

Theorems of Molecular Quantum Mechanics

This chapter discusses theorems that are used in molecular quantum mechanics. Section 14.1 expresses the electron probability density in terms of the wave function. Section 14.2 shows how the dipole moment of a molecule is calculated from the wave function. Section 14.3 gives the procedure for calculating the Hartree–Fock wave function of a molecule. Sections 14.4 to 14.7 discuss the virial theorem and the Hellmann–Feynman theorem, which are helpful in understanding chemical bonding.

14.1 Electron Probability Density

How is the wave function of a many-electron molecule related to the electron probability density? We want to find the probability of finding an electron in the rectangular volume element located at point (x, y, z) in space with edges dx, dy, dz . The electronic wave function ψ is a function of the spatial and spin coordinates of the n electrons. (For simplicity the parametric dependence on the nuclear configuration will not be explicitly indicated.) We know that

$$|\psi(x_1, \dots, z_n, m_{s1}, \dots, m_{sn})|^2 dx_1 dy_1 dz_1 \cdots dx_n dy_n dz_n \quad (14.1)$$

is the probability of simultaneously finding electron 1 with spin m_{s1} in the volume element $dx_1 dy_1 dz_1$ at (x_1, y_1, z_1) , electron 2 with spin m_{s2} in the volume element $dx_2 dy_2 dz_2$ at (x_2, y_2, z_2) , and so on. Since we are not interested in what spin the electron we find at (x, y, z) has, we sum the probability (14.1) over all possible spin states of all electrons to give the probability of simultaneously finding each electron in the appropriate volume element with no regard for spin:

$$\sum_{m_{s1}} \cdots \sum_{m_{sn}} |\psi|^2 dx_1 \cdots dz_n \quad (14.2)$$

Suppose we want the probability of finding electron 1 in the volume element $dx dy dz$ at (x, y, z) . For this probability we do not care where electrons 2 through n are. We therefore add the probabilities for all possible locations for these electrons. This amounts to integrating (14.2) over the coordinates of electrons 2, 3, $\dots$, n :

$$\left[\sum_{\text{all } m_s} \int \cdots \int |\psi(x, y, z, x_2, y_2, z_2, \dots, x_n, y_n, z_n, m_{s1}, \dots, m_{sn})|^2 dx_2 \cdots dz_n \right] dx dy dz \quad (14.3)$$

where there is a $(3n - 3)$ -fold integration over x_2 through z_n .

Now suppose we ask for the probability of finding electron 2 in the volume element $dx dy dz$ at (x, y, z) . By analogy to (14.3), this is

$$\left[\sum_{\text{all } m_s} \int \cdots \int |\psi(x_1, y_1, z_1, x, y, z, x_3, \dots, z_n, m_{s1}, \dots, m_{sn})|^2 dx_1 dy_1 dz_1 dx_3 \cdots dz_n \right] dx dy dz \quad (14.4)$$

Of course, electrons do not come with labels, and this indistinguishability (Section 10.3) means that the probabilities (14.3) and (14.4) must be equal. This equality is readily proved. The wave function ψ is antisymmetric with respect to electron exchange, so $|\psi|^2$ is unchanged by an electron exchange. Interchanging the spatial and spin coordinates of electrons 1 and 2 in ψ in (14.4) and doing some relabeling of dummy variables, we see that (14.4) is equal to (14.3). Thus (14.3) gives the probability of finding any one particular electron in $dx dy dz$. Since the system has n electrons, the probability of finding *an* electron in $dx dy dz$ is n times (14.3). (In drawing this conclusion, we assume that the probability of finding more than one electron in the infinitesimal region $dx dy dz$ is negligible compared with the probability of finding one electron. This is certainly valid since the probability of finding two electrons will involve the product of six infinitesimal quantities as compared with the product of three infinitesimal quantities for the probability of finding one electron.)

Thus the probability density ρ for finding an electron in the neighborhood of point (x, y, z) is

$$\rho(x, y, z) = n \sum_{\text{all } m_s} \int \cdots \int |\psi(x, y, z, x_2, \dots, z_n, m_{s1}, \dots, m_{sn})|^2 dx_2 \cdots dz_n$$

$$\rho(\mathbf{r}) = n \sum_{\text{all } m_s} \int \cdots \int |\psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_n, m_{s1}, \dots, m_{sn})|^2 d\mathbf{r}_2 \cdots d\mathbf{r}_n \quad (14.5)$$

where the vector notation for spatial variables (Section 5.2) is used. The atomic units of ρ are electrons/bohr³.

ρ is the electron probability density. The corresponding electronic charge density averaged over time is equal to $-e\rho(x, y, z)$, where $-e$ is the charge on an electron. In atomic units, the electronic charge density is $-\rho$. In addition, there are the positive charges of the nuclei. The term *electronic charge density* is commonly shortened to *charge density*.

A molecule's ρ is an experimentally observable quantity that can be found from measured x-ray diffraction intensities of molecular crystals or electron-diffraction intensities of gases. See P. Coppens and M. B. Hall (eds.), *Electron Distributions and the Chemical Bond*, Plenum, 1982; D. A. Kohl and L. S. Bartell, *J. Chem. Phys.*, **51**, 2891, 2896 (1969); P. Coppens, *J. Phys. Chem.*, **93**, 7979 (1989); P. Coppens, *Annu. Rev. Phys. Chem.*, **43**, 663 (1992); C. Gatti and P. Macchi (eds.), *Modern Charge-Density Analysis*, Springer, 2012.

To illustrate (14.5), consider the electron density for the simple VB and MO ground-state H_2 wave functions. The wave function is a product of a spatial factor and the spin function (11.60). (For more than two electrons, ψ cannot be factored into a product of a spatial part and a spin part; see Chapter 10.) Summation of (11.60) over m_{s1} and m_{s2} gives one (Section 10.4). Thus (14.5) becomes for H_2

$$\rho(x, y, z) = 2 \iiint |\phi(x, y, z, x_2, y_2, z_2)|^2 dx_2 dy_2 dz_2$$

where ϕ is the spatial factor. When ϕ is taken as the spatial factor in the VB function (13.100) and Prob. 13.33 or the MO function (13.94), we get (Prob. 14.1)

$$\rho_{\text{VB}} = \frac{1s_a^2 + 1s_b^2 + 2S_{ab}1s_a1s_b}{1 + S_{ab}^2}, \quad \rho_{\text{MO}} = \frac{1s_a^2 + 1s_b^2 + 2(1s_a1s_b)}{1 + S_{ab}} \quad (14.6)$$

One finds (Prob. 14.2) that $\rho_{\text{MO}} > \rho_{\text{VB}}$ at the midpoint of the bond, so the MO function (which underestimates electron correlation) piles up more charge between the nuclei than the VB function.

The MO probability density in (14.6) is twice ρ for the H_2^+ -like $1s_A + 1s_B$ MO [Eq. (13.65)]. One can prove that, for a many-electron MO wave function, ρ is found by multiplying the probability-density function of each MO by the number of electrons occupying it and summing the results:

$$\rho(x, y, z) = \sum_j n_j |\phi_j|^2 \quad (14.7)$$

where the sum is over the different orthogonal spatial MOs, and n_j (whose possible values are 0, 1, or 2) is the number of electrons in the MO ϕ_j . [We used (14.7) in Eq. (11.11).]

Calculations of ρ from high-quality wave functions show that for nearly all molecules, local maxima in ρ occur only at the nuclei. One of the few exceptions is the ground electronic state of Li_2 , for which ρ has a small local maximum at the bond midpoint [Bader, Section E2.1; G. I. Bersuker et al., *J. Phys. Chem.*, **97**, 9323 (1993)].

Let $B(\mathbf{r}_i)$ be a function of the spatial coordinates x_i, y_i, z_i of electron i , where the notation of Section 5.2 is used. For an n -electron molecule, consider the average value

$$\left\langle \psi \left| \sum_{i=1}^n B(\mathbf{r}_i) \right| \psi \right\rangle = \int \psi^* \sum_{i=1}^n B(\mathbf{r}_i) \psi d\tau = \sum_{i=1}^n \int |\psi|^2 B(\mathbf{r}_i) d\tau$$

where ψ is the electronic wave function. Since the electrons are indistinguishable, each term in the sum $\sum_i \int |\psi|^2 B d\tau$ must have the same value. Therefore we have $\langle \psi | \sum_{i=1}^n B(\mathbf{r}_i) | \psi \rangle = \int n |\psi|^2 B(\mathbf{r}_1) d\tau$. Since $B(\mathbf{r}_1)$ depends only on x_1, y_1, z_1 , before we integrate over x_1, y_1, z_1 , we can integrate $n |\psi|^2$ over the spatial coordinates of electrons 2 to n and sum over all the spin coordinates. From Eq. (14.5), this produces the electron probability density $\rho(\mathbf{r}_1)$. Therefore, $\langle \psi | \sum_{i=1}^n B(\mathbf{r}_i) | \psi \rangle = \int \rho(\mathbf{r}_1) B(\mathbf{r}_1) d\mathbf{r}_1$. The subscript 1 on the integration variables is not needed, and the final result is

$$\int \psi^* \sum_{i=1}^n B(\mathbf{r}_i) \psi d\tau = \int \rho(\mathbf{r}) B(\mathbf{r}) d\mathbf{r} \quad (14.8)$$

where the integration is over the three spatial coordinates x, y, z . This result will be used later in this chapter and in Chapter 15.

14.2 Dipole Moments

We now show how to calculate molecular dipole moments from wave functions.

The classical expression for the electric dipole moment $\boldsymbol{\mu}_{\text{cl}}$ of a set of discrete charges Q_i is

$$\boldsymbol{\mu}_{\text{cl}} = \sum_i Q_i \mathbf{r}_i \quad (14.9)$$

where $\mathbf{r}_i$ is the position vector from the origin to the i th charge [Eq. (5.33)]. The electric dipole moment is a vector whose x component is

$$\mu_{x,\text{cl}} = \sum_i Q_i x_i \quad (14.10)$$

with similar expressions for the other components. For a continuous charge distribution with charge density $\rho_Q(x, y, z)$, $\boldsymbol{\mu}_{\text{cl}}$ is found by summing over the infinitesimal elements of charge $dQ_i = \rho_Q(x, y, z) dx dy dz$:

$$\boldsymbol{\mu}_{\text{cl}} = \int \rho_Q(x, y, z) \mathbf{r} dx dy dz, \quad \text{where } \mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k} \quad (14.11)$$

Now consider the quantum-mechanical definition of the electric dipole moment. Suppose we apply a uniform external electric field $\mathbf{E}$ to an atom or molecule and ask for the effect on the energy of the system. To form the Hamiltonian operator, we first need the classical expression for the energy. The electric field strength $\mathbf{E}$ is defined as $\mathbf{E} \equiv \mathbf{F}/Q$, where $\mathbf{F}$ is the force the field exerts on a charge Q . We take the z direction as the direction of the applied field: $\mathbf{E} = \mathcal{E}_z \mathbf{k}$. The potential energy V is [Eq. (4.24)]

$$dV/dz = -F_z = -Q\mathcal{E}_z \quad \text{and} \quad V = -Q\mathcal{E}_z z$$

This is the potential energy of a single charge in the field. For a system of charges,

$$V = -\mathcal{E}_z \sum_i Q_i z_i \quad (14.12)$$

where z_i is the z coordinate of charge Q_i . The extension of (14.12) to the case where the electric field points in an arbitrary direction follows from (4.24) and is

$$V = -\mathcal{E}_x \sum_i Q_i x_i - \mathcal{E}_y \sum_i Q_i y_i - \mathcal{E}_z \sum_i Q_i z_i = -\mathbf{E} \cdot \boldsymbol{\mu}_{\text{cl}} \quad (14.13)$$

This is the classical-mechanical expression for the energy of an electric dipole in a uniform applied electric field.

To calculate the quantum-mechanical expression, we use perturbation theory. The perturbation operator $\hat{H}'$ corresponding to (14.13) is $\hat{H}' = -\mathbf{E} \cdot \hat{\boldsymbol{\mu}}$, where the **electric dipole-moment operator** $\hat{\boldsymbol{\mu}}$ is

$$\hat{\boldsymbol{\mu}} = \sum_i Q_i \hat{\mathbf{r}}_i = \mathbf{i}\hat{\mu}_x + \mathbf{j}\hat{\mu}_y + \mathbf{k}\hat{\mu}_z \quad (14.14)$$

$$\hat{\mu}_x = \sum_i Q_i x_i, \quad \hat{\mu}_y = \sum_i Q_i y_i, \quad \hat{\mu}_z = \sum_i Q_i z_i \quad (14.15)$$

The first-order correction to the energy is [Eq. (9.22)]

$$E^{(1)} = -\mathbf{E} \cdot \int \psi^{(0)*} \hat{\boldsymbol{\mu}} \psi^{(0)} d\tau \quad (14.16)$$

where $\psi^{(0)}$ is the unperturbed wave function. Comparison of (14.16) and (14.13) shows that the quantum-mechanical quantity that corresponds to $\boldsymbol{\mu}_{\text{cl}}$ is the integral

$$\boldsymbol{\mu} = \int \psi^{(0)*} \hat{\boldsymbol{\mu}} \psi^{(0)} d\tau \quad (14.17)$$

$\boldsymbol{\mu}$ in (14.17) is the quantum-mechanical **electric dipole moment** of the system.

An objection to taking (14.17) as the dipole moment is that we considered only the first-order energy correction. If we had included $E^{(2)}$ in (14.16), the comparison with (14.13) would not have given (14.17) as the dipole moment. Actually, (14.17) is the dipole

moment of the system in the absence of an applied electric field and is the *permanent* electric dipole moment. Application of the field distorts the wave function from $\psi^{(0)}$, giving rise to an *induced* electric dipole moment in addition to the permanent dipole moment. The induced dipole moment corresponds to the energy correction $E^{(2)}$. (For the details, see *Merzbacher*, Section 17.4.) The induced dipole moment μ_{ind} is related to the applied electric field $\mathbf{E}$ by

$$\mu_{\text{ind}} = \alpha \mathbf{E} \quad (14.18)$$

where α is the **polarizability** of the atom or molecule. The greater the polarizability of molecule B, the greater the London dispersion force (Section 13.7) between two B molecules.

The shift in the energy of a quantum-mechanical system caused by an applied electric field is called the *Stark effect*. The *first-order* (or *linear*) Stark effect is given by (14.16), and from (14.17) it vanishes for a system with no permanent electric dipole moment. The *second-order* (or *quadratic*) Stark effect is given by the energy correction $E^{(2)}$ and is proportional to the square of the applied field.

The electric dipole-moment operator (14.14) is an odd function of the coordinates. If the wave function in (14.17) is either even or odd, then the integrand in (14.17) is an odd function, and the integral over all space vanishes. We conclude that the permanent electric dipole moment μ is zero for states of definite parity.

The permanent electric dipole moment of a molecule in electronic state ψ_{el} is

$$\mu = \int \psi_{\text{el}}^* \hat{\mu} \psi_{\text{el}} d\tau_{\text{el}} \quad (14.19)$$

The electronic wave functions of homonuclear diatomic molecules can be classified as *g* or *u*, according to their parity. Hence, a homonuclear diatomic molecule has a zero permanent electric dipole moment, a result that is not too astonishing. The same holds true for any molecule with a center of symmetry. The electric dipole-moment operator for a molecule includes summation over both the electronic and nuclear charges:

$$\hat{\mu} = \sum_i (-e\mathbf{r}_i) + \sum_{\alpha} Z_{\alpha} e\mathbf{r}_{\alpha} \quad (14.20)$$

where $\mathbf{r}_{\alpha}$ is the vector from the origin to the nucleus of atomic number Z_{α} , and $\mathbf{r}_i$ is the vector to electron i . Since both the dipole-moment operator (14.20) and the electronic wave function depend on the parameters defining the nuclear configuration, the molecular electronic dipole moment μ depends on the nuclear configuration. To indicate this, the quantity (14.19) can be called the dipole-moment *function* of the molecule. In writing (14.19), we ignored the nuclear motion. When the dipole moment of a molecule is experimentally determined, what is measured is the quantity (14.19) averaged over the zero-point vibrations (assuming the temperature is not high enough for there to be appreciable population of higher vibrational levels). We might use μ_0 and μ_e to indicate the dipole moment averaged over zero-point vibrations and the dipole moment at the equilibrium nuclear configuration, respectively.

Since the second sum in (14.20) is independent of the electronic coordinates, we have

$$\begin{aligned} \mu &= \int \psi_{\text{el}}^* \sum_i (-e\mathbf{r}_i) \psi_{\text{el}} d\tau_{\text{el}} + \sum_{\alpha} Z_{\alpha} e\mathbf{r}_{\alpha} \int \psi_{\text{el}}^* \psi_{\text{el}} d\tau_{\text{el}} \\ &= -e \int |\psi_{\text{el}}|^2 \sum_i \mathbf{r}_i d\tau_{\text{el}} + e \sum_{\alpha} Z_{\alpha} \mathbf{r}_{\alpha} \end{aligned}$$

Using (14.8), we have

$$\boldsymbol{\mu} = -e \iiint \rho(x, y, z) \mathbf{r} \, dx \, dy \, dz + e \sum_{\alpha} Z_{\alpha} \mathbf{r}_{\alpha} \quad (14.21)$$

where ρ is the electron probability density. Equation (14.21) is what would be obtained if we pretended that the electrons were smeared out into a continuous charge distribution whose charge density is given by $-e\rho(x, y, z)$ and we used the classical equation (14.11) to calculate $\boldsymbol{\mu}$.

14.3 The Hartree–Fock Method for Molecules

A key development in quantum chemistry has been the computation of accurate self-consistent-field wave functions for many diatomic and polyatomic molecules. The principles of molecular SCF MO calculations are essentially the same as those for atomic SCF calculations (Section 11.1). We shall restrict ourselves to closed-shell configurations. For open shells, the formulas are more complicated.

The molecular Hartree–Fock wave function is written as an antisymmetrized product (Slater determinant) of spin-orbitals, each spin-orbital being a product of a spatial orbital ϕ_i and a spin function (either α or β).

The expression for the Hartree–Fock molecular electronic energy E_{HF} is given by the variation theorem as $E_{\text{HF}} = \langle D | \hat{H}_{\text{el}} + V_{\text{NN}} | D \rangle$, where D is the Slater-determinant Hartree–Fock wave function, and the purely electronic Hamiltonian $\hat{H}_{\text{el}}$ and the internuclear repulsion V_{NN} are given by (13.5) and (13.6). Since V_{NN} doesn't involve electronic coordinates and D is normalized, we have $\langle D | V_{\text{NN}} | D \rangle = V_{\text{NN}} \langle D | D \rangle = V_{\text{NN}}$. The operator $\hat{H}_{\text{el}}$ is the sum of one-electron operators $\hat{f}_i$ and two electron operators $\hat{g}_{ij}$; we have $\hat{H}_{\text{el}} = \sum_i \hat{f}_i + \sum_j \sum_{i>j} \hat{g}_{ij}$, where (in atomic units)

$$\hat{f}_i = -\frac{1}{2} \nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} \quad \text{and} \quad \hat{g}_{ij} = \frac{1}{r_{ij}}$$

The Hamiltonian $\hat{H}_{\text{el}}$ is the same as the Hamiltonian $\hat{H}$ for an atom except that $\sum_{\alpha} Z_{\alpha}/r_{i\alpha}$ replaces Z/r_i in $\hat{f}_i$. Hence Eq. (11.83) can be used to give $\langle D | \hat{H}_{\text{el}} | D \rangle$. Therefore, the Hartree–Fock energy of a diatomic or polyatomic molecule with only closed shells is

$$E_{\text{HF}} = 2 \sum_{i=1}^{n/2} H_{ii}^{\text{core}} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{\text{NN}} \quad (14.22)$$

$$H_{ii}^{\text{core}} \equiv \langle \phi_i(1) | \hat{H}^{\text{core}}(1) | \phi_i(1) \rangle \equiv \left\langle \phi_i(1) \left| -\frac{1}{2} \nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} \right| \phi_i(1) \right\rangle \quad (14.23)$$

$$J_{ij} \equiv \langle \phi_i(1) \phi_j(2) | 1/r_{12} | \phi_i(1) \phi_j(2) \rangle, \quad K_{ij} \equiv \langle \phi_i(1) \phi_j(2) | 1/r_{12} | \phi_j(1) \phi_i(2) \rangle \quad (14.24)$$

where the one-electron-operator symbol was changed from $\hat{f}_1$ to $\hat{H}^{\text{core}}(1)$. The **one-electron core Hamiltonian**

$$\hat{H}^{\text{core}}(1) \equiv -\frac{1}{2} \nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}}$$

is the sum of the kinetic-energy operator for electron 1 and the potential-energy operators for the attractions between electron 1 and the nuclei. $\hat{H}^{\text{core}}(1)$ omits the interactions of electron 1 with the other electrons. The sums over i and j are over the $n/2$ occupied spatial

orbitals ϕ_i of the n -electron molecule. In the **Coulomb integrals** J_{ij} and the **exchange integrals** K_{ij} , the integration goes over the spatial coordinates of electrons 1 and 2.

The Hartree–Fock method looks for those orbitals ϕ_i that minimize the variational integral E_{HF} . Each MO is taken to be normalized: $\langle \phi_i(1) | \phi_i(1) \rangle = 1$. Moreover, for computational convenience one takes the MOs to be orthogonal: $\langle \phi_i(1) | \phi_j(1) \rangle = 0$ for $i \neq j$. It might be thought that a lower energy could be obtained if the orthogonality restriction were omitted, but this is not so. A closed-shell antisymmetric wave function is a Slater determinant, and one can use the properties of determinants to show that a Slater determinant of nonorthogonal orbitals is equal to a Slater determinant in which the orbitals have been orthogonalized by the Schmidt or some other procedure; see Section 15.9 and F. W. Bobrowicz and W. A. Goddard, Chapter 4, Section 3.1 of *Schaefer, Methods of Electronic Structure Theory*. In effect, the Pauli antisymmetry requirement removes nonorthogonalities from the orbitals.

The derivation of the equation that determines the orthonormal ϕ_i 's that minimize E_{HF} is complicated and is omitted. (For the derivation, see *Lowe and Peterson*, Appendix 7; *Szabo and Ostlund*, Sections 3.1 and 3.2; *Parr*, pages 21–23.) One finds that the closed-shell orthogonal Hartree–Fock MOs satisfy

$$\hat{F}(1)\phi_i(1) = \varepsilon_i\phi_i(1) \quad (14.25)$$

where ε_i is the orbital energy and where the **(Hartree–) Fock operator** $\hat{F}$ is (in atomic units)

$$\hat{F}(1) = \hat{H}^{\text{core}}(1) + \sum_{j=1}^{n/2} [2\hat{J}_j(1) - \hat{K}_j(1)] \quad (14.26)$$

$$\hat{H}^{\text{core}}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} \quad (14.27)$$

where the **Coulomb operator** $\hat{J}_j$ and the **exchange operator** $\hat{K}_j$ are defined by

$$\hat{J}_j(1)f(1) = f(1) \int |\phi_j(2)|^2 \frac{1}{r_{12}} dv_2 \quad (14.28)$$

$$\hat{K}_j(1)f(1) = \phi_j(1) \int \frac{\phi_j^*(2)f(2)}{r_{12}} dv_2 \quad (14.29)$$

where f is an arbitrary function and the integrals are definite integrals over all space.

The first term on the right of (14.27) is the operator for the kinetic energy of one electron. The second term is the sum of the potential-energy operators for the attractions between one electron and the nuclei. The Coulomb operator $\hat{J}_j(1)$ is the potential energy of interaction between electron 1 and a smeared-out electron with electronic density $|\phi_j(2)|^2$. The factor 2 in (14.26) occurs because there are two electrons in each spatial orbital. The exchange operator has no simple physical interpretation but arises from the requirement that the wave function be antisymmetric with respect to electron exchange. The exchange operators are absent from the Hartree equations (11.9). The Hartree–Fock MOs ϕ_i in (14.25) are eigenfunctions of the same operator $\hat{F}$, the eigenvalues being the orbital energies ε_i .

The orthogonality of the MOs greatly simplifies MO calculations, causing many integrals to vanish. In contrast, the VB method uses atomic orbitals, and AOs centered on different atoms are not orthogonal. MO calculations are much simpler than VB calculations, and the MO method is used far more often than the VB method.

The true Hamiltonian operator and wave function involve the coordinates of all n electrons. The Hartree–Fock Hamiltonian operator $\hat{F}$ is a one-electron operator (that is, it involves the coordinates of only one electron), and (14.25) is a one-electron differential equation. This has been indicated in (14.25) by writing $\hat{F}$ and ϕ_i as functions of the coordinates of electron 1. Of course, the coordinates of any electron could have been used. The operator $\hat{F}$ is peculiar in that it depends on its own eigenfunctions [see Eqs. (14.26) to (14.29)], which are not known initially. Hence the Hartree–Fock equations must be solved by an iterative process, starting with an initial guess for the MOs.

To obtain the expression for the orbital energies ε_i , we multiply (14.25) by $\phi_i^*(1)$ and integrate over all space. Using the fact that ϕ_i is normalized and using the result of Prob. 14.8, we get $\varepsilon_i = \int \phi_i^*(1) \hat{F}(1) \phi_i(1) dv_1$ and

$$\varepsilon_i = \langle \phi_i(1) | \hat{H}^{\text{core}}(1) | \phi_i(1) \rangle + \sum_j [2 \langle \phi_i(1) | \hat{J}_j(1) | \phi_i(1) \rangle - \langle \phi_i(1) | \hat{K}_j(1) | \phi_i(1) \rangle]$$

$$\varepsilon_i = H_{ii}^{\text{core}} + \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) \quad (14.30)$$

where H_{ii}^{core} , J_{ij} , and K_{ij} are defined by (14.23) and (14.24).

Summation of (14.30) over the $n/2$ occupied orbitals gives

$$\sum_{i=1}^{n/2} \varepsilon_i = \sum_{i=1}^{n/2} H_{ii}^{\text{core}} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) \quad (14.31)$$

Solving this equation for $\sum_i H_{ii}^{\text{core}}$ and substituting the result into (14.22), we obtain the Hartree–Fock energy as

$$E_{\text{HF}} = 2 \sum_{i=1}^{n/2} \varepsilon_i - \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{\text{NN}} \quad (14.32)$$

Since there are two electrons per MO, the quantity $2 \sum_i \varepsilon_i$ is the sum of the orbital energies. Subtraction of the double sum in (14.32) avoids counting each interelectronic repulsion twice, as discussed in Section 11.1.

A key development that made feasible the calculation of accurate molecular SCF wave functions was Roothaan's 1951 proposal to expand the spatial orbitals ϕ_i as linear combinations of a set of one-electron basis functions χ_s :

$$\phi_i = \sum_{s=1}^b c_{si} \chi_s \quad (14.33)$$

To exactly represent the MOs ϕ_i , the basis functions χ_s should form a complete set. This requires an infinite number of basis functions. In practice, one must use a finite number b of basis functions. If b is large enough and the functions χ_s are well chosen, one can represent the MOs with negligible error.

To avoid confusion, we shall use the letters r, s, t, u to label the basis functions χ , and the letters i, j, k, l to label the MOs ϕ . (Often the Greek letters $\mu, \nu, \lambda, \sigma$ are used to label the basis functions.)

Substitution of the expansion (14.33) into the Hartree–Fock equations (14.25) gives

$$\sum_s c_{si} \hat{F} \chi_s = \varepsilon_i \sum_s c_{si} \chi_s$$

Multiplication by χ_r^* and integration gives

$$\sum_{s=1}^b c_{si} (F_{rs} - \varepsilon_i S_{rs}) = 0, \quad r = 1, 2, \dots, b \quad (14.34)$$

$$F_{rs} \equiv \langle \chi_r | \hat{F} | \chi_s \rangle, \quad S_{rs} \equiv \langle \chi_r | \chi_s \rangle \quad (14.35)$$

The equations (14.34) form a set of b simultaneous linear homogeneous equations in the b unknowns c_{si} , $s = 1, 2, \dots, b$, that describe the MO ϕ_i in (14.33). For a nontrivial solution, we must have

$$\det(F_{rs} - \varepsilon_i S_{rs}) = 0 \quad (14.36)$$

This is a secular equation whose roots give the orbital energies ε_i . The **(Hartree–Fock–) Roothaan equations** (14.34) must be solved by an iterative process, since the F_{rs} integrals depend on the orbitals ϕ_i (through the dependence of $\hat{F}$ on the ϕ_i 's), which in turn depend on the unknown coefficients c_{si} .

One starts with guesses for the occupied-MO expressions as linear combinations of the basis functions, as in (14.33). This initial set of MOs is used to compute the Fock operator $\hat{F}$ from (14.26) to (14.29). The matrix elements (14.35) are computed, and the secular equation (14.36) is solved to give an initial set of ε_i 's. These ε_i 's are used to solve (14.34) for an improved set of coefficients, giving an improved set of MOs, which are then used to compute an improved $\hat{F}$, and so on. One continues until no further improvement in MO coefficients and energies occurs from one cycle to the next. The calculations are done using a computer. (The most efficient way to solve the Roothaan equations is to use matrix-algebra methods; see the last part of this section.)

We have used the terms *SCF wave function* and *Hartree–Fock wave function* interchangeably. In practice, the term *SCF wave function* is applied to any wave function obtained by iterative solution of the Roothaan equations, whether or not the basis set is large enough to give a really accurate approximation to the Hartree–Fock SCF wave function. There is only one true Hartree–Fock wave function, which is the best possible wave function that can be written as a Slater determinant of spin-orbitals. With current computer power, one can use very large basis sets for small molecules and obtain wave functions that differ negligibly from the true Hartree–Fock wave functions. Because of deficiencies in properties calculated from Hartree–Fock wave functions, several methods that go beyond the Hartree–Fock method are widely used (see Chapter 16).

The Fock Matrix Elements

To solve the Roothaan equations (14.34), we first must express the *Fock matrix elements* (integrals) F_{rs} in terms of the basis functions χ . The Fock operator $\hat{F}$ is given by (14.26), so

$$F_{rs} = \langle \chi_r(1) | \hat{F}(1) | \chi_s(1) \rangle$$

$$F_{rs} = \langle \chi_r(1) | \hat{H}^{\text{core}}(1) | \chi_s(1) \rangle + \sum_{j=1}^{n/2} [2 \langle \chi_r(1) | \hat{J}_j(1) | \chi_s(1) \rangle - \langle \chi_r(1) | \hat{K}_j(1) | \chi_s(1) \rangle] \quad (14.37)$$

Replacement of f by χ_s in (14.28), followed by use of the expansion (14.33), gives

$$\hat{J}_j(1) \chi_s(1) = \chi_s(1) \int \frac{\phi_j^*(2) \phi_j(2)}{r_{12}} dv_2 = \chi_s(1) \sum_t \sum_u c_{tj}^* c_{uj} \int \frac{\chi_t^*(2) \chi_u(2)}{r_{12}} dv_2$$

Multiplication by $\chi_r^*(1)$ and integration over the coordinates of electron 1 gives

$$\langle \chi_r(1) | \hat{J}_j(1) | \chi_s(1) \rangle = \sum_t \sum_u c_{tj}^* c_{uj} \iint \frac{\chi_r^*(1) \chi_s(1) \chi_t^*(2) \chi_u(2)}{r_{12}} dv_1 dv_2$$

$$\langle \chi_r(1) | \hat{J}_j(1) \chi_s(1) \rangle = \sum_{t=1}^b \sum_{u=1}^b c_{tj}^* c_{uj} (rs|tu) \quad (14.38)$$

where the **two-electron repulsion integral** $(rs|tu)$ is defined as

$$(rs|tu) \equiv \iint \frac{\chi_r^*(1) \chi_s(1) \chi_t^*(2) \chi_u(2)}{r_{12}} dv_1 dv_2 \quad (14.39)$$

The widely used notation of (14.39) should not be misinterpreted as an overlap integral. Other notations, some of which are mutually contradictory, are used for electron repulsion integrals, so it is always wise to check an author's definition.

Similarly, replacement of f by χ_s in (14.29) leads to (Prob. 14.9)

$$\langle \chi_r(1) | \hat{K}_j(1) \chi_s(1) \rangle = \sum_{t=1}^b \sum_{u=1}^b c_{tj}^* c_{uj} (ru|ts) \quad (14.40)$$

Substituting (14.40) and (14.38) into (14.37) and changing the order of summation, we get the desired expression for F_{rs} in terms of integrals over the basis functions χ :

$$F_{rs} = H_{rs}^{\text{core}} + \sum_{t=1}^b \sum_{u=1}^b \sum_{j=1}^{n/2} c_{tj}^* c_{uj} [2(rs|tu) - (ru|ts)]$$

$$F_{rs} = H_{rs}^{\text{core}} + \sum_{t=1}^b \sum_{u=1}^b P_{tu} [(rs|tu) - \frac{1}{2}(ru|ts)] \quad (14.41)$$

$$P_{tu} \equiv 2 \sum_{j=1}^{n/2} c_{tj}^* c_{uj}, \quad t = 1, 2, \dots, b, \quad u = 1, 2, \dots, b \quad (14.42)$$

$$H_{rs}^{\text{core}} \equiv \langle \chi_r(1) | \hat{H}^{\text{core}}(1) | \chi_s(1) \rangle$$

The quantities P_{tu} are called **density matrix elements** or *charge, bond-order matrix elements*. [Some workers use the definition $P_{ut} \equiv 2 \sum_j c_{tj}^* c_{uj}$.] Substitution of the expansion (14.33) into (14.7) for the electron probability density ρ gives for a closed-shell molecule:

$$\rho = 2 \sum_{j=1}^{n/2} \phi_j^* \phi_j = 2 \sum_{r=1}^b \sum_{s=1}^b \sum_{j=1}^{n/2} c_{rj}^* c_{sj} \chi_r^* \chi_s = \sum_{r=1}^b \sum_{s=1}^b P_{rs} \chi_r^* \chi_s \quad (14.43)$$

To express the Hartree–Fock energy in terms of integrals over the basis functions χ , we first solve (14.31) for $\sum_i \sum_j (2J_{ij} - K_{ij})$ and substitute the result into (14.32) to get

$$E_{\text{HF}} = \sum_{i=1}^{n/2} \epsilon_i + \sum_{i=1}^{n/2} H_{ii}^{\text{core}} + V_{\text{NN}}$$

We have, using the expansion (14.33),

$$H_{ii}^{\text{core}} = \langle \phi_i | \hat{H}^{\text{core}} | \phi_i \rangle = \sum_r \sum_s c_{ri}^* c_{si} \langle \chi_r | \hat{H}^{\text{core}} | \chi_s \rangle = \sum_r \sum_s c_{ri}^* c_{si} H_{rs}^{\text{core}}$$

$$E_{\text{HF}} = \sum_{i=1}^{n/2} \epsilon_i + \sum_r \sum_s \sum_{i=1}^{n/2} c_{ri}^* c_{si} H_{rs}^{\text{core}} + V_{\text{NN}}$$

$$E_{\text{HF}} = \sum_{i=1}^{n/2} \epsilon_i + \frac{1}{2} \sum_{r=1}^b \sum_{s=1}^b P_{rs} H_{rs}^{\text{core}} + V_{\text{NN}} \quad (14.44)$$

An alternative expression for E_{HF} is useful. Multiplication of $\hat{F}\phi_i = \varepsilon_i\phi_i$ [Eq. (14.25)] by ϕ_i^* and integration gives $\varepsilon_i = \langle \phi_i | \hat{F} | \phi_i \rangle$. Substitution of $\phi_i = \sum_{s=1}^b c_{si} \chi_s$ [Eq. (14.33)] gives $\varepsilon_i = \sum_r \sum_s c_{ri}^* c_{si} \langle \chi_r | \hat{F} | \chi_s \rangle = \sum_r \sum_s c_{ri}^* c_{si} F_{rs}$. The first sum in (14.44) becomes $\sum_i \varepsilon_i = \sum_r \sum_s \sum_i c_{ri}^* c_{si} F_{rs} = \frac{1}{2} \sum_r \sum_s P_{rs} F_{rs}$, where the definition (14.42) of P_{rs} was used. Equation (14.44) becomes

$$E_{\text{HF}} = \frac{1}{2} \sum_{r=1}^b \sum_{s=1}^b P_{rs} (F_{rs} + H_{rs}^{\text{core}}) + V_{\text{NN}} \quad (14.45)$$

which expresses E_{HF} of a closed-shell molecule in terms of the density, Fock, and core-Hamiltonian matrix elements calculated with the basis functions χ_r .

EXAMPLE

Do an SCF calculation for the helium-atom ground state using a basis set of two 1s STOs with orbital exponents $\zeta_1 = 1.45$ and $\zeta_2 = 2.91$. [By trial and error, these have been found to be the optimum ζ 's to use for this basis set; see C. Roetti and E. Clementi, *J. Chem. Phys.*, **60**, 4725 (1974).]

From (11.14), the normalized basis functions are (in atomic units)

$$\chi_1 = 2\zeta_1^{3/2} e^{-\zeta_1 r} Y_0^0, \quad \chi_2 = 2\zeta_2^{3/2} e^{-\zeta_2 r} Y_0^0, \quad \zeta_1 = 1.45, \quad \zeta_2 = 2.91 \quad (14.46)$$

To solve the Roothaan equations (14.34), we need the integrals F_{rs} and S_{rs} . The overlap integrals S_{rs} are

$$\begin{aligned} S_{11} &= \langle \chi_1 | \chi_1 \rangle = 1, & S_{22} &= \langle \chi_2 | \chi_2 \rangle = 1 \\ S_{12} = S_{21} &= \langle \chi_1 | \chi_2 \rangle = 4\zeta_1^{3/2} \zeta_2^{3/2} \int_0^\infty e^{-(\zeta_1 + \zeta_2)r} r^2 dr = \frac{8\zeta_1^{3/2} \zeta_2^{3/2}}{(\zeta_1 + \zeta_2)^3} = 0.8366 \end{aligned}$$

where the Appendix integral (A.8) was used.

The integrals F_{rs} are given by (14.41) and depend on H_{rs}^{core} , P_{tu} , and $(rs|tu)$. From (14.27), $\hat{H}^{\text{core}} = -\frac{1}{2}\nabla^2 - 2/r = -\frac{1}{2}\nabla^2 - \zeta/r + (\zeta-2)/r$. The integrals H_{rs}^{core} are evaluated the same way that similar integrals were evaluated in the variation treatment of He in Section 9.4. We find (Prob. 14.12)

$$H_{11}^{\text{core}} = \langle \chi_1 | \hat{H}^{\text{core}} | \chi_1 \rangle = -\frac{1}{2}\zeta_1^2 + (\zeta_1 - 2)\zeta_1 = \frac{1}{2}\zeta_1^2 - 2\zeta_1 = -1.8488$$

$$H_{22}^{\text{core}} = \frac{1}{2}\zeta_2^2 - 2\zeta_2 = -1.5860$$

$$H_{12}^{\text{core}} = H_{21}^{\text{core}} = \langle \chi_1 | \hat{H}^{\text{core}} | \chi_2 \rangle = -\frac{1}{2}\zeta_2^2 S_{12} + \frac{4(\zeta_2 - 2)\zeta_1^{3/2} \zeta_2^{3/2}}{(\zeta_1 + \zeta_2)^2}$$

$$H_{12}^{\text{core}} = H_{21}^{\text{core}} = \frac{\zeta_1^{3/2} \zeta_2^{3/2} (4\zeta_1 \zeta_2 - 8\zeta_1 - 8\zeta_2)}{(\zeta_1 + \zeta_2)^3} = -1.8826$$

Many of the electron-repulsion integrals $(rs|tu)$ are equal to one another. For real basis functions, one can show that (Prob. 14.13)

$$(rs|tu) = (sr|tu) = (rs|ut) = (sr|ut) = (tu|rs) = (ut|rs) = (tu|sr) = (ut|sr) \quad (14.47)$$

The electron-repulsion integrals are evaluated using the $1/r_{12}$ expansion (9.124) in Prob. 9.14. One finds [see Eq. (9.53) and Prob. 14.14]

$$(11|11) = \frac{5}{8}\zeta_1 = 0.9062, \quad (22|22) = \frac{5}{8}\zeta_2 = 1.8188$$

$$(11|22) = (22|11) = (\zeta_1^4\zeta_2 + 4\zeta_1^3\zeta_2^2 + \zeta_1\zeta_2^4 + 4\zeta_1^2\zeta_2^3)/(\zeta_1 + \zeta_2)^4 = 1.1826$$

$$(12|12) = (21|12) = (12|21) = (21|21) = 20\zeta_1^3\zeta_2^3/(\zeta_1 + \zeta_2)^5 = 0.9536$$

$$(11|12) = (11|21) = (12|11) = (21|11) = \frac{16\zeta_1^{9/2}\zeta_2^{3/2}}{(3\zeta_1 + \zeta_2)^4} \left[\frac{12\zeta_1 + 8\zeta_2}{(\zeta_1 + \zeta_2)^2} + \frac{9\zeta_1 + \zeta_2}{2\zeta_1^2} \right] = 0.9033$$

$$(12|22) = (22|12) = (21|22) = (22|21)$$

$$= \text{the } (11|12) \text{ expression with 1 and 2 interchanged} = 1.2980$$

To start the calculation, we need an initial guess for the ground-state AO expansion coefficients c_{si} in (14.33) so that we can get an initial estimate of the density matrix elements P_{tu} in (14.41). We saw in Section 9.4 that the optimum orbital exponent for a helium AO that consists of one $1s$ STO is $\frac{27}{16} = 1.6875$. Since the orbital exponent ζ_1 is much closer to 1.6875 than is ζ_2 , we expect that the coefficient of χ_1 in $\phi_1 = c_{11}\chi_1 + c_{21}\chi_2$ will be substantially larger than the coefficient of χ_2 . Let us take as an initial guess $c_{11}/c_{21} \approx 2$. [A more general method to get an initial guess for the c_{si} coefficients is to neglect the electron-repulsion integrals in (14.41) and approximate F_{rs} in the secular equation (14.36) by $F_{rs} \approx H_{rs}^{\text{core}}$; we then solve (14.36) and (14.34). This would give $c_{11}/c_{21} \approx 1.5$ (Prob 14.15).] The normalization condition $\int |\phi_1|^2 d\tau = 1$ gives for real coefficients (Prob. 14.17)

$$c_{21} = (1 + k^2 + 2kS_{12})^{-1/2}, \quad \text{where } k \equiv c_{11}/c_{21} \quad (14.48)$$

Substitution of $k = 2$ and $S_{12} = 0.8366$ gives $c_{21} \approx 0.3461$ and $c_{11} \approx 2c_{21} = 0.6922$.

With $n = 2$ and $b = 2$, Eq. (14.42) gives

$$P_{11} = 2c_{11}^*c_{11}, \quad P_{12} = 2c_{11}^*c_{21}, \quad P_{21} = P_{12}^*, \quad P_{22} = 2c_{21}^*c_{21} \quad (14.49)$$

The initial guess $c_{11} \approx 0.6922$, $c_{21} \approx 0.3461$ gives as the initial density matrix elements

$$P_{11} \approx 0.9583, \quad P_{12} = P_{21} \approx 0.4791, \quad P_{22} \approx 0.2396$$

The Fock matrix elements are found from (14.41) with $b = 2$. Using (14.47) and $P_{12} = P_{21}$ for real functions, we get (Prob. 14.16a)

$$F_{11} = H_{11}^{\text{core}} + \frac{1}{2}P_{11}(11|11) + P_{12}(11|12) + P_{22}[(11|22) - \frac{1}{2}(12|21)]$$

$$F_{12} = F_{21} = H_{12}^{\text{core}} + \frac{1}{2}P_{11}(12|11) + P_{12}[\frac{3}{2}(12|12) - \frac{1}{2}(11|22)] + \frac{1}{2}P_{22}(12|22)$$

$$F_{22} = H_{22}^{\text{core}} + P_{11}[(22|11) - \frac{1}{2}(21|12)] + P_{12}(22|12) + \frac{1}{2}P_{22}(22|22)$$

Substitution of the values of the H_{rs}^{core} and $(rs|tu)$ integrals listed previously gives (Prob. 14.16b)

$$F_{11} = -1.8488 + 0.4531P_{11} + 0.9033P_{12} + 0.7058P_{22} \quad (14.50)$$

$$F_{12} = F_{21} = -1.8826 + 0.4516P_{11} + 0.8391P_{12} + 0.6490P_{22} \quad (14.51)$$

$$F_{22} = -1.5860 + 0.7058P_{11} + 1.2980P_{12} + 0.9094P_{22} \quad (14.52)$$

Substitution of the initial guess for the P_{tu} 's into (14.50) to (14.52) gives as the initial estimates of the F_{rs} matrix elements:

$$F_{11} \approx -0.813, \quad F_{12} = F_{21} \approx -0.892, \quad F_{22} \approx -0.070$$

The initial estimate of the secular equation $\det(F_{rs} - S_{rs}\epsilon_i) = 0$ is

$$\begin{vmatrix} -0.813 - \epsilon_i & -0.892 - 0.8366\epsilon_i \\ -0.892 - 0.8366\epsilon_i & -0.070 - \epsilon_i \end{vmatrix} \approx 0$$

$$0.3001\epsilon_i^2 - 0.6095\epsilon_i - 0.739 \approx 0$$

$$\epsilon_1 \approx -0.854, \quad \epsilon_2 \approx 2.885$$

Substitution of the lower root ϵ_1 into the Roothaan equation (14.34) with $r = 2$ gives

$$\begin{aligned} c_{11}(F_{21} - \epsilon_1 S_{21}) + c_{21}(F_{22} - \epsilon_1 S_{22}) &\approx 0 \\ -0.1775c_{11} + 0.784c_{21} &\approx 0 \\ c_{11}/c_{21} &\approx 4.42 \end{aligned}$$

Substitution of $k = 4.42$ and $S_{12} = 0.8366$ in the normalization condition (14.48) gives

$$c_{21} \approx 0.189, \quad c_{11} = kc_{21} \approx 0.836$$

Substitution of these improved coefficients into (14.49) gives as the improved density matrix elements

$$P_{11} \approx 1.398, \quad P_{12} = P_{21} \approx 0.316, \quad P_{22} \approx 0.071$$

Substitution of these improved P_{tu} 's into (14.50) to (14.52) gives as the improved F_{rs} values

$$F_{11} \approx -0.880, \quad F_{12} = F_{21} \approx -0.940, \quad F_{22} \approx -0.124_6$$

The improved secular equation is

$$\begin{vmatrix} -0.880 - \epsilon_i & -0.940 - 0.8366\epsilon_i \\ -0.940 - 0.8366\epsilon_i & -0.124_6 - \epsilon_i \end{vmatrix} \approx 0$$

$$\epsilon_1 \approx -0.918, \quad \epsilon_2 \approx 2.810$$

The improved ϵ_1 value gives $c_{11}/c_{21} \approx 4.61$ and

$$c_{11} \approx 0.842, \quad c_{21} \approx 0.183$$

Another cycle of calculation yields (Prob. 14.18)

$$\begin{aligned} P_{11} &= 1.418, & P_{12} = P_{21} &= 0.308, & P_{22} &= 0.067 \\ F_{11} &= -0.881, & F_{12} = F_{21} &= -0.940, & F_{22} &= -0.124_5 \end{aligned} \quad (14.53)$$

$$\epsilon_1 = -0.918, \quad \epsilon_2 = 2.809 \quad (14.54)$$

$$c_{11} = 0.842, \quad c_{21} = 0.183$$

These last c 's are the same as those for the previous cycle, so the calculation has converged and we are finished. The He ground-state SCF AO for this basis set is

$$\phi_1 = 0.842\chi_1 + 0.183\chi_2$$

The SCF energy is found from (14.44) with $n = 2$ and $b = 2$ as

$$\begin{aligned} E_{\text{HF}} &= -0.918 + \frac{1}{2}[1.418(-1.8488) + 2(0.308)(-1.8826) + 0.067(-1.5860)] + 0 \\ &= -2.862 \text{ hartrees} = -77.9 \text{ eV} \end{aligned}$$

A more precise calculation with $\zeta_1 = 1.45363$ and $\zeta_2 = 2.91093$ gives an SCF energy of -2.8616726 hartrees, as compared with the limiting Hartree–Fock energy -2.8616799 hartrees found with five basis functions [C. Roetti and E. Clementi, *J. Chem. Phys.*, **60**, 4725 (1974)].

Matrix Form of the Roothaan Equations

The Roothaan equations are most efficiently solved using matrix methods. The Roothaan equations (14.34) read

$$\sum_{s=1}^b F_{rs} c_{si} = \sum_{s=1}^b S_{rs} c_{si} \epsilon_i, \quad r = 1, 2, \dots, b$$

The coefficients c_{si} relate the MOs ϕ_i to the basis functions χ_s according to $\phi_i = \sum_s c_{si} \chi_s$. Let $\mathbf{C}$ be the square matrix of order b whose elements are the coefficients c_{si} . Let $\mathbf{F}$ be the square matrix of order b whose elements are $F_{rs} = \langle \chi_r | \hat{F} | \chi_s \rangle$. Let $\mathbf{S}$ be the square matrix whose elements are $S_{rs} = \langle \chi_r | \chi_s \rangle$. Let $\boldsymbol{\epsilon}$ be the diagonal square matrix whose diagonal elements are the orbital energies $\epsilon_1, \epsilon_2, \dots, \epsilon_b$ so that the elements of $\boldsymbol{\epsilon}$ are $\epsilon_{mi} = \delta_{mi} \epsilon_i$, where δ_{mi} is the Kronecker delta.

Use of the matrix multiplication rule (7.107) gives the (s, i) th element of the matrix product $\mathbf{C}\boldsymbol{\epsilon}$ as $(\mathbf{C}\boldsymbol{\epsilon})_{si} = \sum_m c_{sm} \epsilon_{mi} = \sum_m c_{sm} \delta_{mi} \epsilon_i = c_{si} \epsilon_i$. Hence the Roothaan equations read

$$\sum_{s=1}^b F_{rs} c_{si} = \sum_{s=1}^b S_{rs} (\mathbf{C}\boldsymbol{\epsilon})_{si} \quad (14.55)$$

From the matrix multiplication rule, the left side of (14.55) is the (r, i) th element of $\mathbf{FC}$, and the right side is the (r, i) th element of $\mathbf{S}(\mathbf{C}\boldsymbol{\epsilon})$. Since the general element of $\mathbf{FC}$ equals the general element of $\mathbf{S}\mathbf{C}\boldsymbol{\epsilon}$, these matrices are equal:

$$\mathbf{FC} = \mathbf{S}\mathbf{C}\boldsymbol{\epsilon} \quad (14.56)$$

This is the matrix form of the Roothaan equations.

The set of basis functions χ_s used to expand the MOs is not an orthogonal set. However, one can use the Schmidt or some other procedure to form orthogonal linear combinations of the basis functions to give a new set of basis functions χ'_s that is an orthonormal set: $\chi'_s = \sum_t a_{ts} \chi_t$ and $S'_{rs} = \langle \chi'_r | \chi'_s \rangle = \delta_{rs}$. (See Probs. 8.57 and 8.58 and Szabo and Ostlund, Section 3.4.5, for details of the orthogonalization procedure.) With this orthonormal basis set, the overlap matrix is a unit matrix, and the Roothaan equations (14.56) have the simpler form

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\boldsymbol{\epsilon} \quad (14.57)$$

where $F'_{rs} = \langle \chi'_r | \hat{F} | \chi'_s \rangle$ and $\mathbf{C}'$ is the matrix of the coefficients that relate the MOs ϕ_i to the orthonormal basis functions: $\phi_i = \sum_s c'_{si} \chi'_s$. It was shown in Prob. 8.57c that the $\mathbf{F}$ and $\mathbf{F}'$ matrices and the $\mathbf{C}$ and $\mathbf{C}'$ matrices are related by

$$\mathbf{F}' = \mathbf{A}^\dagger \mathbf{F} \mathbf{A} \quad \text{and} \quad \mathbf{C} = \mathbf{A} \mathbf{C}'$$

where $\mathbf{A}$ is the matrix of coefficients a_{ts} in $\chi'_s = \sum_t a_{ts} \chi_t$, so we can readily calculate $\mathbf{F}'$ from $\mathbf{F}$ and $\mathbf{C}$ from $\mathbf{C}'$. [$\mathbf{H}$ in Prob. 8.57 corresponds to $\mathbf{F}$ in (14.56).]

The matrix equation (14.57) has the same form as Eq. (8.87), which is $\mathbf{H}\mathbf{C} = \mathbf{C}\mathbf{W}$, where $\mathbf{C}$ and $\mathbf{W}$ [defined by (8.86)] are the eigenvector matrix and eigenvalue matrix, respectively, of $\mathbf{H}$. Thus, the orbital energies ϵ_i are the eigenvalues of the Fock matrix $\mathbf{F}'$ and each column of $\mathbf{C}'$ is an eigenvector of $\mathbf{F}'$. Because the Fock operator $\hat{F}$ is Hermitian, the Fock matrix $\mathbf{F}'$ is a Hermitian matrix. As noted in the paragraph preceding Eq. (8.94), the eigenvector matrix $\mathbf{C}'$ of the Hermitian matrix $\mathbf{F}'$ can be chosen to be unitary, meaning that its inverse equals its conjugate transpose [Eq. (8.92)] $\mathbf{C}'^{-1} = \mathbf{C}'^\dagger$. (With a unitary coefficient matrix $\mathbf{C}'$, the MOs ϕ_i are orthonormal; see Prob. 14.22.) Multiplication of (14.57) on the left by $\mathbf{C}'^{-1} = \mathbf{C}'^\dagger$ gives [see Eqs. (8.88) and (8.94)]

$$\mathbf{C}'^\dagger \mathbf{F}' \mathbf{C}' = \boldsymbol{\epsilon} \quad (14.58)$$

which has the same form as Eq. (8.94).

The following procedure is commonly used to do an SCF MO calculation at a specified molecular geometry.

1. Choose a basis set χ_s .
2. Evaluate the H_{rs}^{core} , S_{rs} , and $(rs|tu)$ integrals.
3. Use the overlap integrals S_{rs} and an orthogonalization procedure to calculate the $\mathbf{A}$ matrix of coefficients a_{ts} that will produce orthonormal basis functions $\chi'_s = \sum_t a_{ts} \chi_t$.
4. Make an initial guess for the coefficients c_{si} in the MOs $\phi_i = \sum_s c_{si} \chi_s$. From the initial guess of coefficients, calculate the density matrix $\mathbf{P}$ in (14.42).
5. Use (14.41) to calculate an estimate of the Fock matrix elements F_{rs} from $\mathbf{P}$ and the $(rs|tu)$ and H_{rs}^{core} integrals.
6. Calculate the matrix $\mathbf{F}'$ using $\mathbf{F}' = \mathbf{A}^\dagger \mathbf{F} \mathbf{A}$.
7. Use a matrix-diagonalization method (Section 8.6) to find the eigenvalue and eigenvector matrices $\boldsymbol{\epsilon}$ and $\mathbf{C}'$ of $\mathbf{F}'$.
8. Calculate the coefficient matrix $\mathbf{C} = \mathbf{A} \mathbf{C}'$.
9. Calculate an improved estimate of the density matrix from $\mathbf{C}$ using $\mathbf{P}^* = 2\mathbf{C}\mathbf{C}^\dagger$, which is the matrix form of (14.42) (Prob. 14.10c).
10. Compare the improved $\mathbf{P}$ with the preceding estimate of $\mathbf{P}$. If all corresponding matrix elements differ by negligible amounts from each other, the calculation has converged and one uses the converged SCF wave function to calculate molecular properties. If the calculation has not converged, go back to step (5) to calculate an improved $\mathbf{F}$ matrix from the current $\mathbf{P}$ matrix and then do the succeeding steps.

One way to begin an SCF calculation is to initially estimate the Fock matrix elements by $F_{rs} \approx H_{rs}^{\text{core}}$, which amounts to neglecting the double sum in (14.41). This gives a very crude estimate. More commonly, SCF calculations get the initial estimate of the density matrix by doing a semiempirical calculation (Section 17.4) on the molecule. Semiempirical calculations are very fast. Still another possibility is to construct a guess for the $\mathbf{P}$ matrix by using the density matrices for the atoms composing the molecule. To find the equilibrium geometry of a molecule, one does a series of SCF calculations at many successive geometries (see Section 15.10). For the second and later SCF calculations of the series, one takes the initial guess of $\mathbf{P}$ as $\mathbf{P}$ for the SCF wave function of a nearby geometry.

14.4 The Virial Theorem

We now derive the virial theorem. Let $\hat{H}$ be the time-independent Hamiltonian of a system in the bound stationary state ψ :

$$\hat{H}\psi = E\psi \quad (14.59)$$

Let $\hat{A}$ be a linear, time-independent operator. Consider the integral

$$\int \psi^* [\hat{H}, \hat{A}] \psi d\tau = \langle \psi | \hat{H}\hat{A} - \hat{A}\hat{H} | \psi \rangle = \langle \psi | \hat{H} | \hat{A}\psi \rangle - E \langle \psi | \hat{A} | \psi \rangle \quad (14.60)$$

where (14.59) was used. Since $\hat{H}$ is Hermitian, we have

$$\langle \psi | \hat{H} | \hat{A}\psi \rangle = \langle \hat{A}\psi | \hat{H} | \psi \rangle^* = E^* \langle \hat{A}\psi | \psi \rangle^* = E \langle \psi | \hat{A}\psi \rangle = E \langle \psi | \hat{A} | \psi \rangle$$

and Eq. (14.60) becomes

$$\int \psi^* [\hat{H}, \hat{A}] \psi d\tau = 0 \quad (14.61)$$

Equation (14.61) is the **hypervirial theorem**. [For some of its applications, see J. O. Hirschfelder, *J. Chem. Phys.*, **33**, 1462 (1960); J. H. Epstein and S. T. Epstein, *Am. J. Phys.*, **30**, 266 (1962).] In deriving (14.61), we used the Hermitian property of $\hat{H}$. The proof that $\hat{p}_x$ and $\hat{p}_x^2$ are Hermitian, and hence that $\hat{H}$ is Hermitian, requires that ψ vanish at $\pm\infty$ [see Eq. (7.17)]. Hence the hypervirial theorem does not apply to continuum stationary states, for which ψ does not vanish at ∞ .

We now derive the virial theorem from (14.61). We choose $\hat{A}$ to be

$$\sum_i \hat{q}_i \hat{p}_i = -i\hbar \sum_i q_i \frac{\partial}{\partial q_i} \quad (14.62)$$

where the sum runs over the $3n$ Cartesian coordinates of the n particles. (Particle 1 has Cartesian coordinates q_1, q_2, q_3 and linear-momentum components p_1, p_2, p_3 . In this chapter the symbol q will indicate a *Cartesian* coordinate.) To evaluate $[\hat{H}, \hat{A}]$, we use (5.4), (5.5), (5.8), and (5.9) to get

$$\begin{aligned} \left[\hat{H}, \sum_i \hat{q}_i \hat{p}_i \right] &= \sum_i [\hat{H}, \hat{q}_i \hat{p}_i] = \sum_i \hat{q}_i [\hat{H}, \hat{p}_i] + \sum_i [\hat{H}, \hat{q}_i] \hat{p}_i \\ &= i\hbar \sum_i q_i \frac{\partial V}{\partial q_i} - i\hbar \sum_i \frac{1}{m_i} \hat{p}_i^2 = i\hbar \sum_i q_i \frac{\partial V}{\partial q_i} - 2i\hbar \hat{T} \end{aligned} \quad (14.63)$$

where $\hat{T}$ and $\hat{V}$ are the kinetic- and potential-energy operators for the system. Substitution of (14.63) into (14.61) gives

$$\left\langle \psi \left| \sum_i q_i \frac{\partial V}{\partial q_i} \right| \psi \right\rangle = 2 \langle \psi | \hat{T} | \psi \rangle \quad (14.64)$$

Using $\langle B \rangle$ for the quantum-mechanical average of B , we write (14.64) as

$$\left\langle \sum_i q_i \frac{\partial V}{\partial q_i} \right\rangle = 2 \langle T \rangle \quad (14.65)$$

Equation (14.65) is the quantum-mechanical **virial theorem**. Note that its validity is restricted to bound stationary states. (The word *vires* is Latin for “forces.” In classical mechanics, the derivatives of the potential energy give the negatives of the force components. There is also a classical-mechanical virial theorem.)

For certain systems the virial theorem takes on a simple form. To discuss these systems, we introduce the idea of a homogeneous function. A function $f(x_1, x_2, \dots, x_j)$ of several variables is **homogeneous of degree n** if it satisfies

$$f(sx_1, sx_2, \dots, sx_j) = s^n f(x_1, x_2, \dots, x_j) \quad (14.66)$$

where s is an arbitrary parameter. For example, the function $g = 1/y^3 + x/y^2 z^2$ is homogeneous of degree -3 , since $g(sx, sy, sz) = 1/s^3 y^3 + sx/s^2 y^2 s^2 z^2 = s^{-3} g(x, y, z)$.

Euler's theorem on homogeneous functions states that, if $f(x_1, \dots, x_j)$ is homogeneous of degree n , then

$$\sum_{k=1}^j x_k \frac{\partial f}{\partial x_k} = n f \quad (14.67)$$

The theorem is proved as follows. Let

$$u_1 \equiv sx_1, \quad u_2 \equiv sx_2, \quad \dots, \quad u_j \equiv sx_j$$

Use of the chain rule gives for the partial derivative of the left side of (14.66) with respect to s

$$\begin{aligned}\frac{\partial f(u_1, \dots, u_j)}{\partial s} &= \frac{\partial f}{\partial u_1} \frac{\partial u_1}{\partial s} + \frac{\partial f}{\partial u_2} \frac{\partial u_2}{\partial s} + \dots + \frac{\partial f}{\partial u_j} \frac{\partial u_j}{\partial s} \\ &= x_1 \frac{\partial f}{\partial u_1} + x_2 \frac{\partial f}{\partial u_2} + \dots + x_j \frac{\partial f}{\partial u_j} = \sum_{k=1}^j x_k \frac{\partial f}{\partial u_k}\end{aligned}$$

The partial derivative of Eq. (14.66) with respect to s is thus

$$\sum_{k=1}^j x_k \frac{\partial f(u_1, \dots, u_j)}{\partial u_k} = ns^{n-1} f(x_1, \dots, x_j) \quad (14.68)$$

Let $s = 1$, so that $u_i = x_i$; Eq. (14.68) then gives (14.67). This completes the proof.

Now we return to the virial theorem (14.65). If the potential energy V is a homogeneous function of degree n when expressed in Cartesian coordinates, Euler's theorem gives

$$\sum_i q_i \frac{\partial V}{\partial q_i} = nV \quad (14.69)$$

and the virial theorem (14.65) simplifies to

$$2\langle T \rangle = n\langle V \rangle \quad (14.70)$$

for a bound stationary state. Since (Prob. 6.35)

$$\langle T \rangle + \langle V \rangle = E \quad (14.71)$$

we can write (14.70) in two other forms:

$$\langle V \rangle = \frac{2E}{n+2} \quad (14.72)$$

$$\langle T \rangle = \frac{nE}{n+2} \quad (14.73)$$

EXAMPLE

Apply the virial theorem to (a) the one-dimensional harmonic oscillator; (b) the hydrogen atom; (c) a many-electron atom.

- (a) For the one-dimensional harmonic oscillator, $V = \frac{1}{2} kx^2$, which is homogeneous of degree $n = 2$. Equations (14.70) and (14.72) give

$$\langle T \rangle = \langle V \rangle = \frac{1}{2} E = \frac{1}{2} h\nu \left(v + \frac{1}{2}\right) \quad (14.74)$$

This was verified for the ground state in Prob. 4.9.

- (b) For the H atom, $V = -1/(x^2 + y^2 + z^2)^{1/2}$ in Cartesian coordinates and atomic units. V is a homogeneous function of degree -1 . Hence

$$2\langle T \rangle = -\langle V \rangle \quad (14.75)$$

which was verified for the ground state in Prob. 6.36. For every hydrogen-atom bound stationary state,

$$\langle V \rangle = 2E \quad \text{and} \quad \langle T \rangle = -E \quad (14.76)$$

(c) For a many-electron atom with spin-orbit interaction neglected,

$$V = -Z \sum_{i=1}^n \frac{1}{(x_i^2 + y_i^2 + z_i^2)^{1/2}} + \sum_i \sum_{j>i} \frac{1}{[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2}}$$

Replacing each of the $3n$ coordinates by s times the coordinate, we find that V is homogeneous of degree -1 . Hence Eqs. (14.75) and (14.76) hold for every atom.

Now consider molecules. In the Born-Oppenheimer approximation, the molecular wave function is [Eq. (13.12)]

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

where q_i and q_α symbolize the electronic and nuclear coordinates, respectively. ψ_{el} is found by solving the electronic Schrödinger equation (13.7):

$$\hat{H}_{\text{el}} \psi_{\text{el}}(q_i; q_\alpha) = E_{\text{el}}(q_\alpha) \psi_{\text{el}}(q_i; q_\alpha)$$

where E_{el} is the purely electronic energy and where (in atomic units)

$$\hat{H}_{\text{el}} = \hat{T}_{\text{el}} + \hat{V}_{\text{el}} \quad (14.77)$$

$$\hat{T}_{\text{el}} = -\frac{1}{2} \sum_i \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \quad (14.78)$$

$$\begin{aligned} \hat{V}_{\text{el}} = & - \sum_\alpha \sum_i \frac{Z_\alpha}{[(x_i - x_\alpha)^2 + (y_i - y_\alpha)^2 + (z_i - z_\alpha)^2]^{1/2}} \\ & + \sum_i \sum_{j>i} \frac{1}{[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2}} \end{aligned} \quad (14.79)$$

Let the system be in the electronic stationary state ψ_{el} . If we put the subscript el on $\hat{H}$ and ψ in (14.59) and regard the variables of ψ_{el} to be the electronic coordinates q_i (with the nuclear coordinates q_α being parameters), then the derivation of the virial theorem (14.65) is seen to be valid for the electronic kinetic- and potential-energy operators, and we have

$$2 \langle \psi_{\text{el}} | \hat{T}_{\text{el}} | \psi_{\text{el}} \rangle = \left\langle \psi_{\text{el}} \left| \sum_i q_i \frac{\partial V_{\text{el}}}{\partial q_i} \right| \psi_{\text{el}} \right\rangle \quad (14.80)$$

Viewed as a function of the electronic coordinates, V_{el} is *not* a homogeneous function, since

$$\begin{aligned} & [(sx_i - x_\alpha)^2 + (sy_i - y_\alpha)^2 + (sz_i - z_\alpha)^2]^{-1/2} \\ & \neq s^{-1} [(x_i - x_\alpha)^2 + (y_i - y_\alpha)^2 + (z_i - z_\alpha)^2]^{-1/2} \end{aligned}$$

Thus the virial theorem for the average electronic kinetic and potential energies of a molecule will not have the simple form (14.75), which holds for atoms. We can, however,

view V_{el} as a function of both the electronic and the nuclear Cartesian coordinates. From this viewpoint V_{el} is a homogeneous function of degree -1 , since

$$\begin{aligned} & [(sx_i - sx_\alpha)^2 + (sy_i - sy_\alpha)^2 + (sz_i - sz_\alpha)^2]^{-1/2} \\ &= s^{-1}[(x_i - x_\alpha)^2 + (y_i - y_\alpha)^2 + (z_i - z_\alpha)^2]^{-1/2} \end{aligned}$$

Therefore, considering V_{el} as a function of both electronic and nuclear coordinates and applying Euler's theorem (14.67), we have

$$\sum_i q_i \frac{\partial V_{\text{el}}}{\partial q_i} + \sum_\alpha q_\alpha \frac{\partial V_{\text{el}}}{\partial q_\alpha} = -V_{\text{el}}$$

Using this equation in (14.80), we get

$$2\langle \psi_{\text{el}} | \hat{T}_{\text{el}} | \psi_{\text{el}} \rangle = -\langle \psi_{\text{el}} | \hat{V}_{\text{el}} | \psi_{\text{el}} \rangle - \left\langle \psi_{\text{el}} \left| \sum_\alpha q_\alpha \frac{\partial V_{\text{el}}}{\partial q_\alpha} \right| \psi_{\text{el}} \right\rangle \quad (14.81)$$

which contains an additional term as compared with the atomic virial theorem (14.75). Consider this extra term. We have

$$\left\langle \psi_{\text{el}} \left| \sum_\alpha q_\alpha \frac{\partial V_{\text{el}}}{\partial q_\alpha} \right| \psi_{\text{el}} \right\rangle = \sum_\alpha q_\alpha \int \psi_{\text{el}}^* \frac{\partial V_{\text{el}}}{\partial q_\alpha} \psi_{\text{el}} d\tau_{\text{el}}$$

where the nuclear coordinate q_α was taken outside the integral over electronic coordinates. In Section 14.7 we shall show that [see the bracketed sentence after Eq. (14.126)]

$$\int \psi_{\text{el}}^* \frac{\partial V_{\text{el}}}{\partial q_\alpha} \psi_{\text{el}} d\tau_{\text{el}} = \frac{\partial E_{\text{el}}}{\partial q_\alpha} \quad (14.82)$$

[Equation (14.82) is an example of the Hellmann–Feynman theorem.] Using these last two equations in the molecular electronic virial theorem (14.81), we get

$$\begin{aligned} 2\langle \psi_{\text{el}} | \hat{T}_{\text{el}} | \psi_{\text{el}} \rangle &= -\langle \psi_{\text{el}} | \hat{V}_{\text{el}} | \psi_{\text{el}} \rangle - \sum_\alpha q_\alpha \frac{\partial E_{\text{el}}}{\partial q_\alpha} \\ 2\langle T_{\text{el}} \rangle &= -\langle V_{\text{el}} \rangle - \sum_\alpha q_\alpha \frac{\partial E_{\text{el}}}{\partial q_\alpha} \end{aligned} \quad (14.83)$$

where the q_α 's are the nuclear *Cartesian* coordinates. Using

$$\langle T_{\text{el}} \rangle + \langle V_{\text{el}} \rangle = E_{\text{el}} \quad (14.84)$$

we can eliminate either $\langle T_{\text{el}} \rangle$ or $\langle V_{\text{el}} \rangle$ from (14.83), which is the molecular form of the virial theorem.

Now consider a diatomic molecule. The electronic energy is a function of R , the internuclear distance: $E_{\text{el}} = E_{\text{el}}(R)$. The summation in (14.83) is over the nuclear Cartesian coordinates $x_a, y_a, z_a, x_b, y_b, z_b$. We have

$$\begin{aligned} \frac{\partial E_{\text{el}}}{\partial x_a} &= \frac{dE_{\text{el}}}{dR} \frac{\partial R}{\partial x_a}, & \frac{\partial E_{\text{el}}}{\partial x_b} &= \frac{dE_{\text{el}}}{dR} \frac{\partial R}{\partial x_b} \\ R &= [(x_a - x_b)^2 + (y_a - y_b)^2 + (z_a - z_b)^2]^{1/2} \\ \frac{\partial R}{\partial x_a} &= \frac{x_a - x_b}{R}, & \frac{\partial R}{\partial x_b} &= \frac{x_b - x_a}{R} \end{aligned} \quad (14.85)$$

with similar equations for the y and z coordinates. The sum in (14.83) becomes

$$\begin{aligned}\sum_{\alpha} q_{\alpha} \frac{\partial E_{\text{el}}}{\partial q_{\alpha}} &= \frac{1}{R} \frac{dE_{\text{el}}}{dR} [x_a(x_a - x_b) + x_b(x_b - x_a) + y_a(y_a - y_b) \\ &\quad + y_b(y_b - y_a) + z_a(z_a - z_b) + z_b(z_b - z_a)] \\ \sum_{\alpha} q_{\alpha} \frac{\partial E_{\text{el}}}{\partial q_{\alpha}} &= R \frac{dE_{\text{el}}}{dR}\end{aligned}$$

where $(x_a - x_b)^2 + (y_a - y_b)^2 + (z_a - z_b)^2 = R^2$ was used. The virial theorem (14.83) for a diatomic molecule becomes

$$2\langle T_{\text{el}} \rangle = -\langle V_{\text{el}} \rangle - R \frac{dE_{\text{el}}}{dR} \quad (14.86)$$

Using (14.84), we have the two alternative forms

$$\langle T_{\text{el}} \rangle = -E_{\text{el}} - R \frac{dE_{\text{el}}}{dR} \quad (14.87)$$

$$\langle V_{\text{el}} \rangle = 2E_{\text{el}} + R \frac{dE_{\text{el}}}{dR} \quad (14.88)$$

In deriving the molecular electronic virial theorem (14.83), we omitted the inter-nuclear repulsion

$$V_{NN} = \sum_{\beta} \sum_{\alpha > \beta} \frac{Z_{\alpha} Z_{\beta}}{[(x_{\alpha} - x_{\beta})^2 + (y_{\alpha} - y_{\beta})^2 + (z_{\alpha} - z_{\beta})^2]^{1/2}} \quad (14.89)$$

from the electronic Hamiltonian (14.77) to (14.79). Let

$$V = V_{\text{el}} + V_{NN}$$

where V_{el} is given by (14.79). We can rewrite the electronic Schrödinger equation $\hat{H}_{\text{el}}\psi_{\text{el}} = E_{\text{el}}\psi_{\text{el}}$ as [Eq. (13.4)]

$$(\hat{T}_{\text{el}} + \hat{V})\psi_{\text{el}} = U(q_{\alpha})\psi_{\text{el}}$$

where

$$U(q_{\alpha}) = E_{\text{el}}(q_{\alpha}) + V_{NN}$$

$U(q_{\alpha})$ is the potential-energy function for nuclear motion. Consider what happens to the right side of (14.83) when we add V_{NN} to V_{el} and E_{el} . We have

$$\begin{aligned}-\int \psi_{\text{el}}^* (\hat{V}_{\text{el}} + V_{NN})\psi_{\text{el}} d\tau_{\text{el}} - \sum_{\alpha} q_{\alpha} \frac{\partial U}{\partial q_{\alpha}} \\ = -\langle \psi_{\text{el}} | \hat{V}_{\text{el}} | \psi_{\text{el}} \rangle - V_{NN} - \sum_{\alpha} q_{\alpha} \frac{\partial E_{\text{el}}}{\partial q_{\alpha}} - \sum_{\alpha} q_{\alpha} \frac{\partial V_{NN}}{\partial q_{\alpha}}\end{aligned} \quad (14.90)$$

Since V_{NN} is a homogeneous function of the nuclear Cartesian coordinates of degree -1 , Euler's theorem gives

$$\sum_{\alpha} q_{\alpha} \frac{\partial V_{NN}}{\partial q_{\alpha}} = -V_{NN}$$

and (14.90) becomes

$$-\langle \psi_{\text{el}} | \hat{V}_{\text{el}} + V_{\text{NN}} | \psi_{\text{el}} \rangle - \sum_{\alpha} q_{\alpha} \frac{\partial U}{\partial q_{\alpha}} = -\langle \psi_{\text{el}} | \hat{V}_{\text{el}} | \psi_{\text{el}} \rangle - \sum_{\alpha} q_{\alpha} \frac{\partial E_{\text{el}}}{\partial q_{\alpha}} \quad (14.91)$$

Substitution of (14.91) into (14.83) gives

$$\begin{aligned} 2\langle \psi_{\text{el}} | \hat{T}_{\text{el}} | \psi_{\text{el}} \rangle &= -\langle \psi_{\text{el}} | \hat{V}_{\text{el}} + V_{\text{NN}} | \psi_{\text{el}} \rangle - \sum_{\alpha} q_{\alpha} \frac{\partial U}{\partial q_{\alpha}} \\ 2\langle T_{\text{el}} \rangle &= -\langle V \rangle - \sum_{\alpha} q_{\alpha} \frac{\partial U}{\partial q_{\alpha}} \end{aligned} \quad (14.92)$$

which has the same form as (14.83). Therefore the molecular electronic virial theorem holds whether or not we include the internuclear repulsion. Corresponding to Eqs. (14.86) to (14.88) for diatomic molecules, we have

$$2\langle T_{\text{el}} \rangle = -\langle V \rangle - R(dU/dR) \quad (14.93)$$

$$\langle T_{\text{el}} \rangle = -U - R(dU/dR) \quad (14.94)$$

$$\langle V \rangle = 2U + R(dU/dR) \quad (14.95)$$

The potential energy $V = V_{\text{el}} + V_{\text{NN}}$ takes the zero of energy with all particles (electrons and nuclei) at infinite separation from one another. Therefore, $U(R)$ in (14.93) to (14.95) does not go to zero at $R = \infty$ but goes to the sum of the energies of the separated atoms, which is negative.

The true (nonrelativistic) wave functions for a system with V a homogeneous function of the coordinates must satisfy the form of the virial theorem (14.70). What determines whether an *approximate* wave function for such a system satisfies (14.70)? The answer is that, by inserting a variational parameter as a multiplier of each Cartesian coordinate and choosing this parameter to minimize the variational integral, we can make any trial variation function satisfy the virial theorem. (For the proof, see *Kauzmann*, page 229.) This process is called *scaling*, and the variational parameter multiplying each coordinate is called a *scale factor*. For a molecular trial function, the scaling parameter must be inserted in front of the nuclear Cartesian coordinates, as well as in front of the electronic coordinates.

Consider some examples. The zeroth-order perturbation wave function (9.49) for the heliumlike atom has no scale factor and so does not satisfy the virial theorem. If we were to calculate $\langle T \rangle$ and $\langle V \rangle$ for (9.49), we would find $2\langle T \rangle \neq -\langle V \rangle$; see Prob. 14.26. The Heitler–London trial function for H_2 , Eq. (13.100), has no scale factor and does not satisfy the virial theorem. The Heitler–London–Wang function, which uses a variationally determined orbital exponent, satisfies the virial theorem. Hartree–Fock wave functions satisfy the virial theorem; note the scale factor in the Slater basis functions (11.14).

14.5 The Virial Theorem and Chemical Bonding

We now use the virial theorem to examine the changes in electronic kinetic and potential energy that occur when a covalent chemical bond is formed in a diatomic molecule. For formation of a stable bond, the $U(R)$ curve must have a substantial minimum. At this minimum we have

$$\left. \frac{dU}{dR} \right|_{R_e} = 0 \quad (14.96)$$

and Eqs. (14.93) to (14.95) become

$$2\langle T_{\text{el}} \rangle|_{R_e} = -\langle V \rangle|_{R_e} \quad (14.97)$$

$$\langle T_{\text{el}} \rangle|_{R_e} = -U(R_e) \quad (14.98)$$

$$\langle V \rangle|_{R_e} = 2U(R_e) \quad (14.99)$$

These equations resemble those for atoms [Eqs. (14.75) and (14.76)]. At $R = \infty$ we have the separated atoms, and the atomic virial theorem gives

$$2\langle T_{\text{el}} \rangle|_{\infty} = -\langle V \rangle|_{\infty}, \quad \langle T_{\text{el}} \rangle|_{\infty} = -U(\infty), \quad \langle V \rangle|_{\infty} = 2U(\infty) \quad (14.100)$$

$U(\infty)$ is the sum of the energies of the two separated atoms. Equations (14.98)–(14.100) give

$$\langle T_{\text{el}} \rangle|_{R_e} - \langle T_{\text{el}} \rangle|_{\infty} = U(\infty) - U(R_e) \quad (14.101)$$

$$\langle V \rangle|_{R_e} - \langle V \rangle|_{\infty} = 2[U(R_e) - U(\infty)] \quad (14.102)$$

For bonding, we have $U(R_e) < U(\infty)$. Therefore, Eqs. (14.101) and (14.102) show that the average molecular potential energy at R_e is *less* than the sum of the potential energies of the separated atoms, whereas the average molecular kinetic energy is *greater* at R_e than at ∞ . The decrease in potential energy is twice the increase in kinetic energy, and results from allowing the electrons to feel the attractions of both nuclei and perhaps from an increase in orbital exponents in the molecule (see Section 13.5). The equilibrium dissociation energy (13.9) is $D_e = \frac{1}{2}(\langle V \rangle|_{\infty} - \langle V \rangle|_{R_e})$.

Consider the behavior of the average potential and kinetic energies for large R . The forces between uncharged atoms or molecules (other than those due to bond formation) are called *van der Waals forces*. For two neutral atoms, at least one of which is in an S state, quantum-mechanical perturbation theory shows that the van der Waals force of attraction is proportional to $1/R^7$, and the potential energy behaves like

$$U(R) \approx U(\infty) - \frac{A}{R^6}, \quad R \text{ large} \quad (14.103)$$

where A is a positive constant. (See *Kauzmann*, Chapter 13.) This expression was first derived by London, and van der Waals forces between neutral atoms are called *London forces* or *dispersion forces*. (Recall the discussion near the end of Section 13.7.)

Substitution of (14.103) for U and dU/dR into (14.94) and (14.95), and use of (14.100) gives

$$\langle V \rangle \approx \langle V \rangle|_{\infty} + \frac{4A}{R^6}, \quad \langle T_{\text{el}} \rangle \approx \langle T_{\text{el}} \rangle|_{\infty} - \frac{5A}{R^6}, \quad R \text{ large} \quad (14.104)$$

Hence, as R decreases from infinity, the average potential energy at first increases, while the average kinetic energy at first decreases. The combination of these conclusions with our conclusions about $\langle V \rangle|_{R_e}$ and $\langle T_{\text{el}} \rangle|_{R_e}$ shows that $\langle V \rangle$ must go through a maximum somewhere between R_e and infinity and $\langle T_{\text{el}} \rangle$ must go through a minimum in this region.

Now consider small values of R . One can treat a diatomic molecule by applying perturbation theory to the united atom (UA) formed by merging the two atoms of the molecule. The perturbation is the difference between the molecular and the united-atom Hamiltonians: $H' = \hat{H}_{\text{mol}} - \hat{H}_{\text{UA}}$. One finds that the molecular purely electronic energy has the following form at small R [W. A. Bingel, *J. Chem. Phys.*, **30**, 1250 (1959);

I. N. Levine, *J. Chem. Phys.*, **40**, 3444 (1964); **41**, 2044 (1965); W. Byers Brown and E. Steiner, *J. Chem. Phys.*, **44**, 3934 (1966):

$$E_{\text{el}} = E_{\text{UA}} + aR^2 + bR^3 + cR^4 + dR^5 + eR^5 \ln R + \cdots \quad (14.105)$$

where E_{UA} is the united-atom energy and a, b, c, d, e are constants. For $R \ll R_e$, we can use (14.105) and $U = E_{\text{el}} + V_{\text{NN}}$ [Eq. (13.8)] to write

$$U(R) \approx \frac{Z_a Z_b}{R} + E_{\text{UA}} + aR^2, \quad R \text{ small} \quad (14.106)$$

The virial theorem then gives (in atomic units)

$$\langle T_{\text{el}} \rangle \approx -E_{\text{UA}} - 3aR^2, \quad R \text{ small}$$

$$\langle V \rangle \approx \frac{Z_a Z_b}{R} + 2E_{\text{UA}} + 4aR^2, \quad R \text{ small}$$

Since the virial theorem (14.76) holds for the united atom, we have $\langle T_{\text{el}} \rangle|_0 = -E_{\text{UA}}$ and $\langle V_{\text{el}} \rangle|_0 = 2E_{\text{UA}}$. Therefore,

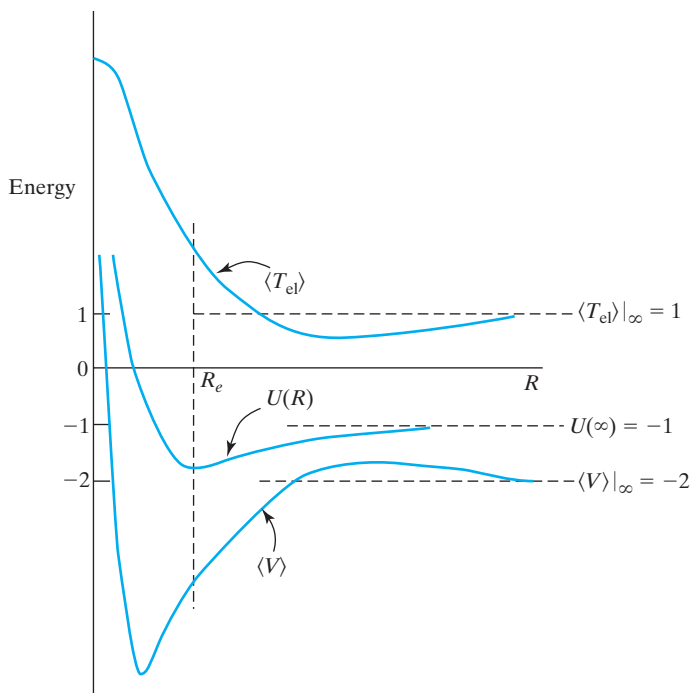
$$\langle T_{\text{el}} \rangle \approx \langle T_{\text{el}} \rangle|_0 - 3aR^2, \quad R \text{ small} \quad (14.107)$$

$$\langle V \rangle \approx \frac{Z_a Z_b}{R} + \langle V_{\text{el}} \rangle|_0 + 4aR^2, \quad R \text{ small} \quad (14.108)$$

$\langle V \rangle$ goes to infinity as R goes to zero, because of the internuclear repulsion.

Having found the general behavior of $\langle V \rangle$ and $\langle T_{\text{el}} \rangle$ as functions of R , we now draw **Fig. 14.1**. This figure is not for any particular molecule but resembles the known curves for H_2 and H_2^+ [W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, **41**, 3663 (1964); Slater,

FIGURE 14.1 Variation of the average potential and kinetic energies of a diatomic molecule. The unit of energy is taken as the electronic kinetic energy of the separated atoms.



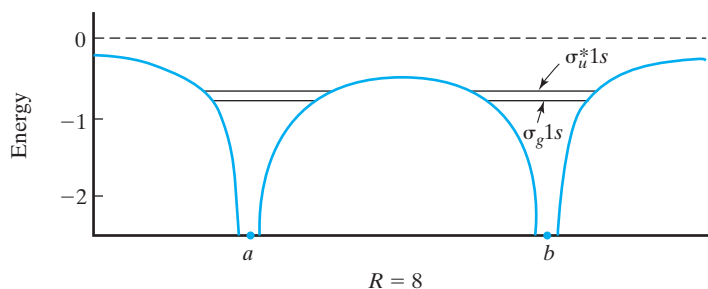


FIGURE 14.2 Potential energy along the internuclear axis for electronic motion in H_2^+ at a large internuclear separation. Atomic units are used.

Quantum Theory of Molecules and Solids, Volume 1, p. 36]. Similar curves hold for other diatomic molecules [see Fig. 1 in J. Hernandez-Trujillo et al., *Faraday Discuss.*, **135**, 79 (2007)].

How can we explain the changes in average kinetic and potential energy with R ? Consider H_2^+ . The electronic potential-energy function is in atomic units

$$V_{\text{el}} = -\frac{1}{r_a} - \frac{1}{r_b} \quad (14.109)$$

If we plot V_{el} for points on the molecular axis for a large value of R , we get a curve like **Fig. 14.2**, which resembles two hydrogen-atom potential-energy curves (Fig. 6.6) placed side by side. We saw that the overlapping of the $1s$ AOs occurring in molecule formation increases the charge probability density between the nuclei for the ground state. However, **Fig. 14.2** shows that the potential energy is relatively *high* in the region midway between the nuclei when R is large. Thus $\langle V \rangle$ initially increases as R decreases from infinity. Now consider the kinetic energy. The uncertainty principle (5.13) gives $(\Delta x)^2(\Delta p_x)^2 \geq \hbar^2/4$. For a stationary state, $\langle p_x \rangle$ is zero [see Eq. (3.92) and Prob. 14.31] and (5.11) gives $(\Delta p_x)^2 = \langle p_x^2 \rangle$. Hence a small value of $(\Delta x)^2$ means a large value of $\langle p_x^2 \rangle$ and a large value of the average kinetic energy, which equals $\langle p^2 \rangle / 2m$. Thus a compact ψ_{el} corresponds to a large electronic kinetic energy. In the separated atoms, the wave function is concentrated in two rather small regions about each nucleus (Fig. 6.7). In the initial stages of molecule formation, the buildup of probability density between the nuclei corresponds to having a wave function that is less compact than it was in the separated atoms. Thus, as R decreases from infinity, the electronic kinetic energy initially decreases. The energies E_{el} of the two lowest H_2^+ states have been indicated in **Fig. 14.2**. For large R the region between the nuclei is classically forbidden, but it is accessible according to quantum mechanics (tunneling).

Now consider what happens as R decreases further. Plotting (14.109) for an intermediate value of R , we find that now the region between the nuclei is a region of *low* potential energy, since an electron in this region feels substantial attractions from both nuclei. (See **Fig. 14.3**.) Hence at intermediate values of R , the overlap charge buildup between the nuclei lowers the potential energy. For intermediate values of R , the wave function has

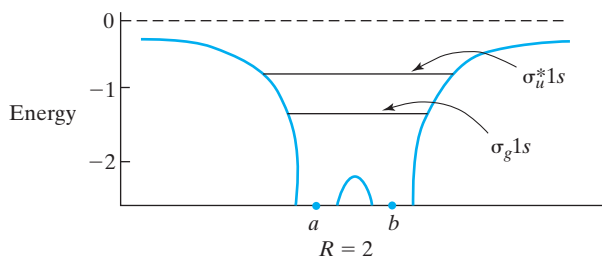


FIGURE 14.3 Potential energy along the internuclear axis for electronic motion in H_2^+ at an intermediate internuclear distance.

become more compact compared with large R , which gives an increase in $\langle T_{\text{el}} \rangle$ as R is reduced. In fact, we see from Fig. 14.1 and Eq. (14.101) that $\langle T_{\text{el}} \rangle$ is *greater* at R_e in the molecule than in the separated atoms. Hence the molecular wave function at R_e is more compact than the separated-atoms wave functions.

For very small R , the average potential energy goes to infinity, because of the internuclear repulsion. *However*, for $R = R_e$, Fig. 14.1 shows that $\langle V \rangle$ is still decreasing sharply with decreasing R , and it is the increase in $\langle T_{\text{el}} \rangle$, and not the nuclear repulsion, that causes the $U(R)$ curve to turn up as R becomes less than R_e . The squeezing of the molecular wave function into a smaller region with the associated increase in $\langle T_{\text{el}} \rangle$ is more important than the internuclear repulsion in causing the initial repulsion between the atoms.

14.6 The Hellmann–Feynman Theorem

Consider a system with a time-independent Hamiltonian $\hat{H}$ that involves parameters. An obvious example is the molecular electronic Hamiltonian (13.5), which depends parametrically on the nuclear coordinates. However, the Hamiltonian of any system contains parameters. For example, in the one-dimensional harmonic-oscillator Hamiltonian operator $-(\hbar^2/2m)(d^2/dx^2) + \frac{1}{2}kx^2$, the force constant k is a parameter, as is the mass m . Although $\hbar$ is a constant, we can consider it as a parameter also. The stationary-state energies E_n are functions of the same parameters as $\hat{H}$. For example, for the harmonic oscillator

$$E_n = (v + \frac{1}{2})\hbar\nu = (v + \frac{1}{2})\hbar(k/m)^{1/2} \quad (14.110)$$

The stationary-state wave functions also depend on the parameters in $\hat{H}$. We now investigate how E_n varies with each of the parameters. More specifically, if λ is one of these parameters, we ask for $\partial E_n / \partial \lambda$, where the partial derivative is taken with all other parameters held constant.

We begin with the Schrödinger equation

$$\hat{H}\psi_n = E_n\psi_n \quad (14.111)$$

where the ψ_n 's are the normalized stationary-state eigenfunctions. Because of normalization, we have

$$E_n = \int \psi_n^* \hat{H} \psi_n d\tau \quad (14.112)$$

$$\frac{\partial E_n}{\partial \lambda} = \frac{\partial}{\partial \lambda} \int \psi_n^* \hat{H} \psi_n d\tau \quad (14.113)$$

The integral in (14.112) is a definite integral over all space, and its value depends parametrically on λ since $\hat{H}$ and ψ_n depend on λ . Provided the integrand is well behaved, we can find the integral's derivative with respect to a parameter by differentiating the integrand with respect to the parameter and then integrating. Thus

$$\frac{\partial E_n}{\partial \lambda} = \int \frac{\partial}{\partial \lambda} (\psi_n^* \hat{H} \psi_n) d\tau = \int \frac{\partial \psi_n^*}{\partial \lambda} \hat{H} \psi_n d\tau + \int \psi_n^* \frac{\partial}{\partial \lambda} (\hat{H} \psi_n) d\tau \quad (14.114)$$

We have

$$\frac{\partial}{\partial \lambda} (\hat{H} \psi_n) = \frac{\partial}{\partial \lambda} (\hat{T} \psi_n) + \frac{\partial}{\partial \lambda} (\hat{V} \psi_n) \quad (14.115)$$

The potential-energy operator is just multiplication by V , so

$$\frac{\partial}{\partial \lambda} (\hat{V}\psi_n) = \frac{\partial V}{\partial \lambda} \psi_n + V \frac{\partial \psi_n}{\partial \lambda} \quad (14.116)$$

The parameter λ will occur in the kinetic-energy operator as part of the factor multiplying one or more of the derivatives with respect to the coordinates. For example, taking λ as the mass of the particle, we have for a one-particle problem

$$\begin{aligned} \hat{T} &= -\frac{\hbar^2}{2\lambda} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \\ \frac{\partial}{\partial \lambda} (\hat{T}\psi) &= -\frac{\hbar^2}{2} \frac{\partial}{\partial \lambda} \left[\frac{1}{\lambda} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) \right] \\ &= \frac{\hbar^2}{2\lambda^2} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) - \frac{\hbar^2}{2\lambda} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \left(\frac{\partial \psi}{\partial \lambda} \right) \end{aligned}$$

since we can change the order of the partial differentiations without affecting the result. We can write this last equation as

$$\frac{\partial}{\partial \lambda} (\hat{T}\psi_n) = \left(\frac{\partial \hat{T}}{\partial \lambda} \right) \psi_n + \hat{T} \left(\frac{\partial \psi_n}{\partial \lambda} \right) \quad (14.117)$$

where $\partial \hat{T} / \partial \lambda$ is found by differentiating $\hat{T}$ with respect to λ just as if it were a function instead of an operator. Although we got (14.117) by considering a specific $\hat{T}$ and λ , the same arguments show it to be generally valid. Combining (14.116) and (14.117), we write

$$\frac{\partial}{\partial \lambda} (\hat{H}\psi_n) = \left(\frac{\partial \hat{H}}{\partial \lambda} \right) \psi_n + \hat{H} \left(\frac{\partial \psi_n}{\partial \lambda} \right) \quad (14.118)$$

Equation (14.114) becomes

$$\frac{\partial E_n}{\partial \lambda} = \int \frac{\partial \psi_n^*}{\partial \lambda} \hat{H} \psi_n d\tau + \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau + \int \psi_n^* \hat{H} \frac{\partial \psi_n}{\partial \lambda} d\tau \quad (14.119)$$

For the first integral in (14.119), we have

$$\int \frac{\partial \psi_n^*}{\partial \lambda} \hat{H} \psi_n d\tau = E_n \int \frac{\partial \psi_n^*}{\partial \lambda} \psi_n d\tau \quad (14.120)$$

The Hermitian property of $\hat{H}$ and (14.111) give for the last integral in (14.119)

$$\int \psi_n^* \hat{H} \frac{\partial \psi_n}{\partial \lambda} d\tau = \int \frac{\partial \psi_n}{\partial \lambda} (\hat{H}\psi_n)^* d\tau = E_n \int \psi_n^* \frac{\partial \psi_n}{\partial \lambda} d\tau$$

Therefore,

$$\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau + E_n \int \frac{\partial \psi_n^*}{\partial \lambda} \psi_n d\tau + E_n \int \psi_n^* \frac{\partial \psi_n}{\partial \lambda} d\tau \quad (14.121)$$

The wave function is normalized, so

$$\begin{aligned}\int \psi_n^* \psi_n d\tau &= 1, & \frac{\partial}{\partial \lambda} \int \psi_n^* \psi_n d\tau &= 0 \\ \int \frac{\partial \psi_n^*}{\partial \lambda} \psi_n d\tau + \int \psi_n^* \frac{\partial \psi_n}{\partial \lambda} d\tau &= 0\end{aligned}\quad (14.122)$$

Using (14.122) in (14.121), we obtain

$$\frac{\partial E_n}{\partial \lambda} = \int \psi_n^* \frac{\partial \hat{H}}{\partial \lambda} \psi_n d\tau \quad (14.123)$$

Equation (14.123) is the **(generalized) Hellmann–Feynman theorem**. [For a discussion of the origin of the Hellmann–Feynman and related theorems, see J. I. Musher, *Am. J. Phys.*, **34**, 267 (1966).]

EXAMPLE

Apply the generalized Hellmann–Feynman theorem to the one-dimensional harmonic oscillator with λ taken as the force constant.

For the harmonic oscillator, $\hat{H} = -(\hbar^2/2m)(d^2/dx^2) + \frac{1}{2}kx^2$ and $\partial \hat{H}/\partial k = \frac{1}{2}x^2$. The energy levels are $E_v = (v + \frac{1}{2})h\nu = (v + \frac{1}{2})h(k/m)^{1/2}/2\pi$. We have

$$\partial E_v / \partial k = \frac{1}{2}(v + \frac{1}{2})h k^{-1/2} m^{-1/2} / 2\pi = \frac{1}{2}(v + \frac{1}{2})h\nu / k$$

Substitution in (14.123) gives

$$\int_{-\infty}^{\infty} \psi_v^* x^2 \psi_v dx = (v + \frac{1}{2})h\nu / k \quad (14.124)$$

We have found $\langle x^2 \rangle$ for any harmonic-oscillator stationary state without evaluating any integrals. This result was also obtained from the virial theorem; see Eq. (14.74). For a third derivation, see *Eyring, Walter, and Kimball*, p. 79.

The derivation of the Hellmann–Feynman theorem assumes that $\partial \psi / \partial \lambda$ exists. For a state belonging to a degenerate energy level, this assumption may not be true and (14.123) need not hold. Changing the parameter's value from λ to $\lambda + d\lambda$ amounts to applying a perturbation $\hat{H}' \equiv \hat{H}(\lambda + d\lambda) - \hat{H}(\lambda) \approx (\partial \hat{H} / \partial \lambda) d\lambda$. This perturbation changes ψ from $\psi(\lambda)$ to $\psi(\lambda + d\lambda)$. If $\psi(\lambda)$ is not one of the correct zeroth-order wave functions (9.73) for the perturbation $\hat{H}'$, then $\psi(\lambda)$ need not equal $\lim_{d\lambda \rightarrow 0} \psi(\lambda + d\lambda)$, so ψ will make a discontinuous jump at $d\lambda = 0$ and $\partial \psi / \partial \lambda$ will not exist at this point. *The Hellmann–Feynman theorem (14.123) applies to the wave functions of a degenerate level only if we use the correct zeroth-order wave functions for the perturbation $\hat{H}'$.* These correct functions are found by solving (9.83) and (9.81) with $\hat{H}' \equiv (\partial \hat{H} / \partial \lambda) d\lambda$. [Since $E_n^{(1)}$ will be proportional to $d\lambda$, we can replace $\hat{H}'$ with $\partial \hat{H} / \partial \lambda$ and $E_n^{(1)}$ with $E_n^{(1)} / d\lambda$ in (9.83) and (9.81).] For further details, see references 4–7 in G. P. Zhang and T. F. George, *Phys. Rev. B*, **69**, 167102 (2004).

Application of the Hellmann–Feynman theorem to the hydrogenlike atom, with Z as the parameter, gives (Prob. 14.37a)

$$\int r^{-1} |\psi|^2 d\tau = \left\langle \frac{1}{r} \right\rangle = \frac{Z}{n^2} \left(\frac{1}{a} \right) \quad (14.125)$$

This result was also obtained from the virial theorem; see Eq. (14.76).

14.7 The Electrostatic Theorem

Hellmann and Feynman independently applied Eq. (14.123) to molecules, taking λ as a nuclear Cartesian coordinate. We now consider their results.

As usual, we are using the Born–Oppenheimer approximation, solving the electronic Schrödinger equation for a fixed nuclear configuration [Eqs. (13.4) to (13.6)]:

$$(\hat{T}_{\text{el}} + \hat{V})\psi_{\text{el}} = (\hat{T}_{\text{el}} + \hat{V}_{\text{el}} + \hat{V}_{\text{NN}})\psi_{\text{el}} = U\psi_{\text{el}}$$

where $\hat{T}_{\text{el}}$, $\hat{V}_{\text{el}}$, and $\hat{V}_{\text{NN}}$ are given by (14.78), (14.79), and (14.89). The Hamiltonian operator $\hat{T}_{\text{el}} + \hat{V}_{\text{el}} + \hat{V}_{\text{NN}}$ depends on the nuclear coordinates as parameters. If x_δ is the x coordinate of nucleus δ , the generalized Hellmann–Feynman theorem (14.123) gives

$$\frac{\partial U}{\partial x_\delta} = \int \psi_{\text{el}}^* \frac{\partial(\hat{T}_{\text{el}} + \hat{V}_{\text{el}} + \hat{V}_{\text{NN}})}{\partial x_\delta} \psi_{\text{el}} d\tau_{\text{el}} = \int \psi_{\text{el}}^* \left(\frac{\partial V_{\text{el}}}{\partial x_\delta} + \frac{\partial V_{\text{NN}}}{\partial x_\delta} \right) \psi_{\text{el}} d\tau_{\text{el}} \quad (14.126)$$

since $\hat{T}_{\text{el}}$ is independent of the nuclear Cartesian coordinates, as can be seen from (14.78). [If we had omitted V_{NN} from V , we would have obtained Eq. (14.82), which was used in deriving the molecular electronic virial theorem.] From (14.79) we get in atomic units

$$\frac{\partial V_{\text{el}}}{\partial x_\delta} = -\sum_i \frac{Z_\delta(x_i - x_\delta)}{r_{i\delta}^3} \quad (14.127)$$

where $r_{i\delta}$ is the distance from electron i to nucleus δ . To find $\partial V_{\text{NN}}/\partial x_\delta$, we need to consider only internuclear repulsion terms that involve nucleus δ . Hence

$$\frac{\partial V_{\text{NN}}}{\partial x_\delta} = \frac{\partial}{\partial x_\delta} \sum_{\alpha \neq \delta} \frac{Z_\alpha Z_\delta}{[(x_\alpha - x_\delta)^2 + (y_\alpha - y_\delta)^2 + (z_\alpha - z_\delta)^2]^{1/2}} = \sum_{\alpha \neq \delta} Z_\alpha Z_\delta \frac{x_\alpha - x_\delta}{R_{\alpha\delta}^3}$$

where $R_{\alpha\delta}$ is the distance between nuclei α and δ . Since $\partial V_{\text{NN}}/\partial x_\delta$ does not involve the electronic coordinates and ψ_{el} is normalized, (14.126) becomes

$$\frac{\partial U}{\partial x_\delta} = -Z_\delta \int |\psi_{\text{el}}|^2 \sum_i \frac{x_i - x_\delta}{r_{i\delta}^3} d\tau_{\text{el}} + \sum_{\alpha \neq \delta} Z_\alpha Z_\delta \frac{x_\alpha - x_\delta}{R_{\alpha\delta}^3} \quad (14.128)$$

Consider the integral in (14.128). Using Eq. (14.8) with $B(\mathbf{r}_i) = (x_i - x_\delta)/r_{i\delta}^3$, we get

$$\frac{\partial U}{\partial x_\delta} = -Z_\delta \iiint \rho(x, y, z) \frac{x - x_\delta}{r_\delta^3} dx dy dz + \sum_{\alpha \neq \delta} Z_\alpha Z_\delta \frac{x_\alpha - x_\delta}{R_{\alpha\delta}^3} \quad (14.129)$$

The variable r_δ is the distance between nucleus δ and point (x, y, z) in space:

$$r_\delta = [(x - x_\delta)^2 + (y - y_\delta)^2 + (z - z_\delta)^2]^{1/2}$$

What is the significance of (14.129)? In the Born–Oppenheimer approximation, $U(x_\alpha, y_\alpha, z_\alpha, x_\beta, y_\beta, z_\beta, \dots)$ is the potential-energy function for nuclear motion, the nuclear Schrödinger equation being

$$\left(-\frac{\hbar^2}{2} \sum_\alpha \frac{1}{m_\alpha} \nabla_\alpha^2 + U \right) \psi_N = E \psi_N \quad (14.130)$$

The quantity $-\partial U/\partial x_\delta$ can thus be viewed [see Eq. (5.31)] as the x component of the effective force on nucleus δ due to the other nuclei and the electrons. In addition to (14.129),

we have two corresponding equations for $\partial U/\partial y_\delta$ and $\partial U/\partial z_\delta$. If $\mathbf{F}_\delta$ is the effective force on nucleus δ , then

$$\mathbf{F}_\delta = -\mathbf{i} \frac{\partial U}{\partial x_\delta} - \mathbf{j} \frac{\partial U}{\partial y_\delta} - \mathbf{k} \frac{\partial U}{\partial z_\delta} \quad (14.131)$$

$$\mathbf{F}_\delta = -Z_\delta \iiint \rho(x, y, z) \frac{\mathbf{r}_\delta}{r_\delta^3} dx dy dz + \sum_{\alpha \neq \delta} Z_\alpha Z_\delta \frac{\mathbf{R}_{\alpha\delta}}{R_{\alpha\delta}^3} \quad (14.132)$$

where $\mathbf{r}_\delta$ is the vector from point (x, y, z) to nucleus δ ,

$$\mathbf{r}_\delta = \mathbf{i}(x_\delta - x) + \mathbf{j}(y_\delta - y) + \mathbf{k}(z_\delta - z) \quad (14.133)$$

and where $\mathbf{R}_{\alpha\delta}$ is the vector from nucleus α to nucleus δ :

$$\mathbf{R}_{\alpha\delta} = \mathbf{i}(x_\delta - x_\alpha) + \mathbf{j}(y_\delta - y_\alpha) + \mathbf{k}(z_\delta - z_\alpha)$$

Equation (14.132) has a simple physical interpretation. Let us imagine the electrons smeared out into a charge distribution whose density in atomic units is $-\rho(x, y, z)$. The force on nucleus δ exerted by the infinitesimal element of electronic charge $-\rho dx dy dz$ is [Eq. (6.56)]

$$-Z_\delta \frac{\mathbf{r}_\delta}{r_\delta^3} \rho dx dy dz \quad (14.134)$$

and integration of (14.134) shows that the total force exerted on δ by this hypothetical electron smear is given by the first term on the right of (14.132). The second term on the right of (14.132) is clearly the Coulomb's law force on nucleus δ due to the electrostatic repulsions of the other nuclei.

Thus *the effective force acting on a nucleus in a molecule can be calculated by simple electrostatics as the sum of the Coulombic forces exerted by the other nuclei and by a hypothetical electron cloud whose charge density $-\rho(x, y, z)$ is found by solving the electronic Schrödinger equation.* This is the **Hellmann–Feynman electrostatic theorem**. The electron probability density depends on the parameters defining the nuclear configuration: $\rho = \rho(x, y, z; x_\alpha, y_\alpha, z_\alpha, x_\beta, \dots)$.

It is quite reasonable that the electrostatic theorem follows from the Born–Oppenheimer approximation, since the rapid motion of the electrons allows the electronic wave function and probability density to adjust immediately to changes in nuclear configuration. The rapid motion of the electrons causes the sluggish nuclei to “see” the electrons as a charge cloud rather than as discrete particles. The fact that the effective forces on the nuclei are electrostatic affirms that there are no “mysterious quantum-mechanical forces” acting in molecules.

Let us consider the implications of the electrostatic theorem for chemical bonding in diatomic molecules. We take the internuclear axis as the z axis (Fig. 14.4). By symmetry the x and y components of the effective forces on the two nuclei are zero. [Also, one can show that the z force components on nuclei a and b are related by $F_{z,a} = -F_{z,b}$ (Prob. 14.40). The effective forces on nuclei a and b are equal in magnitude and opposite in direction.]

From (14.134) and (14.133), the z component of the effective force on nucleus a due to the element of electronic charge in the infinitesimal region about (x, y, z) is

$$-Z_a \rho [(z_a - z)/r_a^3] dx dy dz = Z_a \rho (\cos \theta_a / r_a^2) dx dy dz \quad (14.135)$$

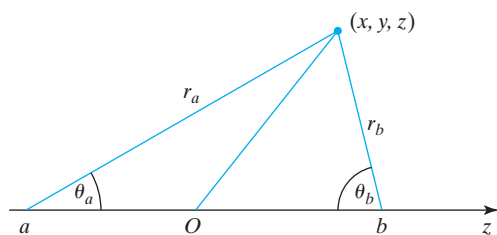


FIGURE 14.4 Coordinate system for a diatomic molecule. The origin is at O .

since $\cos \theta_a = (-z_a + z)/r_a$ (z_a is negative.) Similarly, the z component of force on nucleus b due to this charge is

$$-Z_b \rho (\cos \theta_b / r_b^2) dx dy dz \quad (14.136)$$

A positive value of (14.135) or (14.136) corresponds to a force in the $+z$ direction, that is, to the right in Fig. 14.4. When the force on nucleus a is algebraically greater than the force on nucleus b , then the element of electronic charge tends to draw a toward b . Hence electronic charge that is binding is located in the region where

$$Z_a \rho (\cos \theta_a / r_a^2) dx dy dz > -Z_b \rho (\cos \theta_b / r_b^2) dx dy dz \quad (14.137)$$

Since the probability density ρ is nonnegative, division by ρ preserves the direction of the inequality sign, and the binding region of space is where

$$Z_a \frac{\cos \theta_a}{r_a^2} + Z_b \frac{\cos \theta_b}{r_b^2} > 0 \quad (14.138)$$

When the force on b is algebraically greater than that on a , the electronic charge element tends to draw b away from a . The antibinding region of space is thus characterized by a negative value for the left side of (14.138). The surfaces for which the left side of (14.138) equals zero divide space into the **binding** and **antibinding regions**. [T. Berlin, *J. Chem. Phys.*, **19**, 208 (1951); J. Hinze, *J. Chem. Phys.*, **101**, 6369 (1994); Berlin's ideas are extended to polyatomic molecules in T. Koga et al., *J. Am. Chem. Soc.*, **100**, 7522 (1978); X. Wang and Z. Peng, *Int. J. Quantum. Chem.*, **47**, 393 (1993).]

Figures 14.5 and 14.6 show the binding and antibinding regions for a homonuclear and a heteronuclear diatomic molecule. As might be expected, the binding region for a homonuclear diatomic molecule lies between the nuclei. Charge in this region tends to draw the nuclei together. Bonding leads to a transfer of charge probability density into the region between the nuclei because of the overlap between the bonding AOs. Electronic

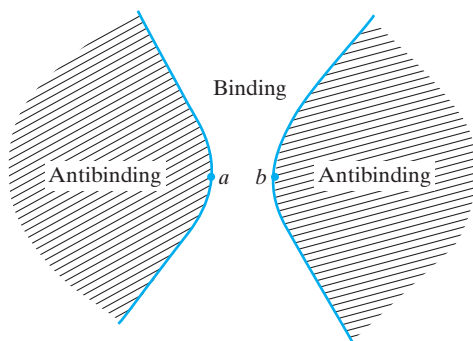
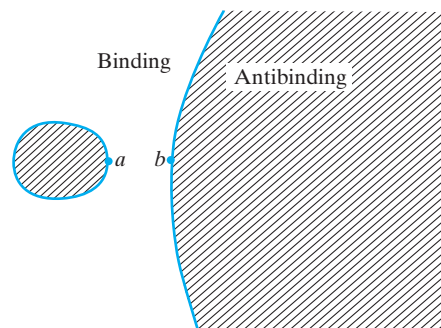


FIGURE 14.5 Cross section of binding and antibinding regions in a homonuclear diatomic molecule. To obtain the three-dimensional regions, rotate the figure about the internuclear axis.

FIGURE 14.6 Binding and antibinding regions for a heteronuclear diatomic molecule with $Z_b > Z_a$.



charge that is “behind” the nuclei (to the left of nucleus a or to the right of nucleus b in Fig. 14.5) exerts a greater attraction on the nucleus that is nearer to it than on the other nucleus and thus tends to pull the nuclei apart.

From the Hellmann–Feynman viewpoint, we seem to be considering chemical bonding solely in terms of potential energy, whereas the virial-theorem discussion involved both potential and kinetic energy. For the purposes of the Hellmann–Feynman discussion, we are imagining the electrons to be smeared out into a continuous charge distribution. Hence we make no reference to electronic kinetic energy. The use of the electrostatic theorem to explain chemical bonding has been criticized by some quantum chemists on the grounds that it hides the role of kinetic energy in bonding. [See the references cited after Eq. (13.66).]

In 1939, Feynman conjectured that the dispersion attraction between two molecules A and B at relatively large intermolecular distances is explainable as follows: The interactions between the two molecules cause the electron probability density of each molecule to be distorted and shifted somewhat toward the other molecule. The attractions of the nuclei in molecule A toward the distorted (polarized) electron density of molecule A and the attractions of the B nuclei toward the polarized B electron density then draw the two molecules together. In 1990, Hunt proved that the dispersion interaction between any two molecules in their ground electronic states results from the attractions of the nuclei in each molecule to the polarized electron density of the same molecule [K. L. C. Hunt, *J. Chem. Phys.*, **92**, 1180 (1990)].

For further applications of the Hellmann–Feynman electrostatic theorem, see B. M. Deb, ed., *The Force Concept in Chemistry*, Van Nostrand Reinhold, 1981.

Summary

The electron probability density ρ of an n -electron molecule is found by summation of $|\psi|^2$ over spins, integration over the spatial coordinates of $n - 1$ electrons, and multiplication by n [Eq. (14.5)]. The dipole moment of a molecule is given by (14.21).

The best possible forms for the MOs ϕ_i of a molecule are the solutions of the Hartree–Fock equations $\hat{F}\phi_i = \varepsilon_i\phi_i$, where $\hat{F}$ is the Fock operator [Eqs. (14.26) to (14.29)] and ε_i is the orbital energy. To solve the Hartree–Fock equations, we expand ϕ_i using a set of basis functions: $\phi_i = \sum_s c_{si}\chi_s$; this leads to the Roothaan equations (14.34) for the coefficients c_{si} and orbital energies ε_i . Since the Fock operator $\hat{F}$ and its matrix elements F_{rs} [Eq. (14.41)] depend on the occupied MOs, which are unknown, the Roothaan equations are solved by an iterative process that starts with an initial guess for the occupied MOs.

For a bound stationary state, the quantum-mechanical virial theorem states that $2\langle T \rangle = \sum_i \langle q_i (\partial V / \partial q_i) \rangle$, where the sum is over the Cartesian coordinates of all the particles.

If V is a homogeneous function of degree n , then $2\langle T \rangle = n\langle V \rangle$. For a diatomic molecule, the virial theorem becomes $\langle T_{\text{el}} \rangle = -U - R(dU/dR)$ and $\langle V \rangle = 2U + R(dU/dR)$, where $U(R)$ is the potential-energy function for nuclear motion. The virial theorem shows that at R_e , $\langle V \rangle$ of a diatomic molecule is less than the total $\langle V \rangle$ of the separated atoms, and $\langle T_{\text{el}} \rangle$ is greater than the total $\langle T_{\text{el}} \rangle$ of the separated atoms.

For a bound stationary state, the generalized Hellmann–Feynman theorem is $\partial E_n / \partial \lambda = \int \psi_n^* (\partial \hat{H} / \partial \lambda) \psi_n d\tau$, where λ is a parameter in the Hamiltonian. (In case of degeneracy, ψ_n must be a correct zeroth-order wave function for the perturbation of changing λ .) Taking λ as a nuclear coordinate, we are led to the Hellmann–Feynman electrostatic theorem, which states that the force on a nucleus in a molecule is the sum of the electrostatic forces exerted by the other nuclei and the electron charge density.

Problems

Sec.	14.1	14.2	14.3	14.4	14.5	14.6	14.7
Probs.	14.1–14.2	14.3–14.5	14.6–14.22	14.23–14.31	14.32–14.36	14.37–14.39	14.40–14.41

- 14.1** Derive (14.6) for ρ_{VB} and ρ_{MO} .
- 14.2** Show that ρ_{MO} of (14.6) is greater than ρ_{VB} of (14.6) at the midpoint of the line joining the nuclei.
- 14.3** Show that the dipole moment (14.9) of a system of charges is independent of the choice of the coordinate origin, *provided* the system has no net charge.
- 14.4** (a) Explain why the permanent dipole moment of a many-electron atom in a stationary state is always zero. (b) Explain why the permanent electric dipole moment of H can be nonzero for certain excited states. (c) Show qualitatively that two of the four correct zeroth-order functions of Prob. 9.23 give nonzero permanent dipole moments.
- 14.5** For NaCl, $R_e = 2.36 \text{ \AA}$. The ionization energy of Na is 5.14 eV, and the electron affinity of Cl is 3.61 eV. Use the simple model of NaCl as a pair of spherical ions in contact to estimate D_e and the dipole moment of NaCl. Compare with the experimental values $D_e = 4.25 \text{ eV}$ and $\mu = 9.0 \text{ D}$. [One debye (D) is $3.33564 \times 10^{-30} \text{ C m}$.]
- 14.6** Prove that the one-electron Hartree–Fock operator (14.26) is Hermitian.
- 14.7** Explain the origin of the extra terms in the molecular Hartree–Fock operator (14.26) as compared with the atomic Hartree operator of (11.9) and (11.7).
- 14.8** Verify that the Coulomb and exchange integrals J_{ij} and K_{ij} can be written in terms of the Coulomb and exchange operators of Section 14.3 as

$$J_{ij} = \langle \phi_i(1) | \hat{J}_j(1) | \phi_i(1) \rangle, \quad K_{ij} = \langle \phi_i(1) | \hat{K}_j(1) | \phi_i(1) \rangle$$

- 14.9** Verify Eq. (14.40) for the $\hat{K}_j$ integral over basis functions.
- 14.10** (a) Use the definition (14.42) of P_{lu} to show that $P_{rs} = P_{sr}^*$, meaning that the density matrix $\mathbf{P}$ is a Hermitian matrix. (b) Show that Eq. (14.45) can be written as $E_{\text{HF}} = \frac{1}{2} \text{Tr}(\mathbf{P}^* \mathbf{F} + \mathbf{P}^* \mathbf{H}^{\text{core}}) + V_{\text{NN}}$, where Tr denotes the trace of a matrix (Section 7.10) and the $\mathbf{P}$, $\mathbf{F}$, and $\mathbf{H}^{\text{core}}$ matrices have elements P_{rs} , F_{rs} , and H_{rs}^{core} . (c) Verify that (14.42) can be written as $\mathbf{P}^* = 2\mathbf{C}\mathbf{C}^\dagger$, where $\mathbf{C}$ is the matrix of coefficients c_{ij} .
- 14.11** From (14.5), show that $\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho dx dy dz = n$, where ρ is the electron probability density of an n -electron molecule. (b) Use the result of (a) and Eq. (14.43) to show that $n = \sum_r \sum_s P_{rs} S_{rs} = \sum_r \sum_s P_{rs} S_{sr}^*$. (c) Show that $n = \text{Tr}(\mathbf{P}\mathbf{S}^*)$, which becomes $n = \text{Tr}(\mathbf{P}\mathbf{S})$ for real basis functions. Here, $\mathbf{P}$ and $\mathbf{S}$ are the density and overlap matrices.
- 14.12** Verify the equations for H_{11}^{core} and H_{22}^{core} in the Section 14.3 example.
- 14.13** Verify the equalities (14.47) for electron-repulsion integrals.
- 14.14** Use Eq. (9.124) of Prob. 9.14 to verify the expressions for the integrals $(11|22)$ and $(22|22)$ in the Section 14.3 example.

- 14.15** For the He-atom SCF calculation in Section 14.3, find the initial estimate of c_{11}/c_{21} given by the approximation $F_{rs} \approx H_{rs}^{\text{core}}$.
- 14.16** (a) Verify the equations for F_{11} , F_{12} , and F_{22} that immediately precede Eq. (14.50). (b) Verify Eqs. (14.50) to (14.52) for F_{11} , F_{12} , and F_{22} .
- 14.17** Derive (14.48) from the normalization condition for ϕ_1 .
- 14.18** Verify the numerical results for P_{11} , P_{12} , P_{22} , F_{11} , F_{12} , F_{22} , ϵ_1 , ϵ_2 , c_{11} , and c_{21} obtained on the last cycle of calculation in the Section 14.3 example [Eqs. (14.53), (14.54), and the preceding and following equations].
- 14.19** Repeat the He SCF calculation of Section 14.3 using the same basis functions but starting with the initial guess $c_{11} = c_{21}$ and c_{21} determined by the normalization condition (14.48).
- 14.20** (a) Write a computer program that will perform the helium-atom SCF calculation of Section 14.3. Have the input to the program be ζ_1 , ζ_2 , and the initial guess for c_{11}/c_{21} . Do not use the Section 14.3 values of the integrals, but have the program calculate all integrals from ζ_1 and ζ_2 . Have the program print c_{11} , c_{21} , ϵ_1 , and ϵ_2 for each cycle of calculation. Use the convergence criterion that c_{11} and c_{21} each differ from the c_{11} and c_{21} values of the previous cycle by less than 10^{-5} atomic units. (b) Use your program with $\zeta_1 = 1.45$ and $\zeta_2 = 2.91$ to find the number of iterations needed to reach convergence for each of these initial guesses for c_{11}/c_{21} : 100, 10, 1, 0, -1 , -10 , -100 . (c) Run the program with $\zeta_1 = 1.45363$ and $\zeta_2 = 2.91093$ to verify the SCF energy given for these ζ 's at the end of the Section 14.3 example. (d) Run the program with ζ_1 changed by $+0.01$ and by -0.01 from the value in (c), and verify that each E_{HF} obtained is higher than that in (c). Repeat for ζ_2 .
- 14.21** Calculate ρ for the He SCF wave function of the Section 14.3 example at $r = 0$ and at $r = 1$ bohr.
- 14.22** Given that $\phi_i = \sum_s c'_{si} \chi'_s$, where the χ'_s functions are orthonormal, show that the orbitals ϕ_i form an orthonormal set if the matrix $\mathbf{C}'$ of coefficients c'_{si} is unitary.
- 14.23** Which of the following functions are homogeneous? Give the degree of homogeneity. (a) $x + 3yz$; (b) 179 ; (c) x^2/yz^3 ; (d) $(ax^3 + by^2)^{1/2}$.
- 14.24** Let 1 and 2 be two bound stationary states of an atom, with $E_2 > E_1$. For which state is the average electronic kinetic energy larger?
- 14.25** Show that the hypervirial theorem follows from Eq. (7.113).
- 14.26** (a) Calculate $\langle T \rangle$ and $\langle V \rangle$ for the helium-atom trial function (9.56). All the needed integrals were evaluated in Chapter 9. (b) Verify that the virial theorem is satisfied for $\zeta = Z - 5/16$ but not for $\zeta = Z$.
- 14.27** A one-dimensional harmonic oscillator in a stationary state has $\langle T \rangle = 5.0 \times 10^{-19}$ J. Find E and $\langle V \rangle$ for this state.
- 14.28** A certain excited stationary state of He has an energy of -59.10 eV [with the zero of energy chosen as in Eq. (11.1)]. Find $\langle T \rangle$ for this state. (Assume relativistic effects are negligible.)
- 14.29** A particle is subject to the potential energy $V = ax^4 + by^4 + cz^4$. If its ground-state energy is 10 eV, calculate $\langle T \rangle$ and $\langle V \rangle$ for the ground state.
- 14.30** The zero level of potential energy is arbitrary and we can always add a constant C to the potential energy function V . (See Prob. 4.52.) If we add C to V , state what happens to each of the following for a stationary state: $\langle V \rangle$, $\langle T \rangle$, E . Do these results contradict the virial theorem? Explain your answer.
- 14.31** Prove that for a bound stationary state: (a) $\langle p_x \rangle = 0$; (b) $\langle \partial V / \partial x \rangle = 0$. *Hint*: Use certain equations in Section 5.1.
- 14.32** The $U(R)$ curve for a diatomic-molecule repulsive electronic state can be roughly approximated by the function $ae^{-bR} - c$, where a , b , and c are positive constants with $a > c$. (This function omits the van der Waals minimum and fails to go to infinity at $R = 0$.) Sketch U , $\langle T_{\text{el}} \rangle$, and $\langle V \rangle$ as functions of R for this function.
- 14.33** Prove that $\partial \langle V \rangle / \partial R$ must be nonnegative at $R = R_e$; that is, $\langle V \rangle$ cannot be increasing with decreasing R as we go through the minimum in the $U(R)$ curve (Fig. 14.1). State and prove the corresponding theorem for $\langle T_{\text{el}} \rangle$.

- 14.34** Let ψ be the complete wave function for a molecule, with the Born–Oppenheimer approximation $\psi = \psi_{\text{el}}\psi_N$ not necessarily holding. Is it true that

$$2\langle\psi|\hat{T}_{\text{el}} + \hat{T}_N|\psi\rangle = -\langle\psi|\hat{V}|\psi\rangle$$

where $\hat{T}_{\text{el}}$ and $\hat{T}_N$ are the kinetic-energy operators for the electrons and nuclei and $\hat{V}$ is the complete potential-energy operator? Justify your answer.

- 14.35** Given that $D_e = 4.75$ eV and $R_e = 0.741$ Å for the ground electronic state of H_2 , find $U(R_e)$, $\langle V \rangle|_{R_e}$, $\langle V_{\text{el}} \rangle|_{R_e}$, and $\langle T_{\text{el}} \rangle|_{R_e}$ for this state.
- 14.36** The Fues potential-energy function for nuclear vibration of a diatomic molecule is $U(R) = U(\infty) + D_e(-2R_e/R + R_e^2/R^2)$. Find the expressions for $\langle T_{\text{el}} \rangle$ and $\langle V \rangle$ predicted by this potential and comment on the results.
- 14.37** (a) Apply the generalized Hellmann–Feynman theorem with Z as the parameter to find $\langle 1/r \rangle$ for the hydrogenlike-atom bound states ψ_{nlm} . (b) Since hydrogenlike functions ψ_{nlm} with the same n but different l or m have the same energy, we must be sure that the functions ψ_{nlm} are the correct zeroth-order functions for the perturbation of varying Z . Use a theorem of Section 9.6 to verify this.
- 14.38** Use the generalized Hellmann–Feynman theorem to find $\langle p_x^2 \rangle$ for the one-dimensional harmonic-oscillator stationary states. Check that the result obtained agrees with the virial theorem.
- 14.39** Differentiate (9.7) and (9.14) with respect to λ , substitute the results into the generalized Hellmann–Feynman theorem, and let $\lambda = 0$ to derive the perturbation-theory equation $E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$.
- 14.40** Use $F_{z,a} = -\partial U / \partial z_a$ and (14.85) to show that in Fig. 14.4, $F_{z,a} = -(\partial U / \partial R)[(z_a - z_b)/R]$. Find a similar equation for $F_{z,b}$ and verify that $F_{z,a} = -F_{z,b}$.
- 14.41** The R_e values for the ground electronic states of HF, HCl, HBr, and HI are 0.92, 1.27, 1.41, and 1.61 Å. The surface enclosing the antibinding region “behind” the proton in these molecules intersects the internuclear axis at two points, one of which is the proton location. Calculate the distance between these two points of intersection for each of the hydrogen halides.