding. The four $2p\pi$ fluorine electrons are nonbonding (there are no π valence AOs on H). The hydrogen $1s$ AO and the fluorine $2p\sigma$ AO have the same symmetry (σ) and have rather similar energies (Fig. 11.2), and a linear combination of these two AOs will form a σ MO for the bonding electron pair:

$$\phi = c_1(1s_H) + c_2(2p\sigma_F)$$

where the contributions of $1s_F$ and $2s_F$ to this MO have been neglected. Since F is more electronegative than H, we expect that $c_2 > c_1$. (In addition, the $1s_H$ and $2p\sigma_F$ AOs form an antibonding MO, which is unoccupied in the ground state.)

The picture of HF just given is only a crude qualitative approximation. A minimal-basis-set SCF calculation using Slater orbitals with optimized exponents gives as the MOs of HF [B. J. Ransil, *Rev. Mod. Phys.*, **32**, 245 (1960)]

$$1\sigma = 1.000(1s_F) + 0.012(2s_{\perp F}) + 0.002(2p\sigma_F) - 0.003(1s_H)$$

$$2\sigma = -0.018(1s_F) + 0.914(2s_{\perp F}) + 0.090(2p\sigma_F) + 0.154(1s_H)$$

$$3\sigma = -0.023(1s_F) - 0.411(2s_{\perp F}) + 0.711(2p\sigma_F) + 0.516(1s_H)$$

$$1\pi_{+1} = (2p\pi_{+1})_F, \quad 1\pi_{-1} = (2p\pi_{-1})_F$$

The ground-state MO configuration of HF is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$. The 1σ MO is virtually identical with the $1s$ fluorine AO. The 2σ MO is pretty close to the $2s$ fluorine AO. The 1π MOs are required by symmetry to be the same as the corresponding fluorine π AOs. The bonding 3σ MO has its largest contribution from the $2p\sigma$ fluorine and $1s$ hydrogen AOs, as would be expected from the discussion of the preceding paragraph. However, the $2s$ fluorine AO makes a substantial contribution to this MO. (Since a single $2s$ function is only an approximation to the $2s$ AO of F, we cannot use this calculation to say exactly how much $2s$ AO character the 3σ HF molecular orbital has.)

For qualitative discussion (but not quantitative work), it is useful to have simple approximations for heteronuclear diatomic MOs. In the crudest approximation, we can take each valence MO of a heteronuclear diatomic molecule as a linear combination of two AOs ϕ_a and ϕ_b , one on each atom. (As the discussions of CO and BF show, this approximation is often quite inaccurate.) From the two AOs, we can form two MOs:

$$c_1\phi_a + c_2\phi_b \quad \text{and} \quad c'_1\phi_a + c'_2\phi_b$$

The lack of symmetry in the heteronuclear diatomic makes the coefficients unequal in magnitude. The coefficients are determined by solving the secular equation [see Eq. (13.45)]

$$\begin{vmatrix} H_{aa} - W & H_{ab} - WS_{ab} \\ H_{ab} - WS_{ab} & H_{bb} - W \end{vmatrix} = 0$$

$$(H_{aa} - W)(H_{bb} - W) - (H_{ab} - WS_{ab})^2 = 0 \quad (13.125)$$

where $\hat{H}$ is some sort of effective one-electron Hamiltonian. Suppose that $H_{aa} > H_{bb}$, and let $f(W)$ be defined as the left side of (13.125). The overlap integral S_{ab} is less than 1 (except at $R = 0$). [A rigorous proof of this follows from Eq. (3-114) in *Margenau and Murphy*.] The coefficient of W^2 in $f(W)$ is $(1 - S_{ab}^2) > 0$; therefore $f(\infty) = f(-\infty) = +\infty > 0$. For $W = H_{aa}$ or H_{bb} , the first product in (13.125) vanishes. Hence $f(H_{aa}) < 0$ and $f(H_{bb}) < 0$. The roots of (13.125) occur where $f(W)$ equals 0. Hence, by continuity, one root must be between $+\infty$ and H_{aa} and the other between H_{bb} and $-\infty$. Therefore, the orbital energy of one MO is less than both H_{aa} and H_{bb} (the energies of the two AOs in the molecule; Section 13.5), and the energy of the other MO is greater than both H_{aa} and H_{bb} . One bonding and one antibonding MO are formed from the two AOs. **Figure 13.22** shows the formation of bonding and antibonding MOs from two AOs, for the homonuclear and heteronuclear cases. These figures are gross oversimplifications, since a given MO has contributions from many AOs, not just two.

The coefficients c_1 and c_2 in the bonding heteronuclear MO in Fig. 13.22 are both positive, so as to build up charge between the nuclei. For the antibonding heteronuclear MO, the coefficients of ϕ_a and ϕ_b have opposite signs, causing charge depletion between the nuclei.

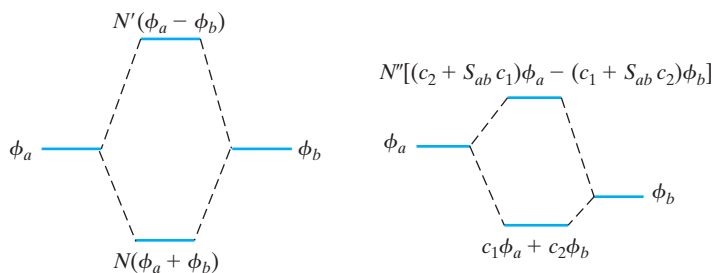


FIGURE 13.22 Formation of bonding and antibonding MOs from AOs in the homonuclear and heteronuclear cases. (See Prob. 13.39.)

13.16 VB Treatment of Heteronuclear Diatomic Molecules

Consider the valence-bond ground state wave function of HF. We expect a single bond to be formed by the pairing of the hydrogen $1s$ electron and the unpaired fluorine $2p\sigma$ electron. The Heitler–London function corresponding to this pairing is [Eq. (13.117)]

$$\phi_{\text{cov}} = |\cdots 1s_{\text{H}} \overline{2p\sigma_{\text{F}}}| - |\cdots \overline{1s_{\text{H}}} 2p\sigma_{\text{F}}| \quad (13.126)$$

where the dots stand for $1s_{\text{F}} \overline{1s_{\text{F}}} 2s_{\text{F}} \overline{2s_{\text{F}}} 2p\pi_{\text{xF}} \overline{2p\pi_{\text{xF}}} 2p\pi_{\text{yF}} \overline{2p\pi_{\text{yF}}}$. This function is essentially covalent, the electrons being shared by the two atoms. However, the high electronegativity of fluorine leads us to include a contribution from an ionic structure as well. An ionic valence-bond function has the form $\phi_a(1)\phi_a(2)$ [Eq. (13.109)]. Introduction of the required antisymmetric spin factor gives as the valence-bond function for an ionic structure in HF:

$$\phi_{\text{ion}} = |\cdots 2p\sigma_{\text{F}} \overline{2p\sigma_{\text{F}}}|$$

The VB wave function is then written as

$$\phi = c_1 \phi_{\text{cov}} + c_2 \phi_{\text{ion}} \quad (13.127)$$

The optimum values of c_1 and c_2 are found by the variation method. This leads to the usual secular equation. We have ionic–covalent “resonance,” involving the structures $\text{H}—\text{F}$ and H^+F^- . The true molecular structure is intermediate between the covalent and ionic structures. A term $c_3 |1s_{\text{H}} \overline{1s_{\text{H}}}|$ corresponding to the ionic structure H^-F^+ could also be included in the wave function, but this should contribute only slightly for HF. For molecules that are less ionic, both ionic structures might well be included.

For a highly ionic molecule such as NaCl, we expect the VB function to have $c_2 \gg c_1$. It might be thought that NaCl would dissociate to Na^+ and Cl^- ions, but this is not true. The ionization energy of Na is 5.1 eV, while the electron affinity of Cl is only 3.6 eV. Hence, in the gas phase the neutral separated ground-state atoms $\text{Na} + \text{Cl}$ are more stable than the ground-state separated ions $\text{Na}^+ + \text{Cl}^-$. (In aqueous solution the ions are more stable because of the hydration energy, which makes the separated ions more stable than even the diatomic NaCl molecule.) If the nuclei are slowly pulled apart, a gas-phase NaCl molecule will dissociate to neutral atoms. Therefore, as R increases from R_e , the ratio c_2/c_1 in (13.127) must decrease, becoming zero at $R = \infty$. For intermediate values of R , the Coulombic attraction between the ions is greater than the 1.5-eV difference between the ionization potential and electron affinity, and the molecule is largely ionic. For very large R , the Coulombic attraction between the ions is less than 1.5 eV, and the molecule is largely covalent. However, if the nuclei in NaCl are pulled apart very rapidly, then the electrons will not have a chance to adjust their wave function from the ionic to the covalent wave function, and both bonding electrons will go with the chlorine nucleus, giving dissociation into ions.

Cesium has the lowest ionization energy, 3.9 eV. Chlorine has the highest electron affinity, 3.6 eV. Thus, even for CsCl and CsF, the separated ground-state neutral atoms are more stable than the separated ground-state ions. There are, however, cases of excited states of diatomic molecules that dissociate to ions.

13.17 The Valence-Electron Approximation

Suppose we want to treat Cs_2 , which has 110 electrons. In the MO method, we would start by writing down a 110×110 Slater determinant of molecular orbitals. We would then approximate the MOs by functions containing variational parameters and go on

to minimize the variational integral. Clearly, the large number of electrons makes this a formidable task. One way to simplify the problem is to divide the electrons into two groups: the 108 **core** electrons and the two 6s **valence** electrons, which provide bonding. We then try to treat the valence electrons separately from the core, taking the molecular energy as the sum of core- and valence-electron energies. This approach, introduced in the 1930s, is called the **valence-electron approximation**.

The simplest approach is to regard the core electrons as point charges coinciding with the nucleus. For Cs_2 this would give a Hamiltonian for the two valence electrons that is identical with the electronic Hamiltonian for H_2 . If we then go ahead and minimize the variational integral for the valence electrons in Cs_2 , with no restrictions on the valence-electron trial functions, we will clearly be in trouble. Such a procedure will cause the valence-electrons' MO to "collapse" to the $\sigma_g 1s$ MO, since the core electrons are considered absent. To avoid this collapse, one can impose the constraint that the variational functions used for the valence electrons be orthogonal to the orbitals of the core electrons. Of course, the task of keeping the valence orbitals orthogonal to the core orbitals means more work. A somewhat different approach is to drop the approximation of treating the core electrons as coinciding with the nucleus, and to treat them as a charge distribution that provides some sort of effective repulsive potential for the motion of the valence electrons. This leads to an effective Hamiltonian for the valence electrons, which is then used in the variational integral. The valence-electron approximation is widely used in approximate treatments of polyatomic molecules (Chapter 17).

Summary

Because electrons are much lighter than nuclei, we can use the Born–Oppenheimer approximation to deal with molecules. This approximation takes the molecular wave function ψ as the product of wave functions for electronic motion and for nuclear motion: $\psi = \psi_{\text{el}}(q_i; q_\alpha) \psi_N(q_\alpha)$, where q_i and q_α are the electronic and nuclear coordinates, respectively. We solve the electronic Schrödinger equation for fixed positions of the nuclei. This equation is $(\hat{H}_{\text{el}} + V_{NN})\psi_{\text{el}} = U\psi_{\text{el}}$, where V_{NN} is the internuclear-repulsion term and $\hat{H}_{\text{el}}$ is the sum of operators for electronic kinetic energy, electron–nuclear attractions, and electron–electron repulsions. U is the electronic energy including internuclear repulsions. After finding $U(q_\alpha)$, we solve the nuclear-motion Schrödinger equation, which is $(\hat{T}_N + U)\psi_N = E\psi_N$, where $\hat{T}_N$ is the nuclear-kinetic-energy operator and E is the (total) molecular energy. Solution of the nuclear-motion Schrödinger equation shows that the molecular energy is approximately the sum of translational, rotational, vibrational, and electronic energies.

Quantum chemists use atomic units, in which energies are measured in hartrees and lengths in bohrs [Eqs. (13.29) and (13.30)].

The electronic Schrödinger equation for H_2^+ can be solved exactly to give wave functions that are eigenfunctions of $\hat{L}_z$, the operator for the component of electronic orbital angular momentum along the internuclear axis. The letters $\sigma, \pi, \delta, \phi, \dots$ denote $\lambda \equiv |m|$ values of 0, 1, 2, 3, $\dots$, respectively, where $m\hbar$ is the $\hat{L}_z$ eigenvalue.

Approximate wave functions for the two lowest electronic states of H_2^+ are $N(1s_a + 1s_b)$ and $N'(1s_a - 1s_b)$, where $1s_a$ and $1s_b$ are 1s AOs centered on nuclei a and b , respectively.

Approximate MOs for homonuclear diatomic molecules were constructed as $N(1s_a \pm 1s_b), N(2s_a \pm 2s_b), \dots$, and in the separated-atoms notation, these were called $\sigma_g 1s, \sigma_u^* 1s, \sigma_g 2s, \sigma_u^* 2s, \dots$, where σ means $\lambda = 0$, g or u denotes even or odd functions, and the star denotes an antibonding MO. An alternative notation, $1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, \dots$,

numbers the MOs of each symmetry type in order of increasing energy. Using these approximate MOs, we examined the electron configurations, bond orders, and spin multiplicities of the ground terms of H_2 , He_2 , Li_2 , . . . , Ne_2 .

A molecular electronic configuration gives rise to one or more electronic terms. Each diatomic-molecule term designation has the form $^{2S+1}(\Lambda)$, where S is the total electronic spin quantum number and (Λ) is a code letter ($\Sigma, \Pi, \Delta, \Phi, \dots$) that gives the $|M_L|$ value (0, 1, 2, 3, . . .), where $M_L\hbar$ is the component of the total electronic orbital angular momentum along the internuclear axis. Σ terms are designated Σ^+ or Σ^- , according to whether the eigenvalue of ψ_{el} for reflection in a plane containing the molecular axis is +1 or -1. For homonuclear diatomic molecules, a g or u subscript is added to the term symbol to show whether ψ_{el} is even or odd.

The simple LCAO-MO wave function for the H_2 ground electronic state is

$$\begin{aligned}\sigma_g 1s(1)\sigma_g 1s(2)2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ \approx N[1s_a(1) + 1s_b(1)][1s_a(2) + 1s_b(2)]2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\end{aligned}$$

The simple covalent VB wave function for ground-state H_2 is constructed by interchange of the bonding electrons between the bonding atoms to give

$$N[1s_a(1)1s_b(2) + 1s_a(2)1s_b(1)]2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The H_2 MO function gives equal weight to covalent and ionic terms and thus underestimates electron correlation, which acts to keep electrons apart and makes the ionic terms less important than the covalent terms. The MO function can be improved by configuration interaction. The H_2 covalent VB wave function can be improved by the addition of a contribution from ionic terms.

The MO wave function for a $^1\Sigma$ diatomic-molecule state is a single Slater determinant of spin-orbitals. The VB wave function is a linear combination of Slater determinants that involve interchanges of spins within the pairs of bonding AOs.

A minimal basis set consists of one basis function for each inner shell and each valence AO. Examples of minimal- and extended-basis-set SCF wave functions for diatomic molecules were given in Sections 13.14 and 13.15. SCF wave functions give pretty accurate molecular geometries and dipole moments, but very inaccurate dissociation energies, due to improper behavior as $R \rightarrow \infty$.

Problems

Sec.	13.1	13.2	13.3	13.5	13.6	13.7
Probs.	13.1–13.6	13.7–13.12	13.13–13.15	13.16–13.23	13.24	13.25–13.26

Sec.	13.8	13.9	13.10	13.12	13.13	13.14	13.15	general
Probs.	13.27–13.31	13.32	13.33	13.34–13.35	13.36	13.37	13.38–13.39	13.40–13.43

- 13.1** True or false? (a) For a diatomic molecule, D_0 is greater than D_e . (b) The electronic wave function of a diatomic molecule changes when the internuclear distance changes. (c) The total energy of a molecule is the sum of the electronic energy (including nuclear repulsion) U and the energy E found by solving the nuclear Schrödinger equation $\hat{H}\psi_N = E\psi_N$.
- 13.2** For the H_2 ground electronic state, $D_0 = 4.4781$ eV. Find ΔH_0° for $\text{H}_2(g) \rightarrow 2\text{H}(g)$ in kJ/mol.
- 13.3** Use the D_0 value of H_2 (4.478 eV) and the D_0 value of H_2^+ (2.651 eV) to calculate the first ionization energy of H_2 (that is, the energy needed to remove an electron from H_2).

- 13.4** The infrared absorption spectrum of $^1\text{H}^{35}\text{Cl}$ has its strongest band at $8.65 \times 10^{13}\text{Hz}$. For this molecule, $D_0 = 4.43\text{ eV}$. (a) Find D_e for $^1\text{H}^{35}\text{Cl}$. (b) Find D_0 for $^2\text{H}^{35}\text{Cl}$.
- 13.5** (a) Verify that if anharmonicity is taken into account by inclusion of the $\nu_e x_e$ term in the vibrational energy, then $D_e = D_0 + \frac{1}{2}h\nu_e - \frac{1}{4}h\nu_e x_e$. (b) The $^7\text{Li}^1\text{H}$ ground electronic state has $D_0 = 2.4287\text{ eV}$, $\nu_e/c = 1405.65\text{ cm}^{-1}$, and $\nu_e x_e/c = 23.20\text{ cm}^{-1}$, where c is the speed of light. (These last two quantities are usually designated ω_e and $\omega_e x_e$ in the literature.) Calculate D_e for $^7\text{Li}^1\text{H}$.
- 13.6** Without consulting the text, write down the complete nonrelativistic Hamiltonian operator for the H_2 molecule. Then write down the purely electronic Hamiltonian operator for H_2 .
- 13.7** Verify the Taylor-series expansion (13.24).
- 13.8** For the Morse-function H_2 example in Section 13.2: (a) Derive the expressions for A and B in terms of $\hbar$, μ , and a . (*Hint:* Use the fact that the argument of an exponential function must be dimensionless.) (b) Calculate the numerical values of A , B , and $D_{e,r}$. (See Table A.3 in the Appendix.)
- 13.9** (a) Use the Numerov method with the endpoints and interval recommended in the Section 13.2 example to find the lowest six Morse-function vibrational levels of H_2 . (b) Calculate $\langle x_r \rangle$ and $\langle R \rangle$ for these six levels. (c) Find the Morse-function $v = 6, 7, 8$, and 9 H_2 vibrational levels.
- 13.10** The $^{127}\text{I}_2$ ground electronic state has $D_e/hc = 12550\text{ cm}^{-1}$, $\nu_e/c = 214.5\text{ cm}^{-1}$, and $R_e = 2.666\text{ \AA}$. Use the Morse function and the Numerov method to calculate the six lowest vibrational energy levels of this electronic state. (The experimental E_{vib}/hc values for $v = 0, 2, 4$ are $107.19, 532.55, 953.01\text{ cm}^{-1}$.)
- 13.11** Analytical solution of the Schrödinger equation for the Morse-function potential energy gives $E_{\text{vib}} = (v + \frac{1}{2})h\nu_e - (v + \frac{1}{2})^2 h^2 \nu_e^2 / 4D_e$. (The Morse-function U becomes infinite at $R = -\infty$. The expression given for E_{vib} corresponds to the boundary conditions that ψ becomes zero at $R = \infty$ and at $R = -\infty$, whereas for a diatomic molecule, we actually require that the vibrational wave function become zero at $R = 0$. This discrepancy is of no significance, since at $R = 0$, the Morse potential energy is very high and the Morse vibrational wave function is very close to zero.) For the $^1\text{H}_2$ ground electronic state, (a) calculate the six lowest analytical Morse vibrational energies to verify the values given in the Section 13.2 example; (b) find the maximum value of v predicted by the Morse function and compare with the true value $v = 14$.
- 13.12** If $\psi_{N,\text{int}}$ is the approximate nuclear wave function of (13.14) and (13.28), verify that $\langle R - R_e \rangle = \int |\psi_{N,\text{int}}|^2 (R - R_e) d\tau = \int_0^\infty |S_v|^2 (R - R_e) dR$.
- 13.13** (a) If Q stands for the dimension electric charge, show that $[4\pi\epsilon_0] = \text{Q}^2\text{M}^{-1}\text{L}^{-3}\text{T}^2$. (b) Derive the expressions for A and B given in Section 13.3. (c) Verify the reduced form of the H-atom Schrödinger equation given in Section 13.3.
- 13.14** (a) Derive the expressions for the atomic units of time and electric dipole moment given in Section 13.3. (b) Find the expression for the atomic unit of electric field strength and calculate its value in volts per meter.
- 13.15** Give the numerical value in atomic units of each of the following quantities: (a) proton mass; (b) electron charge; (c) Planck's constant; (d) He^+ ground-state energy, assuming infinite nuclear mass; (e) one second; (f) c (speed of light); (g) hydrogen-atom ground-state energy, taking internal nuclear motion into account; (h) one debye [$1\text{ debye (D)} \approx 3.33564 \times 10^{-30}\text{ C m}$].
- 13.16** Derive (13.60) for the overlap integral S_{ab} .
- 13.17** (a) Derive (13.61) for the H_{aa} integral as follows. Add and subtract k/r_a in (13.32) to get $\hat{H} = \hat{H}_a + (k-1)/r_a - 1/r_b$, where $\hat{H}_a$ is the Hamiltonian operator for a hydrogenlike atom of nuclear charge k with nucleus at a . Use this expression to write H_{aa} as the sum of three integrals. Evaluate the first integral using $\hat{H}_a 1s_a = -\frac{1}{2}k^2 1s_a$. Evaluate the $1/r_a$ integral using spherical coordinates with origin at a . Use confocal elliptic coordinates and Eqs. (13.59), (13.44), and (13.35) to evaluate the third integral. (b) Derive (13.62) for H_{ab} .

- 13.18** (a) Show that the variational integral W_1 for the ground state of H_2^+ [Eq. (13.63)] can be written as $W_1 = k^2 F(t) + kG(t)$, where $t \equiv kR$ and where F and G are certain functions of t .
 (b) Show that the minimization condition $\partial W_1 / \partial k = 0$ leads to

$$k = -\frac{G(t) + tG'(t)}{2F(t) + tF'(t)}$$

Using this equation, we can find k for a given value of t . We then use $R = t/k$ to find the value of R corresponding to our value of k .

- 13.19** Write a computer program that will calculate the optimum value of the orbital exponent k for the H_2^+ trial function (13.54) for a given R value. Have the program calculate $W_1 + 1/R$ [where W_1 is given by (13.63)] for k ranging from 0 to 3 in steps of 0.001 and have the program pick the k value that gives the smallest $W_1 + 1/R$. Write the program so that the value of R , the initial and final values of k , and the interval between k values are input from the keyboard for each run. Use the program to find k to the nearest 0.001 for R values of 0.5, 1.0, 2.0, 3.0, 4.0, and 6.0. Use the calculated energies to plot the $U(R)$ curve predicted by this trial function. (For more efficient ways to find the minimum of a function of one variable, see *Press et al.*, Chapter 10.)
- 13.20** Write a computer program that will simultaneously find the values of k and R that minimize $W_1 + 1/R$ in (13.63). On the first run, have R range from 0.1 to 6 in steps of 0.01 and have k range from 0 to 3 in steps of 0.01; compute $W_1 + 1/R$ for all possible pairs of k and R values in these ranges and have the computer find the pair of k and R values that gives the smallest $W_1 + 1/R$. Let these values be k' and R' . Rerun the program with k and R ranging from $k' - 0.01$ to $k' + 0.01$ and $R' - 0.01$ to $R' + 0.01$, respectively, each in steps of 0.0001 to find the optimum k and R , each accurate to 0.0001. (For much more efficient ways to find the minimum of a function of two variables, see *Press et al.*, Chapter 10.)
- 13.21** (a) Use Mathcad to create an animation showing how contours and three-dimensional plots of the H_2^+ LCAO MOs ϕ_1 and ϕ_2 [Eqs. (13.57) and (13.58)] for a plane containing the nuclei change as R changes from 3.8 to 0.1 bohr. Proceed as follows. Define the function $U(R, k)$ by adding the internuclear repulsion to (13.63). Include a parameter b in U , such that for $b = 1$ we get U for ϕ_1 and $b = -1$ we get U for ϕ_2 . Specify the b value before defining U . Set R equal to $3.8 - \text{FRAME}/10$, where the animation variable FRAME will later be defined to go from 0 to 37. To find the optimum k value at each R , use the Mathcad function $\text{root}(f(k), k)$, which finds the k value that makes $f(k) = 0$ provided we enter an initial guess for k . Take $f(k)$ as the derivative of $U(R, k)$ with respect to k . Do not find this derivative yourself but use the d/dx facility in Mathcad to have Mathcad take the derivative. Define an initial value for k before setting k equal to the root function. [In some versions of Mathcad, the root function will fail to find the solution for certain initial values of k . Use trial-and-error to find k values that work, and if a single initial k value does not work at all R values, use the if function (or nested if functions) to specify various k values at various R values. Different k values may be needed for the bonding and antibonding MOs.] To make the plot, define x_i and z_i to vary from -2.5 to 2.5 bohrs with increments of $1/6$ bohr. Then use (13.57) and (13.58) to define $\phi_i(x, z)$ as the MO's value in the xz plane. Define the array (matrix) M by defining M_{ij} as $\phi_i(x_i, z_i)$. Create a contour plot, entering -2.5 and 2.5 as the limits for the axes. Also create a three-dimensional-surface plot taking appropriate values for the limits of y . Then create the animation. (b) By adding statements to the worksheet of part (a), use the solve block facility to find the predicted R_e for ϕ_1 and the optimum k at R_e . The conditions to be satisfied are that the derivative of U with respect to R must be zero and the derivative of U with respect to k must be zero. Also include conditions that R and k must be positive.
- 13.22** Use a modified form of the Mathcad worksheet for Prob. 13.21 to find the optimum k for each of the H_2^+ MOs (13.57) and (13.58) at each of these R/bohr values: (a) 10; (b) 6; (c) 4; (d) 2.5; (e) 2; (f) 1; (g) 0.1.
- 13.23** Use a spreadsheet to calculate the k values asked for in Prob. 13.22.
- 13.24** Verify Eq. (13.79) for a σ_h reflection.

- 13.25** Which species of each pair has the greater D_e ? (a) Li_2 or Li_2^+ ; (b) C_2 or C_2^+ ; (c) O_2 or O_2^+ ; (d) F_2 or F_2^+ .
- 13.26** Predict the bond order and the number of unpaired electrons for each of the following molecules: (a) S_2 ; (b) S_2^+ ; (c) S_2^- ; (d) N_2^+ ; (e) N_2^- ; (f) F_2^+ ; (g) F_2^- ; (h) Ne_2^+ ; (i) Na_2^+ ; (j) Na_2^- ; (k) H_2^- ; (l) C_2^+ ; (m) C_2 ; (n) C_2^- .
- 13.27** Use the results of Prob. 13.26 and Table 13.3 to predict the ground term of each molecule in Prob. 13.26.
- 13.28** How many independent electronic wave functions correspond to each of the following diatomic-molecule terms: (a) $^1\Sigma^-$; (b) $^3\Sigma^+$; (c) $^3\Pi$; (d) $^1\Phi$; (e) $^6\Delta$?
- 13.29** Give the levels belonging to each of the terms in Prob. 13.28.
- 13.30** Show that the four functions of (13.89) have the indicated eigenvalues with respect to a $\sigma_v(xz)$ reflection of electronic coordinates. Start by showing that this reflection converts ϕ to $-\phi$ and leaves r_a and r_b unchanged.
- 13.31** Show that for a diatomic molecule $[\hat{L}_z, \hat{O}_{\sigma_v}] \neq 0$.
- 13.32** The ground state of H_2 has $^1\Sigma_g^+$ symmetry. What restriction does this impose on the values of m, n, j , and k in the James and Coolidge wave function (Section 13.9)?
- 13.33** For the VB integrals S_{12} , H_{11} , and H_{12} in (13.97), show that (a) $S_{12} = S_{ab}^2$; (b) $H_{11} = Q - 1$; (c) $H_{12} = A - S_{ab}^2$. Then use these results to verify (13.103).
- 13.34** For the determinant (13.112), add column 1 to column 3 and add column 2 to column 4. Show that the result is equal to $4 |(1s_a + 1s_b)(1s_a - 1s_b)|$. In this determinant, subtract column 3 from column 1 and subtract column 4 from column 2. Then use column interchanges to show that the result equals (13.113). At each step, state which theorem about determinants is being used.
- 13.35** Write down abbreviated expressions for the remaining six determinants of the N_2 VB function of Section 13.12. Use the rule given in that section to find the coefficient of each determinant in the wave function.
- 13.36** (a) Show that the simple MO wave function for the $b^3\Sigma_u^+$ level of H_2 is the same as the Heitler–London VB function for this level. (b) Show that the simple MO wave function for the $B^1\Sigma_u^+$ level of H_2 contains only ionic terms.
- 13.37** Verify that the $2s_\perp$ AO in (13.124) is orthogonal to the $1s$ AO and is normalized. (b) Let an MO ϕ have the form $\phi = a(1s) + b(2s) + \dots$ when expressed using a nonorthogonal $2s$ STO and the form $\phi = c(1s) + d(2s_\perp) + \dots$ when expressed using an orthogonalized $2s$ orbital. Show that $c = a + Sb$ and $d = b(1 - S^2)^{1/2}$, where $S = \langle 1s | 2s \rangle$. (c) Let ζ_1 and ζ_2 be the orbital exponents of $1s$ and $2s$ STOs, respectively. Show that $S = 24\zeta_1^{3/2}\zeta_2^{5/2}/3^{1/2}(\zeta_1 + \zeta_2)^4$.
- 13.38** Use simple MO theory to predict the number of unpaired electrons and the ground term of each of the following: (a) BF ; (b) BN ; (c) BeS ; (d) BO ; (e) NO ; (f) CF ; (g) CP ; (h) NBr ; (i) ClO ; (j) BrCl . Compare your results with the experimentally observed ground terms: (a) $^1\Sigma^+$; (b) $^3\Pi$; (c) $^1\Sigma^+$; (d) $^2\Sigma^+$; (e) $^2\Pi$; (f) $^2\Pi$; (g) $^2\Sigma^+$; (h) $^3\Sigma^-$; (i) $^2\Pi$; (j) $^1\Sigma^+$.
- 13.39** (a) Use orthogonality (Section 8.5 and Prob. 8.40) to derive the expression given in Fig. 13.22 for the heteronuclear antibonding MO. Then do the same for the homonuclear antibonding MO. (b) Verify that the functions (13.57) and (13.58) are orthogonal.
- 13.40** In applying quantum chemistry to chemical reactions, which would be the more accurate approximation, the simple MO or the simple VB method?
- 13.41** In Section 13.14, an experimental value for $U(R_e)$ of F_2 was given. Explain how this value is found from certain other data. *Hint:* See the paragraph after Eq. (13.1).
- 13.42** Use notation such as $1s_a(1)$ to write down without consulting this chapter (a) the simple MO wave function for H_2 including spin; (b) the simple VB wave function for H_2 including spin.
- 13.43** True or false: (a) If $|\psi_1| = |\psi_2|$, then ψ_1 and ψ_2 must represent the same state. (b) The Hartree–Fock $U(R)$ curve for the H_2^+ ground electronic state shows the proper behavior as $R \rightarrow \infty$. (c) The Hartree–Fock $U(R)$ curve for the H_2 ground electronic state shows the proper behavior as $R \rightarrow \infty$.