CHAPTER

THREE

THE HARTREE-FOCK APPROXIMATION

The Hartree-Fock approximation, which is equivalent to the molecular orbital approximation, is central to chemistry. The simple picture, that chemists carry around in their heads, of electrons occupying orbitals is in reality an approximation, sometimes a very good one but, nevertheless, an approximation—the Hartree-Fock approximation. In this chapter we describe, in detail, Hartree-Fock theory and the principles of *ab initio* Hartree-Fock calculations. The length of this chapter testifies to the important role Hartree-Fock theory plays in quantum chemistry. The Hartree-Fock approximation is important not only for its own sake but as a starting point for more accurate approximations, which include the effects of electron correlation. A few of the computational methods of quantum chemistry bypass the Hartree-Fock approximation, but most do not, and all the methods described in the subsequent chapters of this book use the Hartree-Fock approximation as a starting point. Chapters 1 and 2 introduced the basic concepts and mathematical tools important for an indepth understanding of the structure of many-electron theory. We are now in a position to tackle and understand the formalism and computational procedures associated with the Hartree-Fock approximation, at other than a superficial level.

In addition to the basic formalisms of Hartree-Fock theory, this chapter includes a number of *ab initio* calculations. These calculations are not included as a review of available computational results, but as a means of illustrating fundamental ideas. The importance of these calculations to an understanding of the formalisms of this and later chapters cannot be overemphasized. To illustrate the Hartree-Fock approximation, we have performed calculations of each of the quantities discussed in the text (total energies, ionization potentials, equilibrium geometries, dipole moments, etc.), using a standard hierarchy of basis sets (STO-3G, 4-31G, 6-31G* and 6-31G**) and a standard collection of molecules (H_2, CO, N_2, CH_4, NH_3, H_2O, and FH). We thus illustrate the formalism and the accuracy or inaccuracy of the Hartree-Fock approximation with these calculations. In later chapters, we use the same molecules and the same basis sets to illustrate the formalisms of those chapters. In this way we can compare calculations from chapter to chapter to see how a perturbation calculation improves the Hartree-Fock dipole moment of CO, to see how a Green's function calculation improves the Hartree-Fock ionization potentials of N_2, etc. The calculations are intimately related to our discussion of the formal methods of quantum chemistry.

In addition to these larger calculations, we have used two smaller *ab initio* models to illustrate theory. The minimal basis model of H_2, which we introduced in the previous chapter, is applied ubiquitously throughout the book. To specifically illustrate the machinery of Hartree-Fock self-consistent-field (SCF) calculations, we use the minimal basis model of HeH^+. This model is perhaps our most important means of describing the SCF procedure. Appendix A contains a derivation of formulas for all the integrals required in this HeH^+ calculation, and Appendix B contains a short FORTRAN program for performing *ab initio* Hartree-Fock calculations on any two-electron diatomic molecule using the STO-3G basis set. Included is the detailed output for the calculation on HeH^+. The program is written so that it can be easily understood by anyone who has followed the text and has a minimal knowledge of FORTRAN. While it is simple, this program contains the essential ideas (but not the details) of large *ab initio* packages such as Gaussian 80.[1] Appendices A and B and Subsection 3.5.3 are intended to make explicit the basic manipulations of the SCF procedure and take some of the mystery out of such calculations.

In Section 3.1 we present the Hartree-Fock eigenvalue equations and define and discuss associated quantities such as the coulomb, exchange, and Fock operators. The results of this section are presented without derivation as summary of the main equations of Hartree-Fock theory.

Section 3.2 constitutes a derivation of the results of the previous section. The order of presentation of these two sections is such that the derivations of Section 3.2 can be skipped if necessary. For a fuller appreciation of Hartree-Fock theory, however, it is recommended that the derivations be followed. We first present the elements of functional variation and then use this technique to minimize the energy of a single Slater determinant. A unitary transformation of the spin orbitals then leads to the canonical Hartree-Fock equations.

Section 3.3 continues with formal aspects of Hartree-Fock theory. We derive and discuss two important theorems associated with the Hartree-Fock equations: Koopmans' theorem and Brillouin's theorem. The first theorem constitutes an interpretation of the Hartree-Fock orbital energies as ionization potentials and electron affinities. The second theorem states that the matrix element between a Hartree-Fock single determinant and determinants which differ by a single excitation is zero. This theorem is important in multideterminantal theories. Finally, in preparation for perturbation theory (Chapter 6), we define a Hartree-Fock Hamiltonian such that determinants formed from the Hartree-Fock spin orbitals become exact eigenfunctions of this Hamiltonian.

Section 3.4 is the most important section of this chapter. Here we derive the Roothaan equations, which allow one to calculate Hartree-Fock solutions for the ground state of closed-shell molecules. To solve the Hartree-Fock equations, it is necessary to give explicit form to the spin orbitals. This book uses two sets of spin orbitals. The restricted closed-shell set of spin orbitals leads to restricted closed-shell wave functions via the Roothaan equations. An unrestricted open-shell set of spin orbitals leads to unrestricted open-shell wave functions via the Pople-Nesbet equations as discussed in a later section. In this section, the general spin orbital formulation of the Hartree-Fock equations is first reduced to a spatially restricted closed-shell formulation, by replacing the general spin orbitals by a set of restricted closed-shell spin orbitals. A basis set is then introduced; this converts the spatial integro-differential closed-shell Hartree-Fock equations to a set of algebraic equations, the Roothaan equations. The rest of the section then constitutes a detailed discussion of the Roothaan equations, their method of solution (the self-consistent-field (SCF) procedure), and the interpretation of the resulting wave functions.

Section 3.5 contains a detailed illustration of the closed-shell *ab initio* SCF procedure using two simple systems: the minimal basis set descriptions of the homonuclear (H_2) and heteronuclear (HeH^+) two-electron molecules. We first describe the STO-3G minimal basis set used in calculations on these two molecules. We then describe the application of closed-shell Hartree-Fock theory to H_2. This is a very simple model system, which allows one to examine the results of calculations in explicit analytical form. Finally, we apply the Roothaan SCF procedure to HeH^+. Unlike H_2, the final SCF wave function for minimal basis HeH^+ is not symmetry determined and the HeH^+ example provides the simplest possible illustration of the iterative SCF procedure. The description of the *ab initio* HeH^+ calculation given in the text is based on a simple FORTRAN program and the output of a HeH^+ calculation found in Appendix B. By following the details of this simple but, nevertheless, real calculation, the formalism of closed-shell *ab initio* SCF calculations is made concrete.

Section 3.6 describes general aspects of the polyatomic basis sets used in many current calculations. The choice of a basis set for quantum chemical calculations is mainly an art rather than a science, but the principal unifying concepts involved in the choice of a basis set are described. In addition, the basis sets of Pople and co-workers, used in the calculations of this book, are explicitly defined.

In Section 3.7 we perform a number of *ab initio* calculations to illustrate the application and the results of the closed-shell SCF procedure. Our principal aim is to give the reader a feeling for a few of the problems to which *ab initio* SCF calculations can be applied, and the accuracy that can be expected of such Hartree-Fock calculations. To systematize these applications, we apply a standard hierarchy of basis sets to each problem.

In the final Section 3.8, we leave the restricted closed-shell formalism and derive and illustrate unrestricted open-shell calculations. We do not discuss restricted open-shell calculations. By procedures that are strictly analogous to those used in deriving the Roothaan equations of Section 3.4, we derive the corresponding unrestricted open-shell equations of Pople and Nesbet. To illustrate the formalism and the results of unrestricted calculations, we apply our standard basis sets to a description of the electronic structure and ESR spectra of the methyl radical, the ionization potential of N_2, and the orbital structure of the triplet ground state of O_2. Finally, we describe in some detail the application of unrestricted wave functions to the improper behavior of restricted closed-shell wave functions upon dissociation. We again use our minimal basis H_2 model to make the discussion concrete.

3.1 THE HARTREE-FOCK EQUATIONS

In this section we summarize the main results obtained in a derivation of the Hartree-Fock equations. We do this so that the somewhat involved details of the derivation given in the next section (Section 3.2) can be skipped, if desired.

For our purposes, we can equate Hartree-Fock theory to single determinant theory,[2] and we are thus interested in finding a set of spin orbitals $\{\chi_a\}$ such that the single determinant formed from these spin orbitals

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle \tag{3.1}$$

is the best possible approximation to the ground state of the N-electron system described by an electronic Hamiltonian $\mathscr{H}$. According to the variational principle, the "best" spin orbitals are those which minimize the electronic energy

$$\begin{aligned} E_0 = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle &= \sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_{ab}\langle ab||ab\rangle \\ &= \sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_{ab}[aa|bb] - [ab|ba] \end{aligned} \tag{3.2}$$

By a procedure outlined in Section 3.2, we can systematically vary the spin orbitals $\{\chi_a\}$, constraining them only to the extend that they remain orthonormal,

$$\langle \chi_a | \chi_b \rangle = \delta_{ab} \tag{3.3}$$

until the energy E_0 is a minimum. In doing so (in a formal way) one obtains an equation that defines the best spin orbitals, the ones that minimize E_0. This equation for the best (Hartree-Fock) spin orbitals is the Hartree-Fock integro-differential equation

$$h(1)\chi_a(1) + \sum_{b \neq a} \left[\int d\mathbf{x}_2 \, |\chi_b(2)|^2 r_{12}^{-1} \right] \chi_a(1) - \sum_{b \neq a} \left[\int d\mathbf{x}_2 \, \chi_b^*(2) \chi_a(2) r_{12}^{-1} \right] \chi_b(1)$$
$$= \varepsilon_a \chi_a(1) \tag{3.4}$$

where

$$h(1) = -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \tag{3.5}$$

is the kinetic energy and potential energy for attraction to the nuclei, of a single electron chosen to be electron-one. The orbital energy of the spin orbital χ_a is ε_a.

3.1.1 The Coulomb and Exchange Operators

The two terms in Eq. (3.4) involving sums over b are those that in single determinant Hartree-Fock theory represent electron-electron interactions. Without these terms,

$$h(1)\chi_a(1) = \varepsilon_a \chi_a(1) \tag{3.6}$$

would simply be a one-electron Schrödinger equation for the spin orbital states of a single electron in the field of the nuclei. The first of the two-electron terms is the *coulomb* term, which is also present in Hartree theory—a theory which uses a Hartree product wave function rather than an antisymmetrized Hartree product (Slater determinant) wave function. The second two-electron term is the *exchange* term, which arises because of the antisymmetric nature of the determinantal wave function.

The coulomb term has a simple interpretation. In an exact theory, the coulomb interaction is represented by the two-electron operator r_{ij}^{-1}. In the Hartree or Hartree-Fock approximation, as Eq. (3.4) shows, electron-one in χ_a experiences a one-electron coulomb potential

$$v_a^{\text{coul}}(1) = \sum_{b \neq a} \int d\mathbf{x}_2 |\chi_b(2)|^2 r_{12}^{-1} \tag{3.7}$$

Let us consider this potential. Suppose electron 2 occupies χ_b. The *two-electron potential* r_{12}^{-1} felt by electron 1 and associated with the instantaneous position of electron 2 is thus replaced by a *one-electron potential*, obtained by averaging the interaction r_{12}^{-1} of electron 1 and electron 2, over all space and spin coordinates $\mathbf{x}_2$ of electron 2, weighted by the probability $d\mathbf{x}_2\,|\chi_b(2)|^2$ that electron 2 occupies the volume element $d\mathbf{x}_2$ at $\mathbf{x}_2$. By summing over all $b \neq a$, one obtains the total averaged potential acting on the electron in χ_a, arising from the $N-1$ electrons in the other spin orbitals. Associated with this interpretation it is convenient to define a *coulomb operator*

$$\mathscr{J}_b(1) = \int d\mathbf{x}_2\,|\chi_b(2)|^2 r_{12}^{-1} \tag{3.8}$$

which represents the average local potential at $\mathbf{x}_1$ arising from an electron in χ_b.

The exchange term in (3.4), arising from the antisymmetric nature of the single determinant, has a somewhat strange form and does not have a simple classical interpretation like the coulomb term. We can, however, write the Hartree-Fock equation (3.4) as an eigenvalue equation

$$\left[h(1) + \sum_{b \neq a} \mathscr{J}_b(1) - \sum_{b \neq a} \mathscr{K}_b(1)\right]\chi_a(1) = \varepsilon_a \chi_a(1) \tag{3.9}$$

provided we introduce an *exchange operator* $\mathscr{K}_b(1)$, defined by its effect when operating on a spin orbital $\chi_a(1)$,

$$\mathscr{K}_b(1)\chi_a(1) = \left[\int d\mathbf{x}_2\,\chi_b^*(2) r_{12}^{-1} \chi_a(2)\right]\chi_b(1) \tag{3.10}$$

This is to be compared with the previous result (3.8) for the coulomb operator,

$$\mathscr{J}_b(1)\chi_a(1) = \left[\int d\mathbf{x}_2\,\chi_b^*(2) r_{12}^{-1} \chi_b(2)\right]\chi_a(1) \tag{3.11}$$

Operating with $\mathscr{K}_b(1)$ on $\chi_a(1)$ involves an "exchange" of electron 1 and electron 2 to the right of r_{12}^{-1} in (3.10), relative to (3.11). Unlike the *local* coulomb operator, the exchange operator is said to be a *nonlocal* operator, since there does not exist a simple potential $\mathscr{K}_b(\mathbf{x}_1)$ uniquely defined at a local point in space $\mathbf{x}_1$. The result of operating with $\mathscr{K}_b(\mathbf{x}_1)$ on $\chi_a(\mathbf{x}_1)$ depends on the value of χ_a throughout all space, not just at $\mathbf{x}_1$, as is evident from (3.10). One could not, for example, draw contour plots of the exchange potential as one can for the coulomb potential. For an electron in χ_a the expectation values of the coulomb and exchange potentials $\mathscr{J}_b$ and $\mathscr{K}_b$ are just the coulomb and exchange integrals described in the last chapter, i.e.,

$$\langle \chi_a(1)|\mathscr{J}_b(1)|\chi_a(1)\rangle = \int d\mathbf{x}_1\,d\mathbf{x}_2\,\chi_a^*(1)\chi_a(1) r_{12}^{-1} \chi_b^*(2)\chi_b(2) = [aa|bb] \tag{3.12}$$

$$\langle \chi_a(1)|\mathscr{K}_b(1)|\chi_a(1)\rangle = \int d\mathbf{x}_1\,d\mathbf{x}_2\,\chi_a^*(1)\chi_b(1) r_{12}^{-1} \chi_b^*(2)\chi_a(2) = [ab|ba] \tag{3.13}$$

3.1.2 The Fock Operator

The Hartree-Fock equation, as we have written it up to this point, is

$$\left[h(1) + \sum_{b \neq a} \mathscr{J}_b(1) - \sum_{b \neq a} \mathscr{K}_b(1)\right]\chi_a(1) = \varepsilon_a \chi_a(1) \tag{3.14}$$

This is of the eigenvalue form. However, the operator in square brackets appears to be different for every spin orbital χ_a on which it operates (because of the restricted summation over $b \neq a$). Inspecting Eqs. (3.10) and (3.11), it is obvious, however, that

$$[\mathscr{J}_a(1) - \mathscr{K}_a(1)]\chi_a(1) = 0 \tag{3.15}$$

It is thus possible to add this term to (3.14), eliminate the restriction on the summation, and define a *Fock operator* f by

$$f(1) = h(1) + \sum_b \mathscr{J}_b(1) - \mathscr{K}_b(1) \tag{3.16}$$

so that the Hartree-Fock equations become

$$f|\chi_a\rangle = \varepsilon_a|\chi_a\rangle \tag{3.17}$$

This is the usual form of the Hartree-Fock equations. The Fock operator $f(1)$ is the sum of a *core-Hamiltonian operator* $h(1)$ and an effective one-electron potential operator called the *Hartree-Fock potential* $v^{\text{HF}}(1)$,

$$v^{\text{HF}}(1) = \sum_b \mathscr{J}_b(1) - \mathscr{K}_b(1) \tag{3.18}$$

That is,

$$f(1) = h(1) + v^{\text{HF}}(1) \tag{3.19}$$

Sometimes it is convenient to write the exchange potential in terms of an operator $\mathscr{P}_{12}$, which, operating to the right, interchanges electron 1 and electron 2. Thus

$$\begin{aligned}\mathscr{K}_b(1)\chi_a(1) &= \left[\int d\mathbf{x}_2\, \chi_b^*(2) r_{12}^{-1} \chi_a(2)\right]\chi_b(1) \\ &= \left[\int d\mathbf{x}_2\, \chi_b^*(2) r_{12}^{-1} \mathscr{P}_{12} \chi_b(2)\right]\chi_a(1)\end{aligned} \tag{3.20}$$

The Fock operator is thus written, using $\mathscr{P}_{12}$, as

$$\begin{aligned}f(1) &= h(1) + v^{\text{HF}}(1) \\ &= h(1) + \sum_b \int d\mathbf{x}_2\, \chi_b^*(2) r_{12}^{-1}(1 - \mathscr{P}_{12})\chi_b(2)\end{aligned} \tag{3.21}$$

The Hartree-Fock equation

$$f|\chi_a\rangle = \varepsilon_a|\chi_a\rangle \tag{3.22}$$

is an eigenvalue equation with the spin orbitals as eigenfunctions and the energy of the spin orbitals as eigenvalues. The exact solutions to this integro-differential equation correspond to the "exact" Hartree-Fock spin orbitals. In practice it is only possible to solve this equation exactly (i.e., as an integro-differential equation) for atoms. One normally, instead, introduces a set of basis functions for expansion of the spin orbitals and solves a set of matrix equations, as will be described subsequently. Only as the basis set approaches completeness, i.e., as one approaches the Hartree-Fock limit, will the spin orbitals that one obtains approach the exact Hartree-Fock spin orbitals.

While (3.22) is written as a linear eigenvalue equation, it might best be described as a pseudo-eigenvalue equation since the Fock operator has a functional dependence, through the coulomb and exchange operators, on the solutions $\{\chi_a\}$ of the pseudo-eigenvalue equation. Thus the Hartree-Fock equations are really nonlinear equations and will need to be solved by iterative procedures.

Exercise 3.1 Show that the general matrix element of the Fock operator has the form

$$\langle\chi_i|f|\chi_j\rangle = \langle i|h|j\rangle + \sum_b [ij|bb] - [ib|bj] = \langle i|h|j\rangle + \sum_b \langle ib||jb\rangle \tag{3.23}$$

3.2 DERIVATION OF THE HARTREE-FOCK EQUATIONS

In this section we derive the Hartree-Fock equations in their general spin orbital form, i.e., we obtain the eigenvalue equation (3.17) by minimizing the energy expression for a single Slater determinant. The derivation makes no assumptions about the spin orbitals. Later, we will specialize to restricted and unrestricted spin orbitals and introduce a basis set, in order to generate algebraic equations (matrix equations) that can be conveniently solved on a computer. In the meantime, we are concerned only with the derivation of the general integro-differential equations (the Hartree-Fock eigenvalue equations), the nature of these equations, and the nature of their formal solution. To derive the equations we will use the general and useful technique of functional variation.

3.2.1 Functional Variation

Given any trial function $\tilde{\Phi}$, the expectation value $E[\tilde{\Phi}]$ of the Hamiltonian operator $\mathscr{H}$ is a number given by

$$E[\tilde{\Phi}] = \langle\tilde{\Phi}|\mathscr{H}|\tilde{\Phi}\rangle \tag{3.24}$$

We say that $E[\tilde{\Phi}]$ is a functional of $\tilde{\Phi}$ since its value depends on the form of a function, i.e., the function $\tilde{\Phi}$, rather than any single independent variable. Suppose we vary $\tilde{\Phi}$ by an arbitrarily small amount, by changing the parameters upon which $\tilde{\Phi}$ depends, for example. That is,

$$\tilde{\Phi} \rightarrow \tilde{\Phi} + \delta\tilde{\Phi} \tag{3.25}$$

The energy then becomes

$$\begin{aligned} E[\tilde{\Phi} + \delta\tilde{\Phi}] &= \langle \tilde{\Phi} + \delta\tilde{\Phi} | \mathscr{H} | \tilde{\Phi} + \delta\tilde{\Phi} \rangle \\ &= E[\tilde{\Phi}] + \{ \langle \delta\tilde{\Phi} | \mathscr{H} | \tilde{\Phi} \rangle + \langle \tilde{\Phi} | \mathscr{H} | \delta\tilde{\Phi} \rangle \} + \cdots \\ &= E[\tilde{\Phi}] + \delta E + \cdots \end{aligned} \tag{3.26}$$

where δE, which is called the first variation in E, includes all terms that are linear, i.e., first-order, in the variation $\delta\tilde{\Phi}$. Notice that we can treat "δ" just like a differential operator, i.e., $\delta\langle \tilde{\Phi} | \mathscr{H} | \tilde{\Phi} \rangle = \langle \delta\tilde{\Phi} | \mathscr{H} | \tilde{\Phi} \rangle + \langle \tilde{\Phi} | \mathscr{H} | \delta\tilde{\Phi} \rangle$. In the variation method, we are looking for that $\tilde{\Phi}$ for which $E[\tilde{\Phi}]$ is a minimum. In other words, we wish to find that $\tilde{\Phi}$ for which the first variation in $E[\tilde{\Phi}]$ is zero, i.e.,

$$\delta E = 0 \tag{3.27}$$

This condition only ensures that E is *stationary* with respect to any variation in $\tilde{\Phi}$. Normally, however, the stationary point will also be a minimum.

We will illustrate the variational technique by rederiving the matrix eigenvalue equation of the linear variational problem given in Subsection 1.3.2. Given a linear variational trial wave function,

$$|\tilde{\Phi}\rangle = \sum_{i=1}^{N} c_i |\Psi_i\rangle \tag{3.28}$$

we want to minimize the energy

$$E = \langle \tilde{\Phi} | \mathscr{H} | \tilde{\Phi} \rangle = \sum_{ij} c_i^* c_j \langle \Psi_i | \mathscr{H} | \Psi_j \rangle \tag{3.29}$$

subject to the constraint that the trial wave function remains normalized, i.e.,

$$\langle \tilde{\Phi} | \tilde{\Phi} \rangle - 1 = \sum_{ij} c_i^* c_j \langle \Psi_i | \Psi_j \rangle - 1 = 0 \tag{3.30}$$

Using Lagrange's method of undetermined multipliers described in Chapter 1, we therefore minimize, with respect to the coefficients c_i, the following functional

$$\begin{aligned} \mathscr{L} &= \langle \tilde{\Phi} | \mathscr{H} | \tilde{\Phi} \rangle - E(\langle \tilde{\Phi} | \tilde{\Phi} \rangle - 1) \\ &= \sum_{ij} c_i^* c_j \langle \Psi_i | \mathscr{H} | \Psi_j \rangle - E\left(\sum_{ij} c_i^* c_j \langle \Psi_i | \Psi_j \rangle - 1 \right) \end{aligned} \tag{3.31}$$

where E is the Lagrange multiplier. Therefore, we set the first variation in $\mathscr{L}$ equal to zero.

$$\begin{aligned}\delta\mathscr{L} &= \sum_{ij} \delta c_i^* c_j \langle \Psi_i | \mathscr{H} | \Psi_j \rangle - E \sum_{ij} \delta c_i^* c_j \langle \Psi_i | \Psi_j \rangle \\ &\quad + \sum_{ij} c_i^* \delta c_j \langle \Psi_i | \mathscr{H} | \Psi_j \rangle - E \sum_{ij} c_i^* \delta c_j \langle \Psi_i | \Psi_j \rangle = 0 \qquad (3.32)\end{aligned}$$

Since E is real ($\mathscr{L}$ is real), after collecting terms and interchanging indices, we get

$$\sum_i \delta c_i^* \left[\sum_j H_{ij} c_j - E S_{ij} c_j \right] + \text{complex conjugate} = 0 \qquad (3.33)$$

where $H_{ij} = \langle \Psi_i | \mathscr{H} | \Psi_j \rangle$. The linear expansion functions $|\Psi_i\rangle$ are not assumed to be orthonormal, but are assumed to overlap according to

$$\langle \Psi_i | \Psi_j \rangle = S_{ij} \qquad (3.34)$$

Since δc_i^* is arbitrary (c_i^* and c_i are both independent variables), the quantity in square brackets in (3.33) must be zero, or

$$\sum_j H_{ij} c_j = E \sum_j S_{ij} c_j$$

$$\mathbf{Hc} = E\mathbf{Sc} \qquad (3.35)$$

Essentially the same result (with $\mathbf{S} = \mathbf{1}$ and real coefficients) was previously obtained in Subsection 1.3.2. The functional variation technique thus leads to the same result as is obtained by differentiating with respect to the coefficients. Functional variation is a more general technique, however, and we now proceed to derive the Hartree-Fock equations using it.

3.2.2 Minimization of the Energy of a Single Determinant

Given the single determinant $|\Psi_0\rangle = |\chi_1 \chi_2 \cdots \chi_a \chi_b \cdots \chi_N\rangle$, the energy $E_0 = \langle \Psi_0 | \mathscr{H} | \Psi_0 \rangle$ is a functional of the spin orbitals $\{\chi_a\}$. To derive the Hartree-Fock equations we need to minimize $E_0[\{\chi_a\}]$ with respect to the spin orbitals, subject to the constraint that the spin orbitals remain orthonormal,

$$\int d\mathbf{x}_1 \, \chi_a^*(1) \chi_b(1) = [a|b] = \delta_{ab} \qquad (3.36)$$

That is, the constraints are of the form

$$[a|b] - \delta_{ab} = 0 \qquad (3.37)$$

We therefore consider the functional $\mathscr{L}[\{\chi_a\}]$ of the spin orbitals

$$\mathscr{L}[\{\chi_a\}] = E_0[\{\chi_a\}] - \sum_{a=1}^{N} \sum_{b=1}^{N} \varepsilon_{ba}([a|b] - \delta_{ab}) \qquad (3.38)$$

where E_0 is the expectation value of the single determinant $|\Psi_0\rangle$,

$$E_0[\{\chi_a\}] = \sum_{a=1}^{N} [a|h|a] + \frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N} [aa|bb] - [ab|ba] \tag{3.39}$$

and the ε_{ba} constitute a set of Lagrange multipliers. Because $\mathscr{L}$ is real and $[a|b] = [b|a]^*$, the Lagrange multipliers must be elements of a Hermitian matrix

$$\varepsilon_{ba} = \varepsilon_{ab}^* \tag{3.40}$$

Exercise 3.2 Prove Eq. (3.40).

Minimization of E_0, subject to the constraints, is thus obtained by minimizing $\mathscr{L}$. We therefore vary the spin orbitals an arbitrary infinitesimal amount, i.e.,

$$\chi_a \rightarrow \chi_a + \delta\chi_a \tag{3.41}$$

and set the first variation in $\mathscr{L}$ equal to zero,

$$\delta\mathscr{L} = \delta E_0 - \sum_{a=1}^{N}\sum_{b=1}^{N} \varepsilon_{ba}\delta[a|b] = 0 \tag{3.42}$$

This follows directly from Eq. (3.38) since the variation in a constant (δ_{ab}) is zero. Now

$$\delta[a|b] = [\delta\chi_a|\chi_b] + [\chi_a|\delta\chi_b] \tag{3.43}$$

and

$$\begin{aligned}\delta E_0 = {} & \sum_{a=1}^{N} [\delta\chi_a|h|\chi_a] + [\chi_a|h|\delta\chi_a] \\ & + \frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N} [\delta\chi_a\chi_a|\chi_b\chi_b] + [\chi_a\delta\chi_a|\chi_b\chi_b] + [\chi_a\chi_a|\delta\chi_b\chi_b] + [\chi_a\chi_a|\chi_b\delta\chi_b] \\ & - \frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N} [\delta\chi_a\chi_b|\chi_b\chi_a] + [\chi_a\delta\chi_b|\chi_b\chi_a] + [\chi_a\chi_b|\delta\chi_b\chi_a] + [\chi_a\chi_b|\chi_b\delta\chi_a]\end{aligned} \tag{3.44}$$

Exercise 3.3 Manipulate Eq. (3.44) to show that

$$\delta E_0 = \sum_{a=1}^{N} [\delta\chi_a|h|\chi_a] + \sum_{a=1}^{N}\sum_{b=1}^{N} [\delta\chi_a\chi_a|\chi_b\chi_b] - [\delta\chi_a\chi_b|\chi_b\chi_a]$$

$$+ \text{ complex conjugate}$$

Also

$$\begin{aligned}\sum_{ab}\varepsilon_{ba}([\delta\chi_a|\chi_b]+[\chi_a|\delta\chi_b]) &= \sum_{ab}\varepsilon_{ba}[\delta\chi_a|\chi_b]+\sum_{ab}\varepsilon_{ab}[\chi_b|\delta\chi_a]\\ &= \sum_{ab}\varepsilon_{ba}[\delta\chi_a|\chi_b]+\sum_{ab}\varepsilon_{ba}^*[\delta\chi_a|\chi_b]^*\\ &= \sum_{ab}\varepsilon_{ba}[\delta\chi_a|\chi_b]+\text{complex conjugate} \qquad (3.45)\end{aligned}$$

As a result of the above exercise and Eq. (3.45), the first variation in $\mathscr{L}$ of Eq. (3.42) becomes

$$\begin{aligned}\delta\mathscr{L} &= \sum_{a=1}^{N}[\delta\chi_a|h|\chi_a]+\sum_{a=1}^{N}\sum_{b=1}^{N}[\delta\chi_a\chi_a|\chi_b\chi_b]-[\delta\chi_a\chi_b|\chi_b\chi_a]\\ &\quad -\sum_{a=1}^{N}\sum_{b=1}^{N}\varepsilon_{ba}[\delta\chi_a|\chi_b]+\text{complex conjugate}\\ &= 0 \qquad (3.46)\end{aligned}$$

We can use definitions (3.10) and (3.11) for the coulomb and exchange operators to write this result in the form

$$\begin{aligned}\delta\mathscr{L} = \sum_{a=1}^{N}\int d\mathbf{x}_1\,\delta\chi_a^*(1)\left[h(1)\chi_a(1)+\sum_{b=1}^{N}(\mathscr{J}_b(1)-\mathscr{K}_b(1))\chi_a(1)-\sum_{b=1}^{N}\varepsilon_{ba}\chi_b(1)\right]\\ +\text{complex conjugate}=0 \qquad (3.47)\end{aligned}$$

Since $\delta\chi_a^*(1)$ is arbitrary, it must be that the quantity in square brackets is zero for all a. Therefore,

$$\left[h(1)+\sum_{b=1}^{N}\mathscr{J}_b(1)-\mathscr{K}_b(1)\right]\chi_a(1)=\sum_{b=1}^{N}\varepsilon_{ba}\chi_b(1) \qquad a=1,2,\ldots,N \qquad (3.48)$$

The quantity in square brackets above is just our definition of the Fock operator $f(1)$; therefore, the equation for the spin orbitals takes the form

$$f|\chi_a\rangle=\sum_{b=1}^{N}\varepsilon_{ba}|\chi_b\rangle \qquad (3.49)$$

This result is perhaps surprising at first glance since it is not in the canonical (standard) eigenvalue form of Eq. (3.17). The reason is that any single determinant wave function $|\Psi_0\rangle$ formed from a set of spin orbitals $\{\chi_a\}$ retains a certain degree of flexibility in the spin orbitals; the spin orbitals can be mixed among themselves without changing the expectation value $E_0 = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle$. Before obtaining the canonical form of the Hartree-Fock equations, we need to consider unitary transformations of the spin orbitals among themselves.

3.2.3 The Canonical Hartree-Fock Equations

Let us consider a new set of spin orbitals $\{\chi'_a\}$ that are obtained from an old set $\{\chi_a\}$ (those of Eq. (3.49)) by a unitary transformation,

$$\chi'_a = \sum_b \chi_b U_{ba} \tag{3.50}$$

A unitary transformation, which satisfies the relation

$$\mathbf{U}^\dagger = \mathbf{U}^{-1} \tag{3.51}$$

is one which preserves the orthonormality property. That is, if we start with a set $\{\chi_a\}$ of orthonormal spin orbitals, the new set $\{\chi'_a\}$ will also be orthonormal. Let us define a square matrix $\mathbf{A}$

$$\mathbf{A} = \begin{pmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_a(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_a(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & & \vdots & & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_a(N) & \cdots & \chi_N(N) \end{pmatrix} \tag{3.52}$$

such that the wave function $|\Psi_0\rangle$ is just the normalized determinant of this matrix

$$|\Psi_0\rangle = (N!)^{-1/2} \det(\mathbf{A}) \tag{3.53}$$

Using definition (3.50) for the transformed orbitals and the rules for ordinary multiplication, it becomes clear that the matrix $\mathbf{A}'$ which corresponds to $\mathbf{A}$ but contains the transformed spin orbitals is

$$\mathbf{A}' = \mathbf{AU} = \begin{pmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{pmatrix} \begin{pmatrix} U_{11} & U_{12} & \cdots & U_{1N} \\ U_{21} & U_{22} & \cdots & U_{2N} \\ \vdots & \vdots & & \vdots \\ U_{N1} & U_{N2} & \cdots & U_{NN} \end{pmatrix}$$
$$= \begin{pmatrix} \chi'_1(1) & \chi'_2(1) & \cdots & \chi'_N(1) \\ \chi'_1(2) & \chi'_2(2) & \cdots & \chi'_N(2) \\ \vdots & \vdots & & \vdots \\ \chi'_1(N) & \chi'_2(N) & \cdots & \chi'_N(N) \end{pmatrix} \tag{3.54}$$

Therefore, since

$$\det(\mathbf{AB}) = \det(\mathbf{A})\det(\mathbf{B}) \tag{3.55}$$

the determinant of transformed spin orbitals is related to the determinant of the original spin orbitals by

$$\det(\mathbf{A}') = \det(\mathbf{U})\det(\mathbf{A}) \tag{3.56}$$

or, equivalently

$$|\Psi'_0\rangle = \det(\mathbf{U})|\Psi_0\rangle \tag{3.57}$$

Now, since

$$\mathbf{U}^{\dagger}\mathbf{U} = \mathbf{1} \tag{3.58}$$

we have

$$\det(\mathbf{U}^{\dagger}\mathbf{U}) = \det(\mathbf{U}^{\dagger})\det(\mathbf{U}) = (\det(\mathbf{U}))^{*}\det(\mathbf{U}) = |\det(\mathbf{U})|^2 = \det(\mathbf{1}) = 1 \tag{3.59}$$

Therefore,

$$\det(\mathbf{U}) = e^{i\phi} \tag{3.60}$$

and the transformed single determinant $|\Psi'_0\rangle$ of Eq. (3.57) can at most differ from the original determinant $|\Psi_0\rangle$ by a phase factor. If $\mathbf{U}$ is a real matrix then this phase factor is just ± 1. Because any observable property depends on $|\Psi|^2$, for all intents and purposes, the original wave function in terms of the spin orbitals $\{\chi_a\}$ and the transformed wave function in terms of the spin orbitals $\{\chi'_a\}$ are identical. For a single determinant wave function, any expectation value is therefore invariant to an arbitrary unitary transformation of the spin orbitals. Thus the spin orbitals that make the total energy stationary are not unique, and no particular physical significance can be given to a particular set of spin orbitals. Localized spin orbitals, for example, are not more "physical" than delocalized spin orbitals.

We can use the invariance of a single determinant to a unitary transformation of the spin orbitals to simplify Eq. (3.49) and put it in the form of an eigenvalue equation for a particular set of spin orbitals. First, however, we need to determine the effect of the above unitary transformation on the Fock operator f and the Lagrange multipliers ε_{ab}. The only parts of the Fock operator that depend on the spin orbitals are the coulomb and exchange terms. The transformed sum of the coulomb operators is

$$\begin{aligned}\sum_a \mathscr{J}'_a(1) &= \sum_a \int d\mathbf{x}_2\, \chi'^{*}_a(2) r_{12}^{-1} \chi'_a(2) \\ &= \sum_{bc}\left[\sum_a U^{*}_{ba} U_{ca}\right] \int d\mathbf{x}_2\, \chi^{*}_b(2) r_{12}^{-1} \chi_c(2)\end{aligned} \tag{3.61}$$

But

$$\sum_a U^{*}_{ba} U_{ca} = (\mathbf{U}\mathbf{U}^{\dagger})_{cb} = \delta_{cb} \tag{3.62}$$

so that

$$\sum_a \mathscr{J}'_a(1) = \sum_b \int d\mathbf{x}_2\, \chi^{*}_b(2) r_{12}^{-1} \chi_b(2) = \sum_b \mathscr{J}_b(1) \tag{3.63}$$

Thus the sum of coulomb operators is invariant to a unitary transformation of the spin orbitals. In an identical manner it is easy to show that the sum of exchange operators, and hence the Fock operator itself, is invariant to an arbitrary unitary transformation of the spin orbitals, i.e.,

$$f'(1) = f(1) \tag{3.64}$$

We now need to determine the effect of the unitary transformation on the Lagrange multipliers ε_{ba}. Multiplying Equation (3.49) by $\langle\chi_c|$ shows that the Lagrange multipliers are matrix elements of the Fock operator

$$\langle\chi_c|f|\chi_a\rangle = \sum_{b=1}^{N} \varepsilon_{ba}\langle\chi_c|\chi_b\rangle = \varepsilon_{ca} \tag{3.65}$$

Therefore,

$$\begin{aligned}
\varepsilon'_{ab} &= \int d\mathbf{x}_1\, \chi'^*_a(1) f(1) \chi'_b(1) \\
&= \sum_{cd} U^*_{ca} U_{db} \int d\mathbf{x}_1 \chi^*_c(1) f(1) \chi_d(1) \\
&= \sum_{cd} U^*_{ca} \varepsilon_{cd} U_{db}
\end{aligned} \tag{3.66}$$

or in matrix form

$$\boldsymbol{\varepsilon}' = \mathbf{U}^\dagger \boldsymbol{\varepsilon} \mathbf{U} \tag{3.67}$$

From (3.40), $\boldsymbol{\varepsilon}$ is a Hermitian matrix. It is always possible, therefore, to find a unitary matrix $\mathbf{U}$ such that the transformation (3.67) diagonalizes $\boldsymbol{\varepsilon}$. We are not concerned with how to obtain such a matrix, only that such a matrix exists and is unique. There must exist, then, a set of spin orbitals $\{\chi'_a\}$ for which the matrix of Lagrange multipliers is diagonal.

$$f|\chi'_a\rangle = \varepsilon'_a|\chi'_a\rangle \tag{3.68}$$

The unique set of spin orbitals $\{\chi'_a\}$ obtained from a solution of this eigenvalue equation is called the set of *canonical spin orbitals*. We henceforth drop the primes and write the Hartree-Fock equations as

$$f|\chi_a\rangle = \varepsilon_a|\chi_a\rangle \tag{3.69}$$

The canonical spin orbitals, which are a solution to this equation, will generally be delocalized and form a basis for an irreducible representation of the point group of the molecule, i.e., they will have certain symmetry properties characteristic of the symmetry of the molecule or, equivalently, of the Fock operator. Once the canonical spin orbitals have been obtained it would be possible to obtain an infinite number of equivalent sets by a unitary transformation of the canonical set. In particular, there are various criteria (see Further Reading) for choosing a unitary transformation so that the transformed set of spin orbitals is in some sense localized, more in line with our intuitive feeling for chemical bonds.

3.3 INTERPRETATION OF SOLUTIONS TO THE HARTREE-FOCK EQUATIONS

In order to solve the Hartree-Fock equations it is necessary to introduce a basis set and solve a set of matrix equations. Before doing so, however, there are certain aspects of the eigenvalue equation and its solutions that are independent of any basis, and it is appropriate to discuss them at this point.

3.3.1 Orbital Energies and Koopmans' Theorem

For an N-electron system, minimization of the energy of the determinant $|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$ leads to an eigenvalue equation $f|\chi_a\rangle = \varepsilon_a|\chi_a\rangle$ for the N occupied spin orbitals $\{\chi_a\}$. The Fock operator has a functional dependence on these occupied spin orbitals, but once the occupied spin orbitals are known the Fock operator becomes a well-defined Hermitian operator, which will have an infinite number of eigenfunctions, i.e.,

$$f|\chi_j\rangle = \varepsilon_j|\chi_j\rangle \qquad j = 1, 2, \ldots, \infty \tag{3.70}$$

Exercise 3.4 Use the result of Exercise 3.1 to show that the Fock operator is a Hermitian operator, by showing that $f_{ij} = \langle\chi_i|f|\chi_j\rangle$ is an element of a Hermitian matrix.

Each of the solutions $|\chi_j\rangle$ of (3.70) has a spin orbital energy ε_j. The N spin orbitals with the lowest orbital energies are just the spin orbitals occupied in $|\Psi_0\rangle$ for which we use the indices $a, b, \ldots$. The remaining infinite number of spin orbitals with higher energies are the *virtual* or unoccupied spin orbitals, which we label with the indices $r, s, \ldots$. Our main interest here is to obtain expressions for the orbital energies ε_a and ε_r and to investigate what physical significance we can attach to these orbital energies.

Multiplying (3.70) by $\langle\chi_i|$, shows that the matrix representation of the Fock operator in the basis of spin orbital eigenfunctions is diagonal with diagonal elements equal to the orbital energies.

$$\langle\chi_i|f|\chi_j\rangle = \varepsilon_j\langle\chi_i|\chi_j\rangle = \varepsilon_j\delta_{ij} \tag{3.71}$$

Using expression (3.16) for the Fock operator, the orbital energies can be expressed as

$$\begin{aligned}
\varepsilon_i = \langle\chi_i|f|\chi_i\rangle &= \langle\chi_i|h + \sum_b (\mathscr{J}_b - \mathscr{K}_b)|\chi_i\rangle \\
&= \langle\chi_i|h|\chi_i\rangle + \sum_b \langle\chi_i|\mathscr{J}_b|\chi_i\rangle - \langle\chi_i|\mathscr{K}_b|\chi_i\rangle \\
&= \langle i|h|i\rangle + \sum_b \langle ib|ib\rangle - \langle ib|bi\rangle \\
&= \langle i|h|i\rangle + \sum_b \langle ib||ib\rangle
\end{aligned} \tag{3.72}$$

where, from definitions (3.10) and (3.11) of the exchange and coulomb operators, we have used

$$\langle \chi_i | \mathscr{J}_k | \chi_j \rangle = \langle ik | jk \rangle = [ij | kk] \tag{3.73}$$

$$\langle \chi_i | \mathscr{K}_k | \chi_j \rangle = \langle ik | kj \rangle = [ik | kj] \tag{3.74}$$

In particular then

$$\varepsilon_a = \langle a | h | a \rangle + \sum_{b=1}^{N} \langle ab || ab \rangle \tag{3.75}$$

$$\varepsilon_r = \langle r | h | r \rangle + \sum_{b=1}^{N} \langle rb || rb \rangle \tag{3.76}$$

Now, since,

$$\langle aa || aa \rangle = 0 \tag{3.77}$$

we can rewrite these results as

$$\varepsilon_a = \langle a | h | a \rangle + \sum_{b \neq a} \langle ab | ab \rangle - \langle ab | ba \rangle \tag{3.78}$$

$$\varepsilon_r = \langle r | h | r \rangle + \sum_{b} \langle rb | rb \rangle - \langle rb | br \rangle \tag{3.79}$$

Let us examine these last two expressions. The orbital energy ε_a represents the energy of an electron in the spin orbital $|\chi_a\rangle$. From (3.78) this energy is the kinetic energy and attraction to the nuclei ($\langle a|h|a\rangle$) plus a coulomb ($\langle ab|ab\rangle$) and exchange ($-\langle ab|ba\rangle$) interaction with each of the remaining $N-1$ electrons in the $N-1$ spin orbitals $|\chi_b\rangle$, where $b \neq a$. As we have seen before, the integral $\langle ab|ba\rangle$ is nonzero only if the spins of the electrons in $|\chi_a\rangle$ and $|\chi_b\rangle$ are parallel. In the general spin orbital formulation given here, we have not specified the spins of the electrons, so the general term $\langle ab|ba\rangle$ remains for all electron-electron interactions, even though some of these integrals will be zero.

The result for ε_a is as might be expected, but the formula (3.79) for the virtual spin orbital energy ε_r has a different character. It includes the kinetic energy and nuclear attraction of an electron in $|\chi_r\rangle$, i.e., $\langle r|h|r\rangle$, as expected, but includes coulomb ($\langle rb|rb\rangle$) and exchange ($-\langle rb|br\rangle$) interactions *with all N electrons* of the Hartree-Fock ground state $|\Psi_0\rangle$, i.e., interactions with all N electrons in the spin orbitals $\{\chi_b | b = 1, 2, \ldots, N\}$. It is as if an electron had been added to $|\Psi_0\rangle$ to produce an $(N+1)$-electron state and ε_r represented the energy of this extra electron. This is exactly the case. We will return to this point when we describe Koopmans' theorem. First, we want to relate the occupied orbital energies ε_a to the total energy E_0.

If we simply add up the orbital energies ε_a of Eq. (3.75) for each of the N electrons in the ground state $|\Psi_0\rangle$, we get

$$\sum_a^N \varepsilon_a = \sum_a^N \langle a|h|a\rangle + \sum_a^N \sum_b^N \langle ab||ab\rangle \tag{3.80}$$

The correct expectation value $E_0 = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle$ for this state, from Eq. (2.112), for example, is

$$E_0 = \sum_a^N \langle a|h|a\rangle + \frac{1}{2}\sum_a^N \sum_b^N \langle ab||ab\rangle \tag{3.81}$$

It is thus apparent that

$$E_0 \neq \sum_a^N \varepsilon_a \tag{3.82}$$

and the total energy of the state $|\Psi_0\rangle$ is not just the sum of the orbital energies. The reason is as follows. The energy ε_a includes coulomb and exchange interactions between an electron in χ_a and electrons in all other occupied spin orbitals (in particular, χ_b). But ε_b includes coulomb and exchange interactions between an electron in χ_b and electrons in all other occupied spin orbitals (in particular, χ_a). Thus when we add ε_a and ε_b we include the electron-electron interactions between an electron in χ_a and one in χ_b, twice. The sum of orbital energies counts the electron-electron interactions twice. This is the reason for the factor $\frac{1}{2}$ in the correct expression (3.81) for the total energy E_0 relative to the sum of orbital energies (3.80).

If the total energy is not the sum of orbital energies what physical significance can we attach to orbital energies? The answer is provided by investigating the process of adding or subtracting an electron to the N-electron state $|\Psi_0\rangle = |{}^N\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_c\cdots\chi_N\rangle$. Suppose we consider removing an electron from the spin orbital χ_c to produce the $(N-1)$-electron single determinant state $|{}^{N-1}\Psi_c\rangle = |\chi_1\chi_2\cdots\chi_{c-1}\chi_{c+1}\cdots\chi_N\rangle$, where the remaining $N-1$ spin orbitals in $|{}^{N-1}\Psi_c\rangle$ are identical to those in $|{}^N\Psi_0\rangle$. In second quantization, this would be accomplished by annihilating an electron in χ_c, so that to within a sign,

$$|{}^{N-1}\Psi_c\rangle = a_c|{}^N\Psi_0\rangle \tag{3.83}$$

The ionization potential of $|{}^N\Psi_0\rangle$ for this process is

$$\mathrm{IP} = {}^{N-1}E_c - {}^N E_0 \tag{3.84}$$

where ${}^{N-1}E_c$ and ${}^N E_0$ are the expectation values of the energy of the two relevant single determinants.

$${}^N E_0 = \langle {}^N\Psi_0|\mathscr{H}|{}^N\Psi_0\rangle \tag{3.85}$$

$${}^{N-1}E_c = \langle {}^{N-1}\Psi_c|\mathscr{H}|{}^{N-1}\Psi_c\rangle \tag{3.86}$$

Depending from which spin orbital χ_c we remove an electron, the state $|^{N-1}\Psi_c\rangle$ may or may not represent the ground state of the ionized species. Since $|^{N-1}\Psi_c\rangle$ is a different state from $|^{N}\Psi_0\rangle$, one could not in general expect its optimum spin orbitals to be identical with those of $|^{N}\Psi_0\rangle$. With our assumption that the spin orbitals are identical, however, we can calculate the energy difference between the two states. From the rules of the last chapter, the energy of a single determinant is

$$E = \sum_i^{\text{occ}} \langle i|h|i\rangle + \frac{1}{2}\sum_i^{\text{occ}}\sum_j^{\text{occ}} \langle ij||ij\rangle \tag{3.87}$$

where the sums go over all spin orbitals occupied in the determinant. Thus

$$^{N}E_0 = \sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_a\sum_b \langle ab||ab\rangle \tag{3.88}$$

where the indices $a, b, \ldots$ refer to the spin orbitals occupied in $|^{N}\Psi_0\rangle$. With this convention, we have

$$^{N-1}E_c = \sum_{a\neq c} \langle a|h|a\rangle + \frac{1}{2}\sum_{a\neq c}\sum_{b\neq c} \langle ab||ab\rangle \tag{3.89}$$

The ionization potential is the difference between these two results

$$\begin{aligned}
\text{IP} &= {}^{N-1}E_c - {}^{N}E_0 \\
&= -\langle c|h|c\rangle - \frac{1}{2}\sum_{a[b=c]} \langle ab||ab\rangle - \frac{1}{2}\sum_{b[a=c]} \langle ab||ab\rangle \\
&= -\langle c|h|c\rangle - \frac{1}{2}\sum_a \langle ac||ac\rangle - \frac{1}{2}\sum_b \langle cb||cb\rangle \\
&= -\langle c|h|c\rangle - \sum_b \langle cb||cb\rangle
\end{aligned} \tag{3.90}$$

Comparing this with the definition (3.75) of an occupied spin orbital energy, we see that the ionization potential for removing an electron from χ_c is just the negative of the orbital energy ε_c

$$\text{IP} = {}^{N-1}E_c - {}^{N}E_0 = -\varepsilon_c \tag{3.91}$$

Thus occupied spin orbital energies in the single determinant approximation represent the energy (with opposite sign) required to remove an electron from that spin orbital. Orbital energies ε_a are generally negative and ionization potentials are positive.

Exercise 3.5 Show that the energy required to remove an electron from χ_c and one from χ_d to produce the $(N-2)$-electron single determinant $|^{N-2}\Psi_{cd}\rangle$ is $-\varepsilon_c - \varepsilon_d + \langle cd|cd\rangle - \langle cd|dc\rangle$.

Now let us consider the process of adding an electron to one of the virtual spin orbitals χ_r to produce the $(N+1)$-electron single determinant $|^{N+1}\Psi^r\rangle = |\chi_r\chi_1\chi_2 \cdots \chi_N\rangle$, where again the remaining spin orbitals are identical to those in $|^N\Psi_0\rangle$. In second quantization, this would be accomplished by creating an electron in χ_r

$$|^{N+1}\Psi^r\rangle = a_r^\dagger|^N\Psi_0\rangle \tag{3.92}$$

The electron affinity of $|^N\Psi_0\rangle$ for this process is

$$\mathrm{EA} = {}^NE_0 - {}^{N+1}E^r \tag{3.93}$$

where ${}^{N+1}E^r$ is the energy of the single determinant $|^{N+1}\Psi^r\rangle$,

$${}^{N+1}E^r = \langle {}^{N+1}\Psi^r|\mathscr{H}|^{N+1}\Psi^r\rangle \tag{3.94}$$

As in the ionization process, the optimum spin orbitals of the $(N+1)$-electron single determinant will not, in general, be identical with those of $|^N\Psi_0\rangle$. However, with the assumption that they are identical, the electron affinity is readily calculated.

Exercise 3.6 Use Eq. (3.87) to obtain an expression for ${}^{N+1}E^r$ and then subtract it from ${}^NE_0$ (Eq. (3.88)) to show that

$${}^NE_0 - {}^{N+1}E^r = -\langle r|h|r\rangle - \sum_b \langle rb||rb\rangle$$

With the result of the above exercise and Eq. (3.76), we see that the electron affinity for adding an electron to the virtual spin orbital χ_r is just the negative of the orbital energy of that virtual spin orbital, i.e.,

$$\mathrm{EA} = {}^NE_0 - {}^{N+1}E^r = -\varepsilon_r \tag{3.95}$$

This result is consistent with our previous observation that ε_r included interactions with all N other electrons of the ground state $|^N\Psi_0\rangle$ and thus describes an $(N+1)$th electron. If ε_r is negative (i.e., if $|^{N+1}\Psi^r\rangle$ is more stable than $|^N\Psi_0\rangle$), the electron affinity is positive.

The above results were first obtained by Koopmans. We are now in a position to state Koopmans' theorem.

Koopmans' Theorem Given an N-electron Hartree-Fock single determinant $|^N\Psi_0\rangle$ with occupied and virtual spin orbital energies ε_a and ε_r, then the ionization potential to produce an $(N-1)$-electron single determinant $|^{N-1}\Psi_a\rangle$ with identical spin orbitals, obtained by removing an electron from spin orbital χ_a, and the electron affinity to produce an $(N+1)$-electron single determinant $|^{N+1}\Psi^r\rangle$ with identical spin orbitals, obtained by adding an electron to spin orbital χ_r, are just $-\varepsilon_a$ and $-\varepsilon_r$, respectively.

Koopmans' theorem thus gives us a way of calculating approximate ionization potentials and electron affinities. This "frozen orbital" approximation assumes that the spin orbitals in the $(N \pm 1)$-electron states, i.e., the positive and negative ions if $|{}^N\Psi_0\rangle$ is a neutral species, are identical with those of the N-electron state. This approximation neglects relaxation of the spin orbitals in the $(N \pm 1)$-electron states, i.e., the spin orbitals of $|{}^N\Psi_0\rangle$ are not the optimum spin orbitals for $|{}^{N-1}\Psi_a\rangle$ or $|{}^{N+1}\Psi^r\rangle$. Optimizing the spin orbitals of the $(N \pm 1)$-electron single determinants by performing a separate Hartree-Fock calculation on these states would lower the energies ${}^{N-1}E_a$ and ${}^{N+1}E^r$ and thus the neglect of relaxation in Koopmans' theorem calculations tends to produce too positive an ionization potential and too negative an electron affinity. In addition, of course, the approximation of a single determinant wave function leads to errors, and the *correlation effects*, which one obtains in going beyond the Hartree-Fock approximation, will produce further corrections to Koopmans' theorem results. In particular, correlation energies are largest for the system with the highest number of electrons. Therefore, correlation effects tend to cancel the relaxation error for ionization potentials, but add to the relaxation error for electron affinities. In general, Koopmans' ionization potentials are reasonable first approximations to experimental ionization potentials and we shall be discussing a number of such calculations later in this chapter. Koopmans' electron affinities are unfortunately often bad. Many neutral molecules will add an electron to form a stable negative ion. Hartree-Fock calculations on neutral molecules, however, almost always give positive orbital energies for all the virtual orbitals. Electron affinities are considerably more difficult to calculate than ionization potentials and we will not be concerned, to any extent, with electron affinities in this book.

3.3.2 Brillouin's Theorem

The Hartree-Fock equation (3.70) produces a set $\{\chi_i\}$ of spin orbitals. The single determinant $|\Psi_0\rangle$, formed from the N spin orbitals $\{\chi_a\}$ with the lowest orbital energies, is the Hartree-Fock approximation to the ground state. As discussed in the last chapter, there are many other determinants that can be formed from the set $\{\chi_i\}$. Having derived the form of the Fock operator, we are now in a position to prove a theorem about a subset of these determinants. This subset is the set of singly excited determinants $|\Psi_a^r\rangle$ obtained from $|\Psi_0\rangle$ by a single replacement of χ_a with χ_r (Fig. 2.7). In a multideterminantal representation of the exact ground state $|\Phi_0\rangle$, it is these determinants which we might expect, *a priori*, to give the leading correction to the Hartree-Fock ground state $|\Psi_0\rangle$,

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + \sum_{ra} c_a^r|\Psi_a^r\rangle + \cdots \tag{3.96}$$

If we consider only the singly excited determinants as corrections, then the coefficients c_a^r are determined from the variational principle by diagonalizing the Hamiltonian matrix in the basis of the states $\{\Psi_0, \{\Psi_a^r\}\}$. Consider for a moment the matrix eigenvalue problem involving one singly excited state

$$\begin{pmatrix} \langle\Psi_0|\mathscr{H}|\Psi_0\rangle & \langle\Psi_0|\mathscr{H}|\Psi_a^r\rangle \\ \langle\Psi_a^r|\mathscr{H}|\Psi_0\rangle & \langle\Psi_a^r|\mathscr{H}|\Psi_a^r\rangle \end{pmatrix}\begin{pmatrix} c_0 \\ c_a^r \end{pmatrix} = \mathscr{E}_0\begin{pmatrix} c_0 \\ c_a^r \end{pmatrix} \tag{3.97}$$

The mixing of the two states depends on the off-diagonal element $\langle\Psi_0|\mathscr{H}|\Psi_a^r\rangle$. This matrix element is obtained by using the rules for evaluating matrix elements between determinants, and the result can be read directly from Tables 2.5 and 2.6.

$$\langle\Psi_0|\mathscr{H}|\Psi_a^r\rangle = \langle a|h|r\rangle + \sum_b \langle ab||rb\rangle \tag{3.98}$$

The right-hand side of this equation can be simplified; as Exercise 3.1 shows, matrix elements of the Fock operator are given by

$$\langle\chi_i|f|\chi_j\rangle = \langle i|h|j\rangle + \sum_b \langle ib||jb\rangle \tag{3.99}$$

Therefore,

$$\langle\Psi_0|\mathscr{H}|\Psi_a^r\rangle = \langle\chi_a|f|\chi_r\rangle \tag{3.100}$$

The matrix element that mixes singly excited determinants with $|\Psi_0\rangle$ is thus equal to an off-diagonal element of the Fock matrix. Now, by definition, solving the Hartree-Fock eigenvalue problem requires the off-diagonal elements to satisfy $\langle\chi_i|f|\chi_j\rangle = 0, (i \neq j)$. One can then say that solving the Hartree-Fock eigenvalue equation is equivalent to ensuring that $|\Psi_0\rangle$ will not mix with any singly excited determinants. The lowest solution to (3.97) is thus

$$\begin{pmatrix} E_0 & 0 \\ 0 & \langle\Psi_a^r|\mathscr{H}|\Psi_a^r\rangle \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = E_0\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{3.101}$$

The Hartree-Fock ground state is in this sense "stable" since it cannot be improved by mixing it with singly excited determinants. One then expects doubly excited determinants $|\Psi_{ab}^{rs}\rangle$ to provide the leading and most important corrections to $|\Psi_0\rangle$. This does not mean that there are no singly excited determinants $|\Psi_a^r\rangle$ in an exact ground state $|\Phi_0\rangle$. They can mix indirectly with $|\Psi_0\rangle$ through the doubly excited determinants by way of the matrix elements $\langle\Psi_a^r|\mathscr{H}|\Psi_{ab}^{rs}\rangle$ and $\langle\Psi_{ab}^{rs}|\mathscr{H}|\Psi_0\rangle$. The important result we have just derived is termed Brillouin's theorem.

Brillouin's Theorem Singly excited determinants $|\Psi_a^r\rangle$ will not interact directly with a reference Hartree-Fock determinant $|\Psi_0\rangle$, i.e., $\langle\Psi_0|\mathscr{H}|\Psi_a^r\rangle = 0$.

We will have the opportunity to use this theorem many times in later chapters.

3.3.3 The Hartree-Fock Hamiltonian

Until now the Hartree-Fock approximation has been viewed as an approximation in which the Hamiltonian is exact but the wave function is approximated as a single Slater determinant. For later use in the perturbation theory of Chapter 6, we now preview a different but equivalent view of Hartree-Fock theory that focuses on the Hamiltonian.

We have not solved the exact electronic Schrödinger equation

$$\mathscr{H}|\Phi_0\rangle = \mathscr{E}_0|\Phi_0\rangle \tag{3.102}$$

but rather we have used the variational principle to find an approximation $|\Psi_0\rangle$ to $|\Phi_0\rangle$. We now ask the question, "Is there some approximate N-electron Hamiltonian and eigenvalue equation that we have solved exactly, i.e., is there an approximate Hamiltonian for which $|\Psi_0\rangle$ is an exact eigenfunction?" The answer is "Yes." The *Hartree-Fock Hamiltonian* is

$$\mathscr{H}_0 = \sum_{i=1}^{N} f(i) \tag{3.103}$$

where $f(i)$ is a Fock operator for the ith electron.

Exercise 3.7 Use definition (2.115) of a Slater determinant and the fact that $\mathscr{H}_0$ commutes with any operator that permutes the electron labels, to show that $|\Psi_0\rangle$ is an eigenfunction of $\mathscr{H}_0$ with eigenvalue $\sum_a \varepsilon_a$. Why does $\mathscr{H}_0$ commute with the permutation operator?

As the above exercise shows, $|\Psi_0\rangle$ is an eigenfunction of a Hartree-Fock Hamiltonian with an eigenvalue that is not the Hartree-Fock energy E_0, but the sum of orbital energies $\sum_a \varepsilon_a$. We can in fact show that any single determinant formed from the set $\{\chi_i\}$ of eigenfunctions of the Fock operator, f, is an eigenfunction of $\mathscr{H}_0$ with eigenvalue equal to the sum of the orbital energies of the spin orbitals included in the determinant. In the context of perturbation theory, which is extensively discussed in Chapter 6, we have obtained a complete set of eigenfunctions to an unperturbed Hamiltonian $\mathscr{H}_0$, which can form the basis for a perturbation expansion of the exact energy,

$$\mathscr{E}_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \cdots \tag{3.104}$$

The unperturbed zeroth-order energy is just

$$E_0^{(0)} = \sum_a \varepsilon_a \tag{3.105}$$

where

$$\mathscr{H}_0|\Psi_0\rangle = E_0^{(0)}|\Psi_0\rangle \tag{3.106}$$

If

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{V} \tag{3.107}$$

then the perturbation $\mathscr{V}$ is

$$\begin{aligned}\mathscr{V} &= \mathscr{H} - \mathscr{H}_0 \\ &= \sum_{i=1}^{N} h(i) + \sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij}^{-1} - \sum_{i=1}^{N} f(i) \\ &= \sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij}^{-1} - \sum_{i=1}^{N} v^{\mathrm{HF}}(i)\end{aligned} \tag{3.108}$$

or just the difference between the exact electron-electron interaction and the sum of the Hartree-Fock coulomb and exchange potentials. We can now evaluate the Hartree-Fock energy as

$$\begin{aligned}E_0 &= \langle \Psi_0 | \mathscr{H} | \Psi_0 \rangle = \langle \Psi_0 | \mathscr{H}_0 | \Psi_0 \rangle + \langle \Psi_0 | \mathscr{V} | \Psi_0 \rangle \\ &= \sum_a \varepsilon_a + \langle \Psi_0 | \mathscr{V} | \Psi_0 \rangle = E_0^{(0)} + E_0^{(1)}\end{aligned} \tag{3.109}$$

where $\langle \Psi_0 | \mathscr{V} | \Psi_0 \rangle$ has been defined as the first-order energy in the expansion (3.104) for the exact energy. In Chapter 6 we will primarily be concerned with finding the second-order energy $E_0^{(2)}$ and other higher-order energies.

Exercise 3.8 Use expression (3.108) for $\mathscr{V}$, expression (3.18) for the Hartree-Fock potential $v^{\mathrm{HF}}(i)$, and the rules for evaluating matrix elements to explicitly show that $\langle \Psi_0 | \mathscr{V} | \Psi_0 \rangle = -\frac{1}{2} \sum_a \sum_b \langle ab || ab \rangle$ and hence that $E_0^{(1)}$ cancels the double counting of electron-electron repulsions in $E_0^{(0)} = \sum_a \varepsilon_a$ to give the correct Hartree-Fock energy E_0.

3.4 RESTRICTED CLOSED-SHELL HARTREE-FOCK: THE ROOTHAAN EQUATIONS

So far in this chapter we have discussed the Hartree-Fock equations from a formal point of view in terms of a general set of spin orbitals $\{\chi_i\}$. We are now in a position to consider the actual calculation of Hartree-Fock wave functions, and we must be more specific about the form of the spin orbitals. In the last chapter we briefly discussed two types of spin orbitals: restricted spin orbitals, which are constrained to have the same spatial function for α (spin up) and β (spin down) spin functions; and unrestricted spin orbitals, which have different spatial functions for α and β spins. Later in this chapter we will discuss the unrestricted Hartree-Fock formalism and unrestricted calculations. In this section we are concerned with procedures for calculating restricted Hartree-Fock wave functions and, specifically, we consider here only closed-shell calculations. Our molecular states are thus allowed to have only an even number N of electrons, with all electrons paired such that $n = N/2$ spatial orbitals are doubly occupied. In essence this restricts our discussion to closed-shell ground states.[3] For describing open-shell ground states we will use the unrestricted formalism of the last section of this chapter. To describe open-shell excited states we also use unrestricted Hartree-Fock theory. The restricted open-shell formalism is somewhat more involved than our restricted closed-shell or unrestricted open-shell formalism, and we do not describe restricted open-shell Hartree-Fock calculations in this book. An excellent introduction to such calculations is contained in the book by Hurley, suggested for further reading at the end of this chapter.

3.4.1 Closed-Shell Hartree-Fock: Restricted Spin Orbitals

A restricted set of spin orbitals has the form

$$\chi_i(\mathbf{x}) = \begin{cases} \psi_j(\mathbf{r})\alpha(\omega) \\ \psi_j(\mathbf{r})\beta(\omega) \end{cases} \tag{3.110}$$

and the closed-shell restricted ground state is

$$|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_{N-1}\chi_N\rangle = |\psi_1\bar{\psi}_1 \cdots \psi_a\bar{\psi}_a \cdots \psi_{N/2}\bar{\psi}_{N/2}\rangle \tag{3.111}$$

We now want to convert the general spin orbital Hartree-Fock equation $f(1)\chi_i(1) = \varepsilon_i\chi_i(1)$ to a spatial eigenvalue equation where each of the occupied spatial molecular orbitals $\{\psi_a | a = 1, 2, \ldots, N/2\}$ is doubly occupied. The procedure for converting from spin orbitals to spatial orbitals was described in Subsection 2.3.5; we must integrate out the spin functions. Let us first apply this technique to the Hartree-Fock equation

$$f(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \varepsilon_i\chi_i(\mathbf{x}_1) \tag{3.112}$$

The spin orbital $\chi_i(\mathbf{x}_1)$ will have either the α or β spin function. Let us assume α; identical results will be obtained by assuming β,

$$f(\mathbf{x}_1)\psi_j(\mathbf{r}_1)\alpha(\omega_1) = \varepsilon_j\psi_j(\mathbf{r}_1)\alpha(\omega_1) \tag{3.113}$$

where ε_j, the energy of the spatial orbital ψ_j is identical with ε_i, the energy of the spin orbital χ_i. Multiplying on the left by $\alpha^*(\omega_1)$ and integrating over spin gives

$$\left[\int d\omega_1\, \alpha^*(\omega_1)f(\mathbf{x}_1)\alpha(\omega_1)\right]\psi_j(\mathbf{r}_1) = \varepsilon_j\psi_j(\mathbf{r}_1) \tag{3.114}$$

To proceed we must evaluate the left-hand side of (3.114). Let us write the spin orbital Fock operator as

$$f(\mathbf{x}_1) = h(\mathbf{r}_1) + \sum_c^N \int d\mathbf{x}_2\, \chi_c^*(\mathbf{x}_2)r_{12}^{-1}(1 - \mathscr{P}_{12})\chi_c(\mathbf{x}_2) \tag{3.115}$$

so that (3.114) becomes

$$\left[\int d\omega_1\ \alpha^*(\omega_1)f(\mathbf{x}_1)\alpha(\omega_1)\right]\psi_j(\mathbf{r}_1)=\left[\int d\omega_1\ \alpha^*(\omega_1)h(\mathbf{r}_1)\alpha(\omega_1)\right]\psi_j(\mathbf{r}_1)$$
$$+\left[\sum_c\int d\omega_1\ d\mathbf{x}_2\ \alpha^*(\omega_1)\chi_c^*(\mathbf{x}_2)r_{12}^{-1}(1-\mathscr{P}_{12})\chi_c(\mathbf{x}_2)\alpha(\omega_1)\right]\psi_j(\mathbf{r}_1)$$
$$=\varepsilon_j\psi_j(\mathbf{r}_1) \tag{3.116}$$

If we let $f(\mathbf{r}_1)$ be the closed-shell Fock operator

$$f(\mathbf{r}_1)=\int d\omega_1\ \alpha^*(\omega_1)f(\mathbf{x}_1)\alpha(\omega_1) \tag{3.117}$$

then

$$f(\mathbf{r}_1)\psi_j(\mathbf{r}_1)=h(\mathbf{r}_1)\psi_j(\mathbf{r}_1)+\sum_c\int d\omega_1\ d\mathbf{x}_2\ \alpha^*(\omega_1)\chi_c^*(\mathbf{x}_2)r_{12}^{-1}\chi_c(\mathbf{x}_2)\alpha(\omega_1)\psi_j(\mathbf{r}_1)$$
$$-\sum_c\int d\omega_1\ d\mathbf{x}_2\ \alpha^*(\omega_1)\chi_c^*(\mathbf{x}_2)r_{12}^{-1}\chi_c(\mathbf{x}_1)\alpha(\omega_2)\psi_j(\mathbf{r}_2)$$
$$=\varepsilon_j\psi_j(\mathbf{r}_1) \tag{3.118}$$

where we have performed the integration over $d\omega_1$ in the expression involving $h(\mathbf{r}_1)$ and used $\mathscr{P}_{12}$ to generate the explicit exchange term. Now, if we have a closed-shell, the sum over occupied spin orbitals includes an equal sum over those with the α spin function and those with the β spin function

$$\sum_c^N\rightarrow\sum_c^{N/2}+\sum_{\bar{c}}^{N/2} \tag{3.119}$$

and therefore

$$f(\mathbf{r}_1)\psi_j(\mathbf{r}_1)=h(\mathbf{r}_1)\psi_j(\mathbf{r}_1)$$
$$+\sum_c^{N/2}\int d\omega_1\,d\omega_2\,d\mathbf{r}_2\ \alpha^*(\omega_1)\psi_c^*(\mathbf{r}_2)\alpha^*(\omega_2)r_{12}^{-1}\psi_c(\mathbf{r}_2)\alpha(\omega_2)\alpha(\omega_1)\psi_j(\mathbf{r}_1)$$
$$+\sum_c^{N/2}\int d\omega_1\,d\omega_2\,d\mathbf{r}_2\ \alpha^*(\omega_1)\psi_c^*(\mathbf{r}_2)\beta^*(\omega_2)r_{12}^{-1}\psi_c(\mathbf{r}_2)\beta(\omega_2)\alpha(\omega_1)\psi_j(\mathbf{r}_1)$$
$$-\sum_c^{N/2}\int d\omega_1\,d\omega_2\,d\mathbf{r}_2\ \alpha^*(\omega_1)\psi_c^*(\mathbf{r}_2)\alpha^*(\omega_2)r_{12}^{-1}\psi_c(\mathbf{r}_1)\alpha(\omega_1)\alpha(\omega_2)\psi_j(\mathbf{r}_2)$$
$$-\sum_c^{N/2}\int d\omega_1\,d\omega_2\,d\mathbf{r}_2\ \alpha^*(\omega_1)\psi_c^*(\mathbf{r}_2)\beta^*(\omega_2)r_{12}^{-1}\psi_c(\mathbf{r}_1)\beta(\omega_1)\alpha(\omega_2)\psi_j(\mathbf{r}_2)$$
$$=\varepsilon_j\psi_j(\mathbf{r}_1) \tag{3.120}$$

We can now perform the integrations over $d\omega_1$ and $d\omega_2$. The last term of (3.120) disappears because of spin orthogonality. This reflects the fact that there is only an exchange interaction between electrons of parallel spin. The two coulomb terms are equal and thus one obtains

$$\begin{aligned} f(\mathbf{r}_1)\psi_j(\mathbf{r}_1) = h(\mathbf{r}_1)\psi_j(\mathbf{r}_1) &+ \left[2\sum_c^{N/2}\int d\mathbf{r}_2\, \psi_c^*(\mathbf{r}_2)r_{12}^{-1}\psi_c(\mathbf{r}_2)\right]\psi_j(\mathbf{r}_1) \\ &- \left[\sum_c^{N/2}\int d\mathbf{r}_2\, \psi_c^*(\mathbf{r}_2)r_{12}^{-1}\psi_j(\mathbf{r}_2)\right]\psi_c(\mathbf{r}_1) \\ = \varepsilon_j\psi_j(\mathbf{r}_1) & \end{aligned} \tag{3.121}$$

The closed-shell Fock operator thus has the form,

$$f(\mathbf{r}_1) = h(\mathbf{r}_1) + \sum_a^{N/2}\int d\mathbf{r}_2\, \psi_a^*(\mathbf{r}_2)(2 - \mathscr{P}_{12})r_{12}^{-1}\psi_a(\mathbf{r}_2) \tag{3.122}$$

or, equivalently,

$$f(1) = h(1) + \sum_a^{N/2} 2J_a(1) - K_a(1) \tag{3.123}$$

where the closed-shell coulomb and exchange operators are defined by

$$J_a(1) = \int d\mathbf{r}_2\, \psi_a^*(2)r_{12}^{-1}\psi_a(2) \tag{3.124}$$

$$K_a(1)\psi_i(1) = \left[\int d\mathbf{r}_2\, \psi_a^*(2)r_{12}^{-1}\psi_i(2)\right]\psi_a(1) \tag{3.125}$$

These equations are quite analogous to those for spin orbitals, except for the factor of 2 occurring with the coulomb operator. The sum in (3.122) is, of course, over the $N/2$ occupied orbitals $\{\psi_a\}$. The closed-shell spatial Hartree-Fock equation is just

$$f(1)\psi_j(1) = \varepsilon_j\psi_j(1) \tag{3.126}$$

The closed-shell Hartree-Fock energy was derived in Subsection 2.3.5 as an example of the transition from spin orbitals to spatial orbitals. For the closed-shell determinant, $|\Psi_0\rangle = |\psi_1\bar{\psi}_1 \cdots \psi_a\bar{\psi}_a \cdots \psi_{N/2}\bar{\psi}_{N/2}\rangle$, it is

$$\begin{aligned} E_0 = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle &= 2\sum_a (a|h|a) + \sum_a\sum_b 2(aa|bb) - (ab|ba) \\ &= 2\sum_a h_{aa} + \sum_a\sum_b 2J_{ab} - K_{ab} \end{aligned} \tag{3.127}$$

It remains to convert the expression for orbital energies in Eq. (3.72) to the closed-shell spatial orbital form.

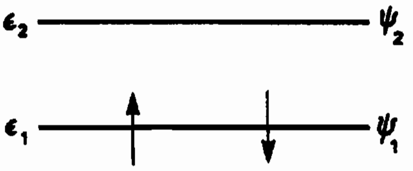
Exercise 3.9 Convert the spin orbital expression for orbital energies

$$\varepsilon_i = \langle\chi_i|h|\chi_i\rangle + \sum_b^N \langle\chi_i\chi_b||\chi_i\chi_b\rangle$$

to the closed-shell expression

$$\varepsilon_i = (\psi_i|h|\psi_i) + \sum_b^{N/2} 2(ii|bb) - (ib|bi) = h_{ii} + \sum_b^{N/2} 2J_{ib} - K_{ib} \qquad (3.128)$$

With the results of this last exercise we now have closed-shell expressions for most quantities of interest. Let us examine these, for a moment, in the context of our minimal basis H_2 model.

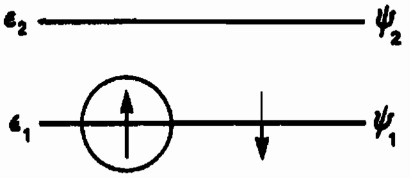


We can evaluate the total energy by inspection. Each of the two electrons has kinetic energy plus attraction to the nuclei of $h_{11} = (\psi_1|h|\psi_1)$. In addition there is the coulomb repulsion between the two electrons $J_{11} = (\psi_1\psi_1|\psi_1\psi_1)$. There are no exchange interactions since the two electrons have antiparallel spins. The Hartree-Fock energy is thus

$$E_0 = 2h_{11} + J_{11} \qquad (3.129)$$

This is an agreement with (3.127) since $J_{ii} = K_{ii}$.

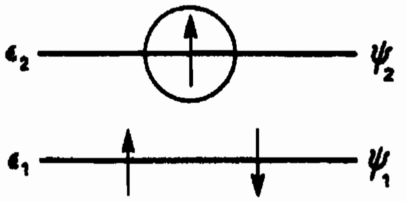
One can evaluate the orbital energies similarly.



To evaluate ε_1 we need only add up the interactions of the circled electron. It has kinetic energy and nuclear attraction h_{11} and a coulomb interaction J_{11} and, therefore,

$$\varepsilon_1 = h_{11} + J_{11} \qquad (3.130)$$

We could do the same for any occupied orbital energy. For virtual orbitals, as we have seen before, the orbital energy corresponds to the interactions of an extra $(N+1)$th electron, in agreement with Koopmans' theorem. For the minimal basis model, we must keep the two electrons of $|\Psi_0\rangle$ and evaluate the interactions of the extra electron in the virtual orbital ψ_2, as shown below.



The circled electron has kinetic energy and nuclear attraction h_{22}. It has two coulomb interactions J_{12}, with each of the other two electrons, and an exchange interaction $-K_{12}$, with the electron of parallel spin. Thus

$$\varepsilon_2 = h_{22} + 2J_{12} - K_{12} \tag{3.131}$$

Both of the results are in agreement with the general expression for closed-shell orbital energies obtained in Exercise 3.9.

3.4.2 Introduction of a Basis: The Roothaan Equations

Now that we have eliminated spin, the calculation of molecular orbitals becomes equivalent to the problem of solving the spatial integro-differential equation

$$f(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = \varepsilon_i\psi_i(\mathbf{r}_1) \tag{3.132}$$

One might attempt to solve this equation numerically; numerical solutions are common in atomic calculations. No practical procedures are presently available, however, for obtaining numerical solutions for molecules. The contribution of Roothaan^4 was to show how, by introducing a set of known spatial basis functions, the differential equation could be converted to a set of algebraic equations and solved by standard matrix techniques.

We, therefore, introduce a set of K known basis functions $\{\phi_\mu(\mathbf{r}) | \mu = 1, 2, \ldots, K\}$ and expand the unknown molecular orbitals in the linear expansion

$$\psi_i = \sum_{\mu=1}^{K} C_{\mu i}\phi_\mu \qquad i = 1, 2, \ldots, K \tag{3.133}$$

If the set $\{\phi_\mu\}$ was complete, this would be an exact expansion, and any complete set $\{\phi_\mu\}$ could be used. Unfortunately, one is always restricted, for practical computational reasons, to a finite set of K basis functions. As such, it is important to choose a basis that will provide, as far as is possible, a reasonably accurate expansion for the exact molecular orbitals $\{\psi_i\}$, particularly, for those molecular orbitals $\{\psi_a\}$ which are occupied in $|\Psi_0\rangle$ and determine the ground state energy E_0. A later section of this chapter discusses the questions involved in the choice of a basis set and describes some of the art of choosing a basis set. For our purposes here, we need only assume that $\{\phi_\mu\}$ is a set of known functions. As the basis set becomes more and more complete, the expansion (3.133) leads to more and more accurate representations of the "exact" molecular orbitals, i.e., the molecular orbitals converge to those of Eq. (3.132), the true eigenfunctions of the Fock operator. For any finite basis set we will obtain molecular orbitals from the truncated expansion (3.133), which are exact only in the space spanned by the basis functions $\{\phi_\mu\}$.

From (3.133), the problem of calculating the Hartree-Fock molecular orbitals reduces to the problem of calculating the set of expansion coefficients

$C_{\mu i}$. We can obtain a matrix equation for the $C_{\mu i}$ by substituting the linear expansion (3.133) into the Hartree-Fock equation (3.132). Using the index ν, gives

$$f(1) \sum_{\nu} C_{\nu i} \phi_{\nu}(1) = \varepsilon_i \sum_{\nu} C_{\nu i} \phi_{\nu}(1) \tag{3.134}$$

By multiplying by $\phi_{\mu}^{*}(1)$ on the left and integrating, we turn the integro-differential equation into a matrix equation,

$$\sum_{\nu} C_{\nu i} \int d\mathbf{r}_1 \, \phi_{\mu}^{*}(1) f(1) \phi_{\nu}(1) = \varepsilon_i \sum_{\nu} C_{\nu i} \int d\mathbf{r}_1 \, \phi_{\mu}^{*}(1) \phi_{\nu}(1) \tag{3.135}$$

We now define two matrices.

1. The *overlap matrix* S has elements

$$S_{\mu\nu} = \int d\mathbf{r}_1 \, \phi_{\mu}^{*}(1) \phi_{\nu}(1) \tag{3.136}$$

and is a $K \times K$ Hermitian (although usually real and symmetric) matrix. The basis functions $\{\phi_{\mu}\}$, although assumed to be normalized and linearly independent, are not in general orthogonal to each other and, hence, overlap with a magnitude $0 \leq |S_{\mu\nu}| \leq 1$, i.e., the diagonal elements of S are unity and the off-diagonal elements are numbers less than one in magnitude. The sign of the off-diagonal elements depends on the relative sign of the two basis functions, and their relative orientation and separation in space. If two off-diagonal elements approach unity (in magnitude) i.e., approach complete overlap, then the two basis functions approach linear dependence. Because the overlap matrix is Hermitian, it can be diagonalized by a unitary matrix, as we will have occasion to do, later. The eigenvalues of the overlap matrix can be shown to be necessarily positive numbers and, hence, the overlap matrix is said to be a positive-definite matrix. Linear dependence in the basis set is associated with eigenvalues of the overlap matrix approaching zero. The overlap matrix is sometimes called the metric matrix.

2. The *Fock matrix* **F** has elements

$$F_{\mu\nu} = \int d\mathbf{r}_1 \, \phi_{\mu}^{*}(1) f(1) \phi_{\nu}(1) \tag{3.137}$$

and is also a $K \times K$ Hermitian (although usually real and symmetric) matrix. The Fock operator $f(1)$ is a one-electron operator, and any set of one-electron functions defines a matrix representation of this operator. We have previously discussed matrix elements of the Fock operator with spin orbitals. The Fock matrix **F** is the matrix representation of the Fock operator with the set of basis functions $\{\phi_{\mu}\}$.

With these definitions of **F** and **S** we can now write the integrated Hartree-Fock equation (3.135) as

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} \qquad i = 1, 2, \ldots, K \tag{3.138}$$

These are the *Roothaan equations*, which can be written more compactly as the single matrix equation

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \tag{3.139}$$

where $\mathbf{C}$ is a $K \times K$ square matrix of the expansion coefficients $C_{\mu i}$

$$\mathbf{C} = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ \vdots & \vdots & & \vdots \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix} \tag{3.140}$$

and $\boldsymbol{\varepsilon}$ is a diagonal matrix of the orbital energies ε_i,

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_1 & & & \\ & \varepsilon_2 & & \mathbf{0} \\ \mathbf{0} & & \ddots & \\ & & & \varepsilon_K \end{pmatrix} \tag{3.141}$$

Note that from (3.133) and (3.140) it is the columns of $\mathbf{C}$ which describe the molecular orbitals, i.e., the coefficients describing ψ_1 are in the first column of $\mathbf{C}$, those describing ψ_2 are in the second column of $\mathbf{C}$, etc.

Exercise 3.10 Show that $\mathbf{C}^\dagger\mathbf{SC} = \mathbf{1}$. *Hint:* Use the fact that the molecular orbitals $\{\psi_i\}$ are orthonormal.

At this point the problem of determining the Hartree-Fock molecular orbitals $\{\psi_i\}$ and orbital energies ε_i involves solving the matrix equation $\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$. To proceed, however, we need an explicit expression for the Fock matrix. It is first of all necessary, however, to introduce the concept of a density matrix.

3.4.3 The Charge Density

If we have an electron described by the spatial wave function $\psi_a(\mathbf{r})$, then the probability of finding that electron in a volume element $d\mathbf{r}$ at a point $\mathbf{r}$ is $|\psi_a(\mathbf{r})|^2\, d\mathbf{r}$. The probability distribution function (charge density) is $|\psi_a(\mathbf{r})|^2$. If we have a closed-shell molecule described by a single determinant wave function with each occupied molecular orbital ψ_a containing two electrons, then the total charge density is just

$$\rho(\mathbf{r}) = 2 \sum_a^{N/2} |\psi_a(\mathbf{r})|^2 \tag{3.142}$$

such that $\rho(\mathbf{r})\, d\mathbf{r}$ is the probability of finding an electron (any electron) in $d\mathbf{r}$ at $\mathbf{r}$. The integral of this charge density is just the total number of electrons,

$$\int d\mathbf{r}\, \rho(\mathbf{r}) = 2 \sum_a^{N/2} \int d\mathbf{r}\, |\psi_a(\mathbf{r})|^2 = 2 \sum_a^{N/2} 1 = N \tag{3.143}$$

For a single determinant, these equations show that the total charge density is just a sum of charge densities for each of the electrons.

Exercise 3.11 Use the density operator $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r})$, the rules for evaluating matrix elements in Chapter 2, and the rules for converting from spin orbitals to spatial orbitals, to derive (3.142) from $\rho(\mathbf{r}) = \langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle$.

Let us now insert the molecular orbital expansion (3.133) into the expression (3.142) for the charge density,

$$\begin{aligned}\rho(\mathbf{r}) &= 2 \sum_{a}^{N/2} \psi_a^*(\mathbf{r}) \psi_a(\mathbf{r}) \\ &= 2 \sum_{a}^{N/2} \sum_{\nu} C_{\nu a}^* \phi_\nu^*(\mathbf{r}) \sum_{\mu} C_{\mu a} \phi_\mu(\mathbf{r}) \\ &= \sum_{\mu\nu} \left[2 \sum_{a}^{N/2} C_{\mu a} C_{\nu a}^* \right] \phi_\mu(\mathbf{r}) \phi_\nu^*(\mathbf{r}) \\ &= \sum_{\mu\nu} P_{\mu\nu} \phi_\mu(\mathbf{r}) \phi_\nu^*(\mathbf{r}) \end{aligned} \tag{3.144}$$

where we have defined a *density matrix* or, as it is sometimes called, a *charge-density bond-order matrix*

$$P_{\mu\nu} = 2 \sum_{a}^{N/2} C_{\mu a} C_{\nu a}^* \tag{3.145}$$

From (3.144), given a set of known basis functions $\{\phi_\mu\}$, the matrix **P** specifies completely the charge density $\rho(\mathbf{r})$. It is directly related to the expansion coefficients **C** by (3.145), and we can characterize the results of closed-shell Hartree-Fock calculations either by the $C_{\mu i}$ or by the $P_{\mu\nu}$.

Exercise 3.12 A matrix **A** is said to be idempotent if $\mathbf{A}^2 = \mathbf{A}$. Use the result of Exercise 3.10 to show that $\mathbf{PSP} = 2\mathbf{P}$, i.e., show that $\frac{1}{2}\mathbf{P}$ would be idempotent in an orthonormal basis.

Exercise 3.13 Use the expression (3.122) for the closed-shell Fock operator to show that

$$\begin{aligned} f(\mathbf{r}_1) &= h(\mathbf{r}_1) + v^{\mathrm{HF}}(\mathbf{r}_1) \\ &= h(\mathbf{r}_1) + \frac{1}{2} \sum_{\lambda\sigma} P_{\lambda\sigma} \left[\int d\mathbf{r}_2 \, \phi_\sigma^*(\mathbf{r}_2)(2 - \mathscr{P}_{12}) r_{12}^{-1} \phi_\lambda(\mathbf{r}_2) \right] \end{aligned} \tag{3.146}$$

The result of the above exercise expresses the Fock operator in terms of the density matrix. We can use this expression to indicate in an intuitive way how the Hartree-Fock procedure operates. We first guess a density matrix

P, i.e., we guess the charge density $\rho(\mathbf{r})$ describing the positions of the electrons. Later we will say something about how to obtain such a guess. We then use this charge density to calculate an effective one-electron potential $v^{\mathrm{HF}}(\mathbf{r}_1)$ for the electrons according to (3.146). We thus have an effective one-electron Hamiltonian (the Fock operator), and we can solve a one-electron Schrödinger-like equation to determine the states $\{\psi_i\}$ of an electron in the effective potential. The new one-electron states (molecular orbitals ψ_i) can then be used to obtain a better approximation to the density, using (3.142), for example. With this new charge density we can calculate a new Hartree-Fock potential and repeat the procedure until the Hartree-Fock potential (and, consequently, an effective electrostatic field) no longer changes, i.e., until the field which produced a particular charge density (by solving a one-electron Schrödinger-like equation, the Hartree-Fock eigenvalue equation) is consistent (identical) with the field which would be calculated from that charge density (using (3.146)). This is why the Hartree-Fock equations are commonly called the *self-consistent-field* (SCF) equations. This is a way of viewing the physics involved in solving the Roothaan equations. To return to the actual algebraic procedure, we need an explicit expression for the Fock matrix **F**.

3.4.4 Expression for the Fock Matrix

The Fock matrix **F** is the matrix representation of the Fock operator

$$f(1) = h(1) + \sum_{a}^{N/2} 2J_a(1) - K_a(1) \tag{3.147}$$

in the basis $\{\phi_\mu\}$, i.e.,

$$\begin{aligned} F_{\mu\nu} &= \int d\mathbf{r}_1\, \phi_\mu^*(1) f(1) \phi_\nu(1) \\ &= \int d\mathbf{r}_1\, \phi_\mu^*(1) h(1) \phi_\nu(1) + \sum_{a}^{N/2} \int d\mathbf{r}_1\, \phi_\mu^*(1)[2J_a(1) - K_a(1)]\phi_\nu(1) \\ &= H_{\mu\nu}^{\mathrm{core}} + \sum_{a}^{N/2} 2(\mu\nu|aa) - (\mu a|a\nu) \end{aligned} \tag{3.148}$$

where we have defined a *core-Hamiltonian* matrix

$$H_{\mu\nu}^{\mathrm{core}} = \int d\mathbf{r}_1\, \phi_\mu^*(1) h(1) \phi_\nu(1) \tag{3.149}$$

The elements of the core-Hamiltonian matrix are integrals involving the one-electron operator $h(1)$, describing the kinetic energy and nuclear attraction of an electron, i.e.,

$$h(1) = -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|} \tag{3.150}$$

Calculating the elements of the core-Hamiltonian matrix thus involves the kinetic energy integrals

$$T_{\mu\nu} = \int d\mathbf{r}_1\, \phi_\mu^*(1)[-\tfrac{1}{2}\nabla_1^2]\phi_\nu(1) \tag{3.151}$$

and the nuclear attraction integrals

$$V_{\mu\nu}^{\text{nucl}} = \int d\mathbf{r}_1\, \phi_\mu^*(1)\left[-\sum_A \frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_A|}\right]\phi_\nu(1) \tag{3.152}$$

where

$$H_{\mu\nu}^{\text{core}} = T_{\mu\nu} + V_{\mu\nu}^{\text{nucl}} \tag{3.153}$$

Given a particular basis set $\{\phi_\mu\}$, the integrals of $\mathbf{T}$ and $\mathbf{V}^{\text{nucl}}$ need to be evaluated and the core-Hamiltonian matrix formed. The core-Hamiltonian matrix, unlike the full Fock matrix, needs only to be evaluated once as it remains constant during the iterative calculation. The calculation of kinetic energy and nuclear attraction integrals is described in Appendix A.

To return to expression (3.148) for the Fock matrix, we now insert the linear expansion for the molecular orbitals (3.133) into the two-electron terms to get

$$\begin{aligned} F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} + \sum_a^{N/2} \sum_{\lambda\sigma} C_{\lambda a} C_{\sigma a}^* [2(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] \\ &= H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - \tfrac{1}{2}(\mu\lambda|\sigma\nu)] \\ &= H_{\mu\nu}^{\text{core}} + G_{\mu\nu} \end{aligned} \tag{3.154}$$

where $G_{\mu\nu}$ is the two-electron part of the Fock matrix. This is our final expression for the Fock matrix. It contains a one-electron part $\mathbf{H}^{\text{core}}$ which is fixed, given the basis set, and a two-electron part $\mathbf{G}$ which depends on the density matrix $\mathbf{P}$ and a set of two-electron integrals

$$(\mu\nu|\lambda\sigma) = \int d\mathbf{r}_1\, d\mathbf{r}_2\, \phi_\mu^*(1)\phi_\nu(1) r_{12}^{-1} \phi_\lambda^*(2)\phi_\sigma(2) \tag{3.155}$$

Because of their large number, the evaluation and manipulation of these two-electron integrals is the major difficulty in a Hartree-Fock calculation.

Exercise 3.14 Assume that the basis functions are real and use the symmetry of the two-electron integrals $[(\mu\nu|\lambda\sigma) = (\nu\mu|\lambda\sigma) = (\lambda\sigma|\mu\nu)$, etc.$]$ to show that for a basis set of size $K = 100$ there are $12{,}753{,}775 = O(K^4/8)$ unique two-electron integrals.

Because the Fock matrix depends on the density matrix,

$$\mathbf{F} = \mathbf{F}(\mathbf{P}) \tag{3.156}$$

or, equivalently, on the expansion coefficients,

$$\mathbf{F} = \mathbf{F}(\mathbf{C}) \tag{3.157}$$

the Roothaan equations are nonlinear, i.e.,

$$\mathbf{F}(\mathbf{C})\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\varepsilon} \tag{3.158}$$

and they will need to be solved in an iterative fashion. Before considering how such iterations should proceed, we need to discuss the solution of the matrix equation

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\varepsilon} \tag{3.159}$$

at each step in the iteration. If S were the unit matrix (i.e., if we had an orthonormal basis set), then we would have

$$\mathbf{F}\mathbf{C} = \mathbf{C}\boldsymbol{\varepsilon} \tag{3.160}$$

and Roothaan's equations would just have the form of the usual matrix eigenvalue problem, and we could find the eigenvectors **C** and eigenvalues $\boldsymbol{\varepsilon}$ by diagonalizing **F**. Because of the nonorthogonal basis, we need to reformulate the eigenvalue problem $\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$.

3.4.5 Orthogonalization of the Basis

The basis sets that are used in molecular calculations are not orthonormal sets. The basis functions are normalized, but they are not orthogonal to each other. This gives rise to the overlap matrix in Roothaan's equations. In order to put Roothaan's equations into the form of the usual matrix eigenvalue problem, we need to consider procedures for orthogonalizing the basis functions.

If we have a set of functions $\{\phi_\mu\}$ that are not orthogonal, i.e.,

$$\int d\mathbf{r}\ \phi_\mu^*(\mathbf{r})\phi_\nu(\mathbf{r}) = S_{\mu\nu} \tag{3.161}$$

then it will always be possible to find a transformation matrix **X** (not unitary) such that a transformed set of functions $\{\phi'_\mu\}$ given by

$$\phi'_\mu = \sum_\nu X_{\nu\mu}\phi_\nu \qquad \mu = 1, 2, \ldots, K \tag{3.162}$$

do form an orthonormal set, i.e.,

$$\int d\mathbf{r}\ \phi'^*_\mu(\mathbf{r})\phi'_\nu(\mathbf{r}) = \delta_{\mu\nu} \tag{3.163}$$

To derive the properties of $\mathbf{X}$, we substitute the transformation (3.162) into (3.163) to get

$$\begin{aligned}\int d\mathbf{r}\; \phi'^*_\mu(\mathbf{r})\phi'_\nu(\mathbf{r}) &= \int d\mathbf{r} \left[\sum_\lambda X^*_{\lambda\mu}\phi^*_\lambda(\mathbf{r})\right]\left[\sum_\sigma X_{\sigma\nu}\phi_\sigma(\mathbf{r})\right] \\ &= \sum_\lambda\sum_\sigma X^*_{\lambda\mu}\int d\mathbf{r}\; \phi^*_\lambda(\mathbf{r})\phi_\sigma(\mathbf{r})X_{\sigma\nu} \\ &= \sum_\lambda\sum_\sigma X^*_{\lambda\mu}S_{\lambda\sigma}X_{\sigma\nu} = \delta_{\mu\nu} \qquad (3.164)\end{aligned}$$

This last equation can be written as the matrix equation

$$\mathbf{X}^\dagger\mathbf{S}\mathbf{X} = \mathbf{1} \qquad (3.165)$$

and defines the relation that the matrix $\mathbf{X}$ must satisfy if the transformed orbitals are to form an orthonormal set. As we shall see later, $\mathbf{X}$ must also be nonsingular, i.e., it must possess an inverse $\mathbf{X}^{-1}$. We now proceed to show how to obtain two different transformation matrices $\mathbf{X}$. Since $\mathbf{S}$ is Hermitian it can be diagonalized by a unitary matrix $\mathbf{U}$,

$$\mathbf{U}^\dagger\mathbf{S}\mathbf{U} = \mathbf{s} \qquad (3.166)$$

where $\mathbf{s}$ is a diagonal matrix of the eigenvalues of $\mathbf{S}$.

Exercise 3.15 Use the definition of $S_{\mu\nu} = \int d\mathbf{r}\; \phi^*_\mu\phi_\nu$ to show that the eigenvalues of $\mathbf{S}$ are all positive. *Hint:* consider $\sum_\nu S_{\mu\nu}c^i_\nu = s_i c^i_\mu$, multiply by c^{i*}_μ and sum, where $\mathbf{c}^i$ is the ith column of $\mathbf{U}$.

There are two ways of orthogonalizing the basis set $\{\phi_\mu\}$ in common use. The first procedure, called *symmetric orthogonalization*, uses the inverse square root of $\mathbf{S}$ for $\mathbf{X}$

$$\mathbf{X} \equiv \mathbf{S}^{-1/2} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger \qquad (3.167)$$

If you will recall from the discussion of functions of a matrix in Chapter 1, we can form $\mathbf{S}^{-1/2}$ by diagonalizing $\mathbf{S}$ to form $\mathbf{s}$, then taking the inverse square root of each of the eigenvalues to form the diagonal matrix $\mathbf{s}^{-1/2}$ and then "undiagonalizing" by the transformation in (3.167). If $\mathbf{S}$ is Hermitian then $\mathbf{S}^{-1/2}$ is also Hermitian. Substituting (3.167) into (3.165),

$$\mathbf{S}^{-1/2}\mathbf{S}\mathbf{S}^{-1/2} = \mathbf{S}^{-1/2}\mathbf{S}^{1/2} = \mathbf{S}^0 = \mathbf{1} \qquad (3.168)$$

shows that $\mathbf{X} = \mathbf{S}^{-1/2}$ is indeed an orthogonalizing transformation matrix. Since the eigenvalues of $\mathbf{S}$ are all positive (Exercise 3.15), there is no difficulty in (3.167) of taking square roots. However, if there is linear dependence or near linear dependence in the basis set, then some of the eigenvalues will approach zero and (3.167) will involve dividing by quantities that are nearly zero. Thus symmetric orthogonalization will lead to problems in numerical precision for basis sets with near linear dependence.

A second way of obtaining an orthonormal set of basis functions is called *canonical orthogonalization*. It uses the transformation matrix

$$\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2} \tag{3.169}$$

that is, the columns of the unitary matrix $\mathbf{U}$ are divided by the square root of the corresponding eigenvalue

$$X_{ij} = U_{ij}/s_j^{1/2} \tag{3.170}$$

Substituting this definition of $\mathbf{X}$ into (3.165) gives

$$\mathbf{X}^\dagger\mathbf{S}\mathbf{X} = (\mathbf{U}\mathbf{s}^{-1/2})^\dagger\mathbf{S}\mathbf{U}\mathbf{s}^{-1/2} = \mathbf{s}^{-1/2}\mathbf{U}^\dagger\mathbf{S}\mathbf{U}\mathbf{s}^{-1/2} = \mathbf{s}^{-1/2}\mathbf{s}\mathbf{s}^{-1/2} = \mathbf{1} \tag{3.171}$$

showing that $\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2}$ is also an orthogonalizing transformation matrix. It appears, from (3.170), that this orthogonalization procedure will also entail difficulties if there is linear dependence in the basis set, i.e., if any of the eigenvalues s_i approach zero. We can circumvent this problem with canonical orthogonalization, however. In the matrix eigenvalue problem (3.166), we can order the eigenvalues in any way in the diagonal matrix $\mathbf{s}$, provided we order the columns of $\mathbf{U}$ in the same way. Suppose we order the positive eigenvalues s_i in the order $s_1 > s_2 > s_3 > \cdots$. Upon inspection we may decide that the last m of these are too small and will give numerical problems. We can then use as a transformation matrix, the truncated matrix $\tilde{\mathbf{X}}$,

$$\tilde{\mathbf{X}} = \begin{pmatrix} U_{1,1}/s_1^{1/2} & U_{1,2}/s_2^{1/2} & \cdots & U_{1,K-m}/s_{K-m}^{1/2} \\ U_{2,1}/s_1^{1/2} & U_{2,2}/s_2^{1/2} & \cdots & U_{2,K-m}/s_{K-m}^{1/2} \\ \vdots & \vdots & & \vdots \\ U_{K,1}/s_1^{1/2} & U_{K,2}/s_2^{1/2} & \cdots & U_{K,K-m}/s_{K-m}^{1/2} \end{pmatrix} \tag{3.172}$$

where we have eliminated the last m columns of $\mathbf{X}$ to give the $K \times (K-m)$ matrix $\tilde{\mathbf{X}}$. With this truncated transformation matrix, we get only $K-m$ transformed orthonormal basis functions

$$\phi'_\mu = \sum_{\nu=1}^{K} \tilde{X}_{\nu\mu}\phi_\nu \qquad \mu = 1, 2, \ldots, K-m \tag{3.173}$$

These would span exactly the same region of space as the original set, provided the eliminated eigenvalues were exactly zero. In practice, one often finds linear dependence problems with eigenvalues in the region $s_i \leq 10^{-4}$ (depending, of course, on the machine precision of the calculation). In eliminating the columns with these eigenvalues one is "throwing away" part of the basis set, but only a very small part.

One way of dealing with the problem of a nonorthogonal basis set would thus be to orthogonalize the functions $\{\phi_\mu\}$ to obtain the transformed basis functions $\{\phi'_\mu\}$ and work with these orthonormal functions throughout. This would eliminate the overlap matrix S from Roothaan's equations, which could then be solved just by diagonalizing the Fock matrix. This would mean, however, that we would have to calculate all our two-electron integrals using the new orbitals or else transform all the old integrals $(\mu\nu|\lambda\sigma)$ to set $(\mu'\nu'|\lambda'\sigma')$. In practice this is very time consuming, and we can solve the same problem in a more efficient way. Consider a new coefficient matrix $\mathbf{C}'$ related to the old coefficient matrix $\mathbf{C}$ by

$$\mathbf{C}' = \mathbf{X}^{-1}\mathbf{C} \qquad \mathbf{C} = \mathbf{X}\mathbf{C}' \tag{3.174}$$

where we have assumed that $\mathbf{X}$ possesses an inverse. This will be the case if we have eliminated linear dependencies. Substituting $\mathbf{C} = \mathbf{X}\mathbf{C}'$ into the Roothaan equations gives

$$\mathbf{F}\mathbf{X}\mathbf{C}' = \mathbf{S}\mathbf{X}\mathbf{C}'\boldsymbol{\varepsilon} \tag{3.175}$$

Multiplying on the left by $\mathbf{X}^\dagger$ gives

$$(\mathbf{X}^\dagger\mathbf{F}\mathbf{X})\mathbf{C}' = (\mathbf{X}^\dagger\mathbf{S}\mathbf{X})\mathbf{C}'\boldsymbol{\varepsilon} \tag{3.176}$$

If we define a new matrix $\mathbf{F}'$ by

$$\mathbf{F}' = \mathbf{X}^\dagger\mathbf{F}\mathbf{X} \tag{3.177}$$

and use (3.165), then

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\boldsymbol{\varepsilon} \tag{3.178}$$

These are the transformed Roothaan equations, which can be solved for $\mathbf{C}'$ by diagonalizing $\mathbf{F}'$. Given $\mathbf{C}'$, then $\mathbf{C}$ can be obtained from (3.174). Therefore, given $\mathbf{F}$, we can use (3.177), (3.178), and (3.174) to solve the Roothaan equations $\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$ for $\mathbf{C}$ and $\boldsymbol{\varepsilon}$. The intermediate primed matrices are just the Fock matrix and expansion coefficients in the orthogonalized basis, i.e.,

$$\psi_i = \sum_{\mu=1}^{K} C'_{\mu i}\phi'_\mu \qquad i = 1, 2, \ldots, K \tag{3.179}$$

$$F'_{\mu\nu} = \int d\mathbf{r}_1\ \phi'^*_\mu(1)f(1)\phi'_\nu(1) \tag{3.180}$$

Exercise 3.16 Use (3.179), (3.180), and (3.162) to derive (3.174) and (3.177).

3.4.6 The SCF Procedure

With the background of the previous sections we are now in a position to describe the actual computational procedure for obtaining restricted closed-shell Hartree-Fock wave functions for molecules, i.e., wave functions $|\Psi_0\rangle$. Some authors restrict the term Hartree-Fock solution to one that is at the

Hartree-Fock limit, where the basis set is essentially complete, and use the term self-consistent-field (SCF) solution for one obtained with a finite, possibly small, basis set. We use the terms Hartree-Fock and SCF interchangeably, however, and specifically refer to the Hartree-Fock limit when necessary. The SCF procedure is as follows:

1. Specify a molecule (a set of nuclear coordinates $\{\mathbf{R}_A\}$, atomic numbers $\{Z_A\}$, and number of electrons N) and a basis set $\{\phi_\mu\}$.
2. Calculate all required molecular integrals, $S_{\mu\nu}$, $H_{\mu\nu}^{\text{core}}$, and $(\mu\nu|\lambda\sigma)$.
3. Diagonalize the overlap matrix $\mathbf{S}$ and obtain a transformation matrix $\mathbf{X}$ from either (3.167) or (3.169).
4. Obtain a guess at the density matrix $\mathbf{P}$.
5. Calculate the matrix $\mathbf{G}$ of equation (3.154) from the density matrix $\mathbf{P}$ and the two-electron integrals $(\mu\nu|\lambda\sigma)$.
6. Add $\mathbf{G}$ to the core-Hamiltonian to obtain the Fock matrix $\mathbf{F} = \mathbf{H}^{\text{core}} + \mathbf{G}$.
7. Calculate the transformed Fock matrix $\mathbf{F}' = \mathbf{X}^\dagger\mathbf{F}\mathbf{X}$.
8. Diagonalize $\mathbf{F}'$ to obtain $\mathbf{C}'$ and $\boldsymbol{\varepsilon}$.
9. Calculate $\mathbf{C} = \mathbf{X}\mathbf{C}'$.
10. Form a new density matrix $\mathbf{P}$ from $\mathbf{C}$ using Eq. (3.145).
11. Determine whether the procedure has converged, i.e., determine whether the new density matrix of step (10) is the same as the previous density matrix within a specified criterion. If the procedure has not converged, return to step (5) with the new density matrix.
12. If the procedure has converged, then use the resultant solution, represented by $\mathbf{C}, \mathbf{P}, \mathbf{F}$, etc., to calculate expectation values and other quantities of interest.

We will describe the calculation of expectation values like the energy, dipole moment, etc., and other quantities of interest like population analyses shortly (Subsection 3.4.7) but let us first consider some of the practical questions involved in each of the twelve steps.

Within the Born-Oppenheimer approximation, what we have done in the above procedure is to determine an electronic wave function $|\Psi_0\rangle$ (and hence an electronic energy E_0) for a collection of N electrons in the field of a set of M point charges (the M nuclei with charges Z_A). By adding the classical nuclear-nuclear repulsion to the electronic energy we will have a total energy as a function of a set of nuclear coordinates $\{\mathbf{R}_A\}$. By repeating the calculation for different nuclear coordinates we can then explore the potential energy surface for nuclear motion. A common calculation is to find the set $\{\mathbf{R}_A\}$ which minimize this total energy; this is a calculation of the equilibrium geometry of a molecule. The procedure is valid for any collection of point charges. In particular, "supermolecule" calculations, which use a set of nuclear charges representative of more than one molecule, are common for exploring, for example, intermolecular forces.

Having chosen a set of nuclear coordinates, the calculation of a restricted closed-shell single determinant wave function is then completely specified by the set of basis functions $\{\phi_\mu\}$. As such, this is an example of an *ab initio* calculation which makes no approximation to the integrals or the electronic Hamiltonian, but is completely specified by the choice of a basis set and the coordinates of the nuclei. The choice of a basis set is more of an art than a science. One is obviously limited by computer facilities, budget, etc. to a rather small, finite set of functions. One must, therefore, be rather judicious in the choice of a basis set. Only Slater- and Gaussian-type functions are currently in common use. If one uses a very small set of functions per atom, then Slater-type functions give definitely superior energies. As the number of functions per atom increases, the clear cut superiority of Slater-type functions is somewhat diminished. As well as the ability of the basis set to span the function space, however, one has to consider, for practical reasons, the time required to evaluate molecular integrals. Most polyatomic calculations now use Gaussian orbitals because of the speed with which integrals can be evaluated, and in this book we will emphasize Gaussian basis functions. Basis functions are discussed in Section 3.6 of this chapter, and the 1*s* STO-3G basis is discussed in Subsection 3.5.1, prior to its use in model calculations on H_2 and HeH^+.

Having defined a basis set, one then needs to calculate and store a number of different types of integrals. Appendix A describes molecular integral evaluation using Gaussian basis functions; we will only mention a few pertinent points here. The overlap integrals and the one-electron integrals that are needed for the core-Hamiltonian and one-electron expectation values, described later, are relatively trivial compared to the two-electron repulsion integrals, primarily because of the much smaller number of one-electron integrals. The major difficulty of a large calculation is the evaluation and handling of large numbers of two-electron integrals. If there are K basis functions, then there will be of the order of $K^4/8$ (see Exercise 3.14) unique two-electron integrals. These can quickly run into the millions even for small basis sets on moderately sized molecules. The problem is not quite this bad since many integrals will be effectively zero for large molecules, as the distance between basis functions becomes large. A number of integrals may also be zero because of molecular symmetry. There will almost always be, however, too many two-electrons integrals to store them all in main computer memory. One common procedure is to store all nonzero integrals in random order on an external magnetic disk or tape, associating with each integral a label identifying the indices μ, ν, λ, and σ.

In the last subsection we described two ways of orthogonalizing the basis set or deriving a transformation $\mathbf{X}$, which enables one to solve Roothaan's equations by a diagonalization. The use of $\mathbf{X} = \mathbf{S}^{-1/2}$ is conceptually simple, and only in unusual situations, where linear dependence in the basis set is a problem, does one need to use canonical orthogonalization. With canonical orthogonalization, columns of $\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2}$ can just be dropped to give a rectangular matrix. If m columns of $\mathbf{X}$ are deleted, one will effectively be using a basis set of size $K - m$ and one will obtain $K - m$ molecular orbitals ψ_i, i.e., $\mathbf{F}'$ will be a $(K - m) \times (K - m)$ matrix and $\mathbf{C}'$ will be a $K \times (K - m)$ matrix, with columns describing the $K - m$ molecular orbitals in terms of the original K basis functions.

The simplest possible guess at the density matrix $\mathbf{P}$ is to use a null (zero) matrix. This is equivalent to approximating $\mathbf{F}$ as $\mathbf{H}^{\text{core}}$ and neglecting all electron-electron interactions in the first iteration. This is a very convenient way of starting the iteration procedure. It corresponds to approximating the converged molecular orbitals by those describing a single electron in the field of the nuclear point charges. The molecular orbitals for the N-electron molecule may be quite different from those for the corresponding one-electron molecule, however, and the SCF procedure will often not converge with the core-Hamiltonian as an initial guess to the Fock matrix. A semi-empirical extended Hückel type calculation, with an "effective" $\mathbf{F}$, is often used for an initial guess at the wave function and, commonly, provides a better guess than just using the core-Hamiltonian. There are clearly many ways one could generate an initial guess.

The major time-consuming part of the actual iteration procedure is the assembling of the two-electron integrals and density matrix into the matrix $\mathbf{G}$ in step (5). If the integrals are stored in random order with associated labels on an external device, then as they are read into main memory one uses the label, i.e., the indices μ, ν, λ, and σ identifying the integral, to determine which elements of the density matrix to multiply by and to which elements of the $\mathbf{G}$ matrix the products must be added, according to the expression for the $\mathbf{G}$ matrix given by Eq. (3.154).

In most calculations, the matrix operations in steps (6) to (10) are not time consuming relative to the formation of the $\mathbf{G}$ matrix, provided one uses an efficient diagonalization procedure.

Because the Roothan equations are nonlinear equations, the simple iteration procedure we have outlined here will not always converge. It may oscillate or diverge, possibly because of a poor initial guess. If it oscillates, averaging successive density matrices may help. If it does converge, it may do so only slowly. With two or more successive density matrices, various extrapolation procedures can be devised. Convergence problems are not unusual, but also are not a major problem for many calculations. The iterative procedure we have described is perhaps the simplest procedure one might try, but it also is somewhat naive. A number of other techniques have been suggested for ensuring or accelerating convergence to the SCF solution.

One, of course, requires a criterion for establishing convergence, and it is not uncommon simply to observe the total electronic energy of each iteration and require that two successive values differ by no more than a small quantity δ. A value of $\delta = 10^{-6}$ Hartrees is adequate for most purposes. We will show shortly that the energy of each iteration can be calculated without due expense. Alternatively, one might require convergence for elements of the density matrix, by requiring the standard deviation of successive density matrix elements, i.e., the quantity

$$\left[K^{-2} \sum_{\mu} \sum_{\nu} [P_{\mu\nu}^{(i)} - P_{\mu\nu}^{(i-1)}]^2\right]^{1/2}$$

to be less than δ. A value of $\delta = 10^{-4}$ for the error in the density matrix will usually give an error in the energy of less than 10^{-6} Hartrees.

We have only been able to touch on a few aspects of the SCF procedure. Research efforts by many groups and large numbers of man-years of programming have gone into the large computer programs, which are currently available, for performing *ab initio* SCF calculations.

3.4.7 Expectation Values and Population Analysis

Once we have a converged value for the density matrix, Fock matrix, etc., there are a number of ways we might use our wave function $|\Psi_0\rangle$ or analyze the results of our calculation. Only some of the more common quantities will be discussed.

The eigenvalues of $\mathbf{F}'$ are the orbital energies ε_i. As we discussed when describing Koopmans' theorem, the occupied orbital energies ε_a constitute a prediction of ionization potentials and the virtual orbital energies ε_r constitute a prediction of electron affinities. The values of $-\varepsilon_a$ are commonly a reasonable approximation to the observed ionization potentials, but $-\varepsilon_r$ is usually of little use, even for a qualitative understanding of electron affinities.

The total electronic energy is the expectation value $E_0 = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle$ and, as we have seen a number of times now, it is given by

$$E_0 = 2 \sum_{a}^{N/2} h_{aa} + \sum_{a}^{N/2} \sum_{b}^{N/2} 2J_{ab} - K_{ab} \tag{3.181}$$

With definition (3.147) of the Fock operator, we have

$$\varepsilon_a = f_{aa} = h_{aa} + \sum_{b}^{N/2} 2J_{ab} - K_{ab} \tag{3.182}$$

and, therefore, we can write the energy as

$$E_0 = \sum_{a}^{N/2} (h_{aa} + f_{aa}) = \sum_{a}^{N/2} (h_{aa} + \varepsilon_a) \tag{3.183}$$

This is a convenient result; if we substitute the basis function expansion (3.133) for the molecular orbitals into this expression, we obtain a formula for the energy, which is readily evaluated from quantities available at any stage of the SCF iteration procedure, i.e.,

$$E_0 = \frac{1}{2}\sum_{\mu}\sum_{\nu} P_{\nu\mu}(H_{\mu\nu}^{\text{core}} + F_{\mu\nu}) \tag{3.184}$$

Exercise 3.17 Derive Equation (3.184) from (3.183)

If E_0 is calculated from (3.184) using the same matrix **P** as was used to form **F**, then E_0 will be an upper bound to the true energy at any stage of the iteration and will usually converge monotonically from above to the converged result. If one adds the nuclear-nuclear repulsion to the electronic energy E_0 one obtains the total energy E_{tot}

$$E_{\text{tot}} = E_0 + \sum_{A}\sum_{B>A} \frac{Z_A Z_B}{R_{AB}} \tag{3.185}$$

This is commonly the quantity of most interest, particularly in structure determinations, because the predicted equilibrium geometry of a molecule occurs when E_{tot} is a minimum.

Most of the properties of molecules that one might evaluate from a molecular wave function, such as the dipole moment, quadrupole moment, field gradient at a nucleus, diamagnetic susceptibility, etc., are described by sums of one-electron operators of the general form

$$\mathscr{O}_1 = \sum_{i=1}^{N} h(i) \tag{3.186}$$

where $h(i)$ is not necessarily the core-Hamiltonian here, but any operator depending only on the coordinates of a single electron. From the rules for matrix elements, expectation values for such operators will always have the form

$$\langle \mathscr{O}_1 \rangle = \langle \Psi_0 | \mathscr{O}_1 | \Psi_0 \rangle = \sum_{a}^{N/2} (\psi_a | h | \psi_a) = \sum_{\mu\nu} P_{\mu\nu} (\nu | h | \mu) \tag{3.187}$$

so that, in addition to the density matrix, we need only evaluate the set of one-electron integrals $(\mu|h|\nu)$ to calculate one-electron expectation values. We will use the dipole moment to illustrate such a calculation.

The classical definition of the dipole moment of a collection of charges q_i with position vectors $\mathbf{r}_i$ is

$$\vec{\mu} = \sum_{i} q_i \mathbf{r}_i \tag{3.188}$$

The corresponding definition for a quantum mechanical calculation on a molecule is

$$\vec{\mu} = \left\langle \Psi_0 \middle| -\sum_{i=1}^{N} \mathbf{r}_i \middle| \Psi_0 \right\rangle + \sum_{A} Z_A \mathbf{R}_A \tag{3.189}$$

where the first term is the contribution (quantum mechanical) of the electrons, of charge -1, and the second term is the contribution (classical) of the nuclei, of charge Z_A, to the dipole moment. The electronic dipole operator is $-\sum_{i=1}^{N} \mathbf{r}_i$, a sum of one-electron operators. Therefore, using (3.187), we have

$$\vec{\mu} = -\sum_{\mu}\sum_{\nu} P_{\mu\nu}(\nu|\mathbf{r}|\mu) + \sum_{A} Z_A \mathbf{R}_A \tag{3.190}$$

this is a vector equation with components (for example the x component) given by

$$\mu_x = -\sum_{\mu}\sum_{\nu} P_{\mu\nu}(\nu|x|\mu) + \sum_{A} Z_A X_A \tag{3.191}$$

and to calculate the dipole moment we need in addition to **P** only the dipole integrals

$$(\nu|x|\mu) = \int d\mathbf{r}_1 \, \phi_\nu^*(\mathbf{r}_1) x_1 \phi_\mu(\mathbf{r}_1) \tag{3.192}$$

with corresponding values for the y and z components.

The charge density

$$\rho(\mathbf{r}) = \sum_{\mu}\sum_{\nu} P_{\mu\nu}\phi_\mu(\mathbf{r})\phi_\nu^*(\mathbf{r}) \tag{3.193}$$

representing the probability of finding an electron in various regions of space, is commonly pictured by contour maps for various planes drawn through the molecule. There is no unique definition of the number of electrons to be associated with a given atom or nucleus in a molecule, but it is still sometimes useful to perform such population analyses. Since

$$N = 2\sum_{a}^{N/2} \int d\mathbf{r} |\psi_a(\mathbf{r})|^2 \tag{3.194}$$

divides the total number of electrons into two electrons per molecular orbital, by substituting the basis expansion of ψ_a into (3.194), we have

$$N = \sum_{\mu}\sum_{\nu} P_{\mu\nu}S_{\nu\mu} = \sum_{\mu} (\mathbf{PS})_{\mu\mu} = \operatorname{tr} \mathbf{PS} \tag{3.195}$$

and it is possible to interpret $(\mathbf{PS})_{\mu\mu}$ as the number of electrons to be associated with ϕ_μ. This is called a *Mulliken population analysis.* Assuming the basis functions are centered on atomic nuclei, the corresponding number of electrons to be associated with a given atom in a molecule are obtained by summing over all basis functions centered on that atom. The net charge associated with an atom is then given by

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu} \tag{3.196}$$

where Z_A is the charge of atomic nucleus A; the index of summation indicates that we only sum over the basis functions centered on A.

The definition (3.195) is by no means unique. Since tr **AB** = tr **BA**,

$$N = \sum_{\mu} (\mathbf{S}^{\alpha}\mathbf{P}\mathbf{S}^{1-\alpha})_{\mu\mu} \tag{3.197}$$

for any α. With $\alpha = 1/2$, we have

$$N = \sum_{\mu} (\mathbf{S}^{1/2}\mathbf{P}\mathbf{S}^{1/2})_{\mu\mu} = \sum_{\mu} \mathbf{P}'_{\mu\mu} \tag{3.198}$$

where we can show that $\mathbf{P}'$ is the density matrix in terms of a symmetrically orthogonalized basis set,

$$\rho(\mathbf{r}) = \sum_{\mu}\sum_{\nu} P'_{\mu\nu}\phi'_{\mu}(\mathbf{r})\phi'^{*}_{\nu}(\mathbf{r}) \tag{3.199}$$

$$\phi'_{\mu}(\mathbf{r}) = \sum_{\nu} (\mathbf{S}^{-1/2})_{\nu\mu}\phi_{\nu}(\mathbf{r}) \tag{3.200}$$

The diagonal elements of $\mathbf{P}'$ are commonly used for a *Löwdin population analysis*

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{S}^{1/2}\mathbf{P}\mathbf{S}^{1/2})_{\mu\mu} \tag{3.201}$$

Exercise 3.18 Derive the right-hand side of Eq. (3.198), i.e., show that $\alpha = 1/2$ is equivalent to a population analysis based on the diagonal elements of $\mathbf{P}'$.

None of these population analysis schemes is unique, but they are often useful when comparing different molecules using the same type of basis set for each molecule. The basis sets must be "balanced" as can be illustrated by a simple example. It is possible to have a complete set of basis functions by placing them all at one center, on oxygen, for example, in an H_2O calculation. A population analysis would then suggest that the H atoms in water have a charge of +1 and that all the electrons reside on the oxygen. This example makes it obvious that care must be used in assigning physical significance to any population analysis.

3.5 MODEL CALCULATIONS ON H_2 AND HeH^+

We have discussed and will subsequently discuss a number of formal mathematical procedures associated with solutions to the many-electron problem. The ideas and concepts that we are presenting may appear to be rather formidable and difficult to the uninitiated. With only a formal presentation, it is unlikely that this situation would be radically altered. We want, for the reader's benefit, to avoid the burden of endless formalism, without hint of application. We particularly feel that what appears at the outset as a somewhat obscure formal theory is usually made clear by application to a simple, but nevertheless realistic, model system. In this section we apply the closed-shell Hartree-Fock procedure to the model systems H_2 and HeH^+.

The two-electron molecules H_2 and HeH^+ are prototypes for homonuclear and heteronuclear diatomic molecules. We will consider both molecules in the approximation of a *minimal basis set*, i.e., a basis set $\{\phi_\mu\}$ consisting of only two functions, one on each nucleus. The limitation of these models is only in the basis set (and the usual assumption of a nonrelativistic, Born-Oppenheimer electronic Hamiltonian). Larger basis sets would lead to correspondingly more accurate results. Since both molecules are simple two-electron systems, essentially exact calculations, corresponding to an infinite basis set, will be available for comparison with our very approximate calculations. Before describing these calculations, however, we need to introduce the basis set that we will be using.

3.5.1 The 1*s* Minimal STO-3G Basis Set

In Section 3.6 we will describe basis sets for the general polyatomic molecule calculation, including *s*, *p*, and *d*-type basis functions. Here we introduce some of the basic ideas involved in the choice of a basis set, by describing basis functions of the 1*s* type, i.e., those that will be used in our simple calculations on H_2 and HeH^+. Better calculations would use many 1*s* functions and/or 2*p*, 3*d*, etc. functions in the basis set $\{\phi_\mu\}$. The extension of most of the concepts introduced here, for 1*s* functions, to the general case is fairly straightforward.

In a strictly mathematical sense many different kinds of basis set functions ϕ_μ could be used. A variety of choices have been suggested but only two types of basis functions have found common use. The normalized 1*s* *Slater-type function*, centered at $\mathbf{R}_A$, has the form

$$\phi_{1s}^{SF}(\zeta, \mathbf{r} - \mathbf{R}_A) = (\zeta^3/\pi)^{1/2} e^{-\zeta|\mathbf{r} - \mathbf{R}_A|} \tag{3.202}$$

where ζ is the *Slater orbital exponent*. The normalized 1*s* *Gaussian-type function*, centered at $\mathbf{R}_A$, has the form

$$\phi_{1s}^{GF}(\alpha, \mathbf{r} - \mathbf{R}_A) = (2\alpha/\pi)^{3/4} e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2} \tag{3.203}$$

where α is the *Gaussian orbital exponent*. The 2*p*, 3*d*, etc. Slater and Gaussian functions are generalizations of (3.202) and (3.203) that have polynomials in the components of $\mathbf{r} - \mathbf{R}_A$ ($x - X_A$, etc.) multiplying the same exponential ($e^{-\zeta r}$) or Gaussian ($e^{-\alpha r^2}$) fall-off. The orbital exponents, which are positive numbers larger than zero, determine the diffuseness or "size" of the basis functions; a large exponent implies a small dense function, a small exponent implies a large diffuse function. The major differences between the two functions $e^{-\zeta r}$ and $e^{-\alpha r^2}$ occur at $r = 0$ and at large r. At $r = 0$, the Slater function has a finite slope and the Gaussian function has a zero slope,

$$[d/dr\, e^{-\zeta r}]_{r=0} \neq 0 \tag{3.204}$$

$$[d/dr\, e^{-\alpha r^2}]_{r=0} = 0 \tag{3.205}$$

At large values of r, the Gaussian function $e^{-\alpha r^2}$ decays much more rapidly than the Slater function $e^{-\zeta r}$.

For electronic wave function calculations one would prefer to use the Slater functions. They more correctly describe the qualitative features of the molecular orbitals ψ_i than do Gaussian functions, and fewer Slater basis functions than Gaussian basis functions would be needed in the basis function expansion of ψ_i, for comparable results. It is possible to show, for example, that at large distances molecular orbitals decay as $\psi_i \sim e^{-a_i r}$, which is of the Slater rather than the Gaussian form. In particular, the exact solution for the $1s$ orbital of the hydrogen atom is the Slater function $(\pi)^{-1/2}e^{-r}$.

The reason why one considers Gaussian functions at all is that, in an SCF calculation, one must calculate of the order of $K^4/8$ two-electron integrals $(\mu\nu|\lambda\sigma)$. These integrals are of the form

$$(\mu_A\nu_B|\lambda_C\sigma_D) = \int d\mathbf{r}_1\, d\mathbf{r}_2\; \phi_\mu^{A*}(\mathbf{r}_1)\phi_\nu^{B}(\mathbf{r}_1) r_{12}^{-1} \phi_\lambda^{C*}(\mathbf{r}_2)\phi_\sigma^{D}(\mathbf{r}_2) \tag{3.206}$$

where ϕ_μ^A is a basis function on nucleus A, i.e., centered at $\mathbf{R}_A$. The general integral involves four different centers: $\mathbf{R}_A$, $\mathbf{R}_B$, $\mathbf{R}_C$, and $\mathbf{R}_D$. Evaluation of these four-center integrals is very difficult and time-consuming with Slater basis functions. These integrals are relatively easy to evaluate with Gaussian basis functions, however. The reason is that the product of two $1s$ Gaussian functions, each on different centers, is, apart from a constant, a $1s$ Gaussian function on a third center. Thus

$$\phi_{1s}^{\mathrm{GF}}(\alpha, \mathbf{r} - \mathbf{R}_A)\phi_{1s}^{\mathrm{GF}}(\beta, \mathbf{r} - \mathbf{R}_B) = K_{AB}\phi_{1s}^{\mathrm{GF}}(p, \mathbf{r} - \mathbf{R}_P) \tag{3.207}$$

where the constant K_{AB} is

$$K_{AB} = (2\alpha\beta/[(\alpha + \beta)\pi])^{3/4} \exp[-\alpha\beta/(\alpha + \beta)|\mathbf{R}_A - \mathbf{R}_B|^2] \tag{3.208}$$

The exponent of the new Gaussian centered at $\mathbf{R}_P$ is

$$p = \alpha + \beta \tag{3.209}$$

and the third center P is on a line joining the centers A and B,

$$\mathbf{R}_P = (\alpha\mathbf{R}_A + \beta\mathbf{R}_B)/(\alpha + \beta) \tag{3.210}$$

This relationship is shown in Fig. 3.1

Exercise 3.19 Derive Eq. (3.207)

As a result of (3.207), the four-center integral in (3.206) immediately reduces, for $1s$ Gaussians, to the two-center integral

$$(\mu_A\nu_B|\lambda_C\sigma_D) = K_{AB}K_{CD} \int d\mathbf{r}_1\, d\mathbf{r}_2\; \phi_{1s}^{\mathrm{GF}}(p, \mathbf{r}_1 - \mathbf{R}_P) r_{12}^{-1} \phi_{1s}^{\mathrm{GF}}(q, \mathbf{r}_2 - \mathbf{R}_Q) \tag{3.211}$$

These integrals can be readily evaluated as described in Appendix A.

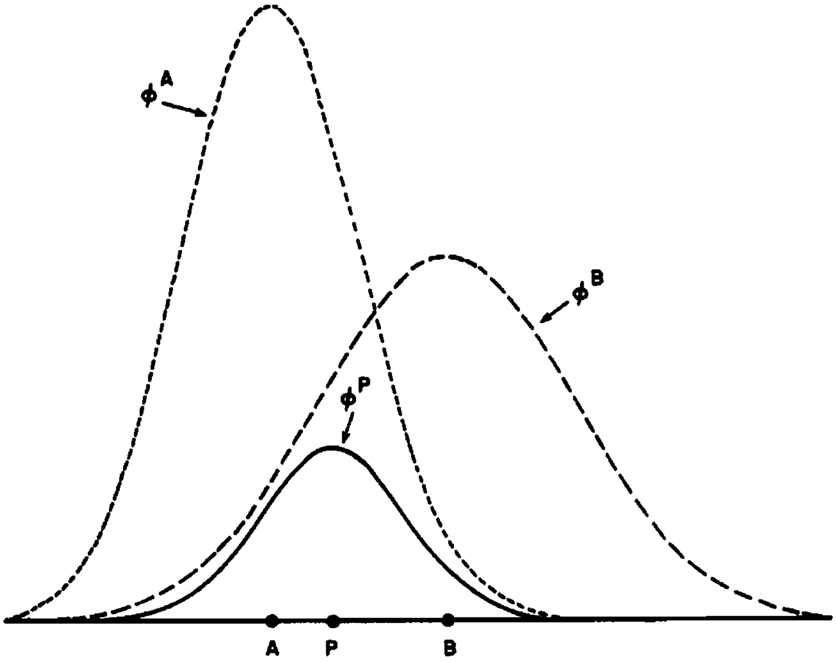


Figure 3.1 The product of two 1*s* Gaussians is a third 1*s* Gaussian.

One is thus faced with somewhat of a dilemma. Two-electron integrals can be calculated rapidly and efficiently with Gaussian functions, but Gaussian functions are not optimum basis functions and have functional behavior different from the known functional behavior of molecular orbitals. One would prefer to use better basis functions. One way around this problem is to use as basis functions fixed linear combinations of the primitive Gaussian functions ϕ_p^{GF}. These linear combinations, called *contractions*, lead to *contracted Gaussian functions* (CGF),

$$\phi_\mu^{\mathrm{CGF}}(\mathbf{r}-\mathbf{R}_A)=\sum_{p=1}^{L} d_{p\mu}\phi_p^{\mathrm{GF}}(\alpha_{p\mu},\mathbf{r}-\mathbf{R}_A) \tag{3.212}$$

where L is the length of the contraction and $d_{p\mu}$ is a contraction coefficient. The pth normalized primitive Gaussian ϕ_p^{GF} in the basis function ϕ_μ^{CGF} has a functional dependence on the Gaussian orbital exponent (contraction exponent) $\alpha_{p\mu}$. By a proper choice of the contraction length, the contraction coefficients, and the contraction exponents, the contracted Gaussian function can be made to assume any functional form consistent with the primitive functions used. If the primitive functions are all 1*s* Gaussians at the same center, then ϕ_μ^{CGF} can only be of *s*-symmetry. Although we will not pursue such possibilities, if the primitive functions were allowed to reside on different centers, the expansion (3.212) could in principle describe any basis function. The idea behind the use of contracted Gaussian functions is to choose in advance the contraction length, contraction coefficients, and contraction exponents that fit the right-hand side of (3.212) to a desirable set of basis functions ϕ_μ^{CGF} and then to use these fixed functions in molecular wave function calculations. That is, the contraction coefficients, etc. are not allowed to change in the course of an SCF calculation. The two-electron integrals $(\mu\nu|\lambda\sigma)$ for the contracted basis set functions $\{\phi_\mu^{\mathrm{CGF}}\}$ can, from (3.212), be evaluated as sums of rapidly calculated two-electron integrals over the primitive Gaussian functions.

By proper choice of the contraction parameters one can thus use basis functions that are approximate atomic Hartree-Fock functions, Slater-type functions, etc., while still evaluating integrals only with primitive Gaussian functions. A procedure that has come into wide use is to fit a Slater-type orbital (STO) to a linear combination of $L = 1, 2, 3, \ldots$ primitive Gaussian functions. This is the STO-LG procedure (the procedure is commonly referred to as STO-NG, but since N represents the number of electrons everywhere in this book, we prefer an alternative symbol). In particular, STO-3G basis sets are often used in polyatomic calculations, in preference to evaluating integrals with Slater functions. We will use STO-3G basis sets for our model calculations on H_2 and HeH^+. We need to explicitly consider the form that the contraction (3.212) takes if ϕ_{1s}^{CGF} is to approximate a $1s$ Slater-type function.

Let us first consider fitting a Slater function having Slater exponent $\zeta = 1.0$. Later we will return to consider other exponents. We will only consider contractions up to length three so that the three fits we seek to find are

$$\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \text{STO-1G}) = \phi_{1s}^{\mathrm{GF}}(\alpha_{11}) \tag{3.213}$$

$$\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \text{STO-2G}) = d_{12}\phi_{1s}^{\mathrm{GF}}(\alpha_{12}) + d_{22}\phi_{1s}^{\mathrm{GF}}(\alpha_{22}) \tag{3.214}$$

$$\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \text{STO-3G}) = d_{13}\phi_{1s}^{\mathrm{GF}}(\alpha_{13}) + d_{23}\phi_{1s}^{\mathrm{GF}}(\alpha_{23}) + d_{33}\phi_{1s}^{\mathrm{GF}}(\alpha_{33}) \tag{3.215}$$

where the ϕ_{1s}^{CGF} ($\zeta = 1.0$, STO-LG) are the basis functions that approximate as best as possible a Slater-type function with $\zeta = 1.0$. We therefore need to find the coefficients $d_{p\mu}$ and exponents $\alpha_{p\mu}$ in (3.213) to (3.215) that provide the best fit. The fitting criterion is one that fits the contracted Gaussian function to the Slater function in a least-squares sense, i.e., we seek to minimize the integral

$$I = \int d\mathbf{r}\, [\phi_{1s}^{\mathrm{SF}}(\zeta = 1.0, \mathbf{r}) - \phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \text{STO-LG}, \mathbf{r})]^2 \tag{3.216}$$

Equivalently, since the two functions in this equation are normalized, one maximizes the overlap between the two functions, i.e., one maximizes

$$S = \int d\mathbf{r}\, \phi_{1s}^{\mathrm{SF}}(\zeta = 1.0, \mathbf{r})\, \phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \text{STO-LG}, \mathbf{r}) \tag{3.217}$$

For the STO-1G case there are no contraction coefficients, and we only need to find the primitive Gaussian exponent α which maximizes the overlap

$$S = (\pi)^{-1/2}(2\alpha/\pi)^{3/4} \int d\mathbf{r}\, e^{-r} e^{-\alpha r^2} \tag{3.218}$$

Table 3.1 Overlap of a 1*s* Slater function ($\zeta = 1.0$) and a 1*s* Gaussian function

$$S = \int d\mathbf{r}\, \phi_{1s}^{\mathrm{SF}}(\zeta = 1.0)\, \phi_{1s}^{\mathrm{GF}}(\alpha)$$

α	S
0.1	0.8641
0.2	0.9673
0.3	0.9772
0.4	0.9606
0.5	0.9355

$\alpha_{\mathrm{optimum}} = 0.270950$

This overlap is shown in Table 3.1. The optimum fit occurs for $\alpha = 0.270950$ and is shown in Fig. 3.2a. The corresponding radial distribution functions ($4\pi r^2|\phi_{1s}(r)|^2$) are compared in Fig. 3.2b. Notice the different behavior near the origin and the more rapid fall-off of the Gaussian function at large r. The overlaps S of (3.217) can be maximized for the STO-2G and STO-3G cases also and, if one does so, the optimum fits are as follows:

$$\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \text{STO-1G}) = \phi_{1s}^{\mathrm{GF}}(0.270950) \tag{3.219}$$

$$\begin{aligned}\phi_{1s}^{\mathrm{CGF}}&(\zeta = 1.0, \text{STO-2G})\\ &= 0.678914\phi_{1s}^{\mathrm{GF}}(0.151623) + 0.430129\phi_{1s}^{\mathrm{GF}}(0.851819)\end{aligned} \tag{3.220}$$

$$\begin{aligned}\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \text{STO-3G}) &= 0.444635\phi_{1s}^{\mathrm{GF}}(0.109818) + 0.535328\,\phi_{1s}^{\mathrm{GF}}(0.405771)\\ &\quad + 0.154329\phi_{1s}^{\mathrm{GF}}(2.22766)\end{aligned} \tag{3.221}$$

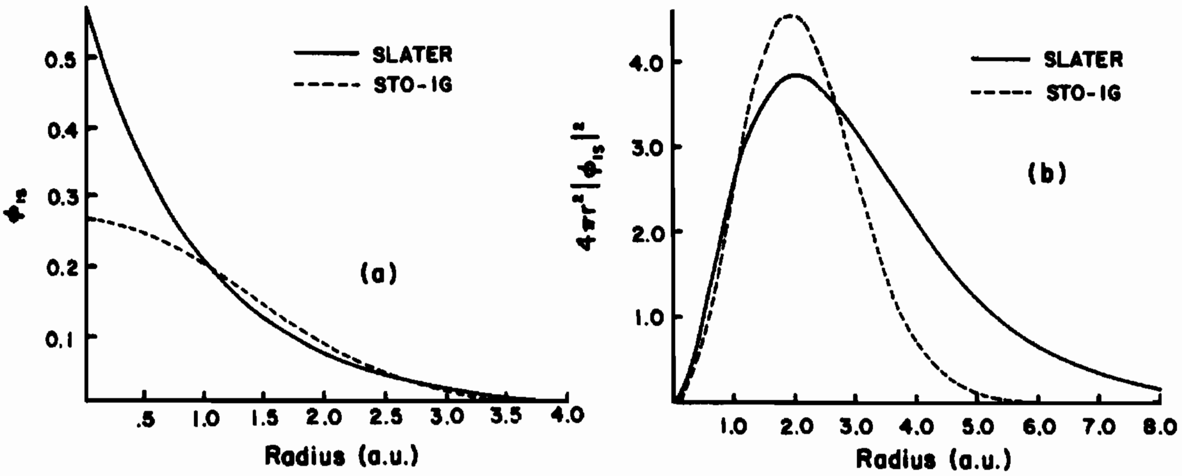


Figure 3.2 Comparison of a Slater function with a Gaussian function: a) least squares fit of a 1*s* Slater function ($\zeta = 1.0$) by a single STO-1G 1*s* Gaussian function ($\alpha = 0.270950$); b) comparison of the corresponding radial distribution functions ($4\pi r^2|\phi_{1s}(r)|^2$).

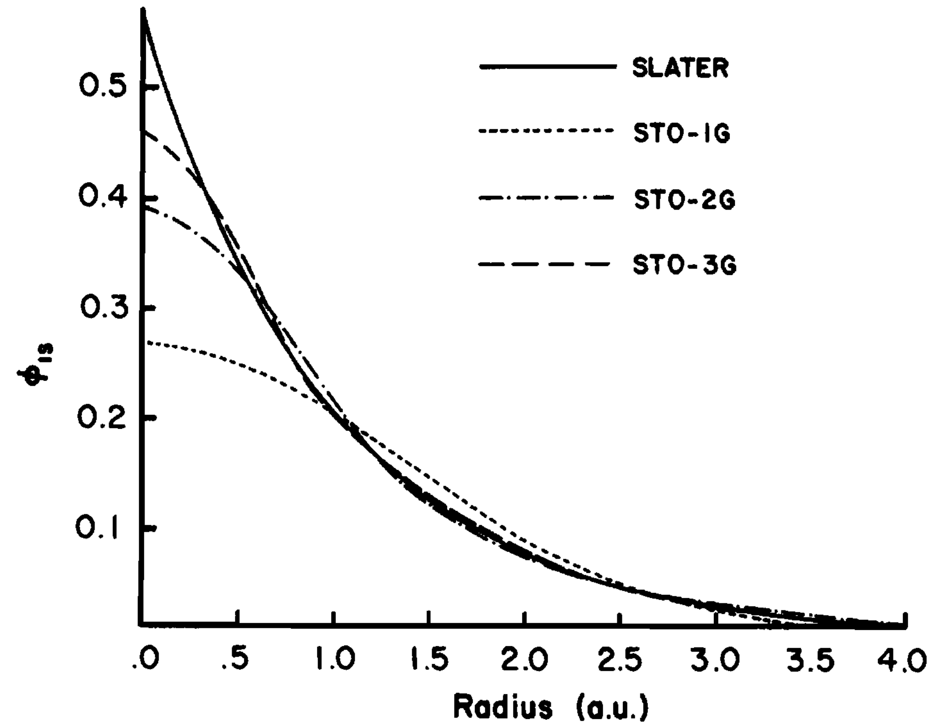


Figure 3.3 Comparison of the quality of the least-squares fit of a 1*s* Slater function ($\zeta = 1.0$) obtained at the STO-1G, STO-2G, and STO-3G levels.

Figure 3.3 illustrates the improvement of the fit to a Slater 1*s* function ($\zeta = 1.0$) obtained by increasing the number of Gaussians in the contraction (i.e., upon going from STO-1G to STO-2G to STO-3G).

Exercise 3.20 Calculate the values of $\phi(\mathbf{r})$ at the origin for the three STO-LG contracted functions and compare with the value of $(\pi)^{-1/2}$ for a Slater function ($\zeta = 1.0$).

The STO-LG fits to a Slater function, given in Eqs. (3.219) to (3.221), are for a Slater exponent of $\zeta = 1.0$. How does one obtain a fit to a Slater function with a different orbital exponent? The orbital exponents are scale factors which scale the function in r, i.e., they expand or contract the function, but do not change its functional form. Because the scale factors multiply r as follows,

$$e^{-[\zeta r]} \leftrightarrow e^{-[\sqrt{\alpha} r]^2} \tag{3.222}$$

the proper scaling is

$$\zeta'/\zeta = [\alpha'/\alpha]^{1/2} \tag{3.223}$$

The appropriate contraction exponents α for fitting to a Slater function with orbital exponent ζ are thus

$$\alpha = \alpha(\zeta = 1.0) \times \zeta^2 \tag{3.224}$$

If the Slater exponent doubles, the contraction exponents should be multiplied by a factor of four. This scaling procedure is quite general and contraction parameters need only be determined once for a given type of basis function ϕ_μ^{CGF}. If a different scale factor for ϕ_μ^{CGF} is required, the contraction exponents can be appropriately scaled. The usual description of the STO-3G basis set includes a standard set of Slater orbital exponents ζ, for basis functions centered on particular atoms. For example, the standard exponent for the 1*s* basis function of hydrogen is $\zeta = 1.24$. This is larger than the $\zeta = 1.0$ exponent of the hydrogen atom, since the hydrogen 1*s* orbital in average molecules is known to be "smaller" or "denser" than in the atom. Using the scaling relation (3.224), the standard STO-3G basis function for hydrogen becomes,

$$\begin{aligned}\phi_{1s}^{\text{CGF}}(\zeta = 1.24, \text{STO-3G}) = {} & 0.444635\phi_{1s}^{\text{GF}}(0.168856) + 0.535328\phi_{1s}^{\text{GF}}(0.623913) \\ & + 0.154329\phi_{1s}^{\text{GF}}(3.42525) \qquad (3.225)\end{aligned}$$

This is the basis function we will use for H in our following calculations.

3.5.2 STO-3G H_2

In Subsection 2.2.5 we presented our minimal basis H_2 model, which has only one occupied molecular orbital and one virtual molecular orbital. With the description of the 1*s* minimal STO-3G basis set given in the last subsection we are now in a position to illustrate *ab initio* Hartree-Fock calculations on H_2. The model is simple but extension to larger basis sets is relatively straightforward and most of the aspects of Hartree-Fock theory that we wish to illustrate here are independent of the actual size of the basis set. Unfortunately, however, the model is too simple to be able to illustrate the iterative nature of the SCF procedure. In the next subsection we describe a minimal basis calculation on HeH^+, in order to illustrate this aspect of Hartree-Fock theory.

In this subsection, we describe restricted closed-shell calculations on the ground state of H_2. As we will see, there is a very basic deficiency in such calculations at long bond lengths. Later in this chapter, when we describe unrestricted open-shell calculations, we will return to minimal basis H_2 and partially correct this deficiency. Some of the results obtained here will also be used in later chapters when we use the minimal basis H_2 model to illustrate procedures that go beyond the Hartree-Fock approximation.

According to the steps involved in an SCF calculation, as outlined in Subsection 3.4.6, we must first of all choose a geometry for the nuclear framework. We will use the coordinate system of Fig. 2.5 with an internuclear distance $R = |\mathbf{R}_{12}|$ equal to the experimental value of 1.4 atomic units (Bohr). Our basis set is the standard STO-3G basis set, consisting of two functions ϕ_1 and ϕ_2 where each of these functions is a contraction of three primitive Gaussians such that each constitutes a least-squares fit to a Slater function with orbital exponent $\zeta = 1.24$, as previously illustrated in Eq. (3.225). That is,

$$\begin{aligned} \phi_1(\mathbf{r}) &\simeq (\zeta^3/\pi)^{1/2} e^{-\zeta|\mathbf{r}-\mathbf{R}_1|} \\ \phi_2(\mathbf{r}) &\simeq (\zeta^3/\pi)^{1/2} e^{-\zeta|\mathbf{r}-\mathbf{R}_2|} \\ \zeta &= 1.24 \end{aligned} \tag{3.226}$$

It is important to remember, however, that each basis function has the definite form of (3.225) and that, while the functions approximate Slater functions, there is no approximation being made, other than the Hartree-Fock approximation, once the basis functions are chosen. The next step in the SCF calculation involves the evaluation of all integrals over the basis set $\{\phi_\mu\}$, i.e., $S_{\mu\nu}$, $H_{\mu\nu}^{\text{core}}$, and the two-electron integrals $(\mu\nu|\lambda\sigma)$. All these integrals can be evaluated using formulas developed in Appendix A. Consider the overlap integral,

$$S_{\mu\nu} = \int d\mathbf{r}\; \phi_\mu^{\text{CGF}}(\mathbf{r} - \mathbf{R}_A)\phi_\nu^{\text{CGF}}(\mathbf{r} - \mathbf{R}_B) \tag{3.227}$$

Substituting the general contraction (3.212), this integral reduces to the sum of overlap integrals involving primitive Gaussians. That is,

$$\begin{aligned} S_{\mu\nu} &= \int d\mathbf{r} \sum_{p=1}^{L} d_{p\mu}^* \phi_p^{\text{GF}*}(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_A) \sum_{q=1}^{L} d_{q\nu}\phi_q^{\text{GF}}(\alpha_{q\nu}, \mathbf{r} - \mathbf{R}_B) \\ &= \sum_{p=1}^{L}\sum_{q=1}^{L} d_{p\mu}^* d_{q\nu} \int d\mathbf{r}\; \phi_p^{\text{GF}*}(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_A)\phi_q^{\text{GF}}(\alpha_{q\nu}, \mathbf{r} - \mathbf{R}_B) \\ &= \sum_{p=1}^{L}\sum_{q=1}^{L} d_{p\mu}^* d_{q\nu} S_{pq} \end{aligned} \tag{3.228}$$

In a similar manner, if other integrals over primitive Gaussian functions are evaluated using the methods of Appendix A, they can be summed to give integrals over any specific contracted function of interest, such as that of (3.225). One finds that the overlap S_{12} for the functions ϕ_1 and ϕ_2 of minimal basis H_2 at $R = 1.4$ a.u. is 0.6593. The overlap matrix is thus

$$\mathbf{S} = \begin{pmatrix} 1.0 & 0.6593 \\ 0.6593 & 1.0 \end{pmatrix} \tag{3.229}$$

At longer bond lengths the overlap S_{12} would decrease towards zero. At $R = 0$ the overlap S_{12} is, of course, 1.0.

Exercise 3.21 Use definition (3.219) for the STO-1G function and the scaling relation (3.224) to show that the STO-1G overlap for an orbital exponent $\zeta = 1.24$ at $R = 1.4$ a.u., corresponding to result (3.229), is $S_{12} = 0.6648$. Use the formula in Appendix A for overlap integrals. Do not forget normalization.

The elements $H_{\mu\nu}^{\text{core}}$ of the core-Hamiltonian are the sum of elements $T_{\mu\nu}$ describing the kinetic energy and elements describing the coulomb attraction of an electron for the first nucleus ($V_{\mu\nu}^{1}$) and the second nucleus ($V_{\mu\nu}^{2}$). From Appendix A these integrals can be calculated to be

$$\mathbf{T} = \begin{pmatrix} 0.7600 & 0.2365 \\ 0.2365 & 0.7600 \end{pmatrix} \tag{3.230}$$

$$\mathbf{V}^1 = \begin{pmatrix} -1.2266 & -0.5974 \\ -0.5974 & -0.6538 \end{pmatrix} \tag{3.231}$$

$$\mathbf{V}^2 = \begin{pmatrix} -0.6538 & -0.5974 \\ -0.5974 & -1.2266 \end{pmatrix} \tag{3.232}$$

If the basis functions were the hydrogen atom solutions $(\pi)^{-1/2}e^{-r}$, then T_{11} would be 0.5, the kinetic energy of an electron in the hydrogen atom, and $V_{11}^{1} = V_{22}^{2}$ would be -1.0, the potential energy of an electron in the hydrogen atom. The present values reflect the larger exponent $\zeta = 1.24$, which leads to a "smaller" orbital than in the hydrogen atom. The electron is therefore closer to the nucleus, leading to a more negative value of the potential energy (-1.2266), and it "travels faster to avoid collapsing into the nucleus," leading to a larger kinetic energy (0.7600). The energy of a hydrogen atom in this basis is just $T_{11} + V_{11}^{1} = 0.7600 - 1.2266 = -0.4666$ a.u. to be compared with the exact value of -0.5 a.u. If an electron in ϕ_1 were somehow to be localized exactly at the position of nucleus 1, its attraction for nucleus 2 would be $-1/1.4 = -0.7143$. The actual value of this attraction, shown in Fig. 3.4, is $V_{11}^{2} = -0.6538$, at $R = 1.4$ a.u. As the internuclear distance R increases, V_{11}^{2} will converge asymptotically to $-R^{-1}$. The off-diagonal elements of $\mathbf{T}$ and $\mathbf{V}^{\text{nucl}}$ cannot be given such simple classical interpretations and they constitute the basic quantum mechanical effects of bonding. As the internuclear distance R becomes large, the off-diagonal elements go to zero.

The core-Hamiltonian matrix is the sum of the above three matrices,

$$\mathbf{H}^{\text{core}} = \mathbf{T} + \mathbf{V}^1 + \mathbf{V}^2 = \begin{pmatrix} -1.1204 & -0.9584 \\ -0.9584 & -1.1204 \end{pmatrix} \tag{3.233}$$

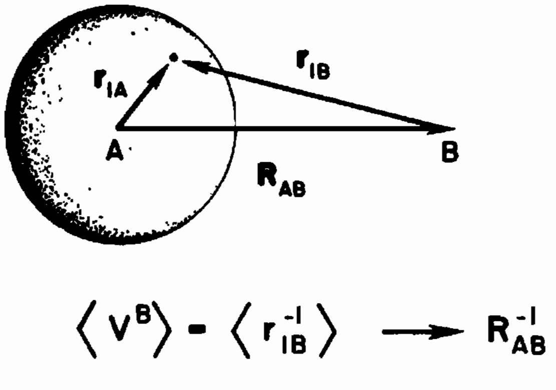


Figure 3.4 Attraction of an electron for an adjacent nucleus.

This is the Hamiltonian matrix for a single electron in the field of the nuclei, in this case for H_2^+. Solving the matrix eigenvalue problem

$$\mathbf{H}^{\text{core}}\mathbf{C} = \mathbf{SC}\boldsymbol{\varepsilon} \tag{3.234}$$

would lead to the orbital energies and molecular orbitals of H_2^+. For other cases such as H_2O, it would lead to the orbitals energies and molecular orbitals of H_2O^{9+}, which are not of particular interest.

Of the $2^4 = 16$ possible two-electron integrals $(\mu\nu|\lambda\sigma)$ in the minimal basis model, there are only four unique values,

$$\begin{aligned}
(\phi_1\phi_1|\phi_1\phi_1) &= (\phi_2\phi_2|\phi_2\phi_2) = 0.7746 \text{ a.u.}\\
(\phi_1\phi_1|\phi_2\phi_2) &= 0.5697 \text{ a.u.}\\
(\phi_2\phi_1|\phi_1\phi_1) &= (\phi_2\phi_2|\phi_2\phi_1) = 0.4441 \text{ a.u.}\\
(\phi_2\phi_1|\phi_2\phi_1) &= 0.2970 \text{ a.u.}
\end{aligned} \tag{3.235}$$

The other integrals are related to the above by simple interchange of indices, for example, $(\mu\nu|\lambda\sigma) = (\mu\nu|\sigma\lambda) = (\lambda\sigma|\mu\nu)$. The one-center integrals $(\phi_1\phi_1|\phi_1\phi_1)$ and $(\phi_2\phi_2|\phi_2\phi_2)$ just represent the average value of the electron-electron repulsion of two electrons in the same $1s$ orbital. The two-center integral $(\phi_1\phi_1|\phi_2\phi_2)$ is the repulsion between an electron in an orbital on center 1 and an electron in an orbital on center 2. Its value, which is 0.5697 a.u. at $R = 1.4$ a.u., will tend to $1/R$ as the internuclear distance R increases. The other two integrals do not have classical interpretations. They both go to zero at long bond lengths as the overlap S_{12} goes to zero. Having calculated all basic integrals we could proceed to solve Roothaan's equations by the procedure we have previously given, i.e., guess at the density matrix, form the Fock matrix, transform the Fock matrix to a basis of orthonormal orbitals, diagonalize the transformed Fock matrix, etc. Our minimal basis model for H_2 is, however, simple enough that the solutions to Roothaan's equations are determined by simple symmetry arguments. The canonical molecular orbitals will form a representation of the point group of the molecule. That is, for a homonuclear diatomic they can be labeled as having the symmetry σ_g, σ_u, π_g, π_u, etc. With our minimal basis set there are only two molecular orbitals. The lowest energy one will be the occupied molecular orbital, a bonding orbital of σ_g symmetry,

$$\psi_1 = [2(1 + S_{12})]^{-1/2}(\phi_1 + \phi_2) \tag{3.236}$$

The virtual molecular orbital will be the corresponding antibonding combination of σ_u symmetry,

$$\psi_2 = [2(1 - S_{12})]^{-1/2}(\phi_1 - \phi_2) \tag{3.237}$$

The final coefficient matrix for this problem is, therefore,

$$\mathbf{C} = \begin{pmatrix} [2(1+S_{12})]^{-1/2} & [2(1-S_{12})]^{-1/2} \\ [2(1+S_{12})]^{-1/2} & -[2(1-S_{12})]^{-1/2} \end{pmatrix} \tag{3.238}$$

and the final density matrix is

$$\mathbf{P} = \begin{pmatrix} (1+S_{12})^{-1} & (1+S_{12})^{-1} \\ (1+S_{12})^{-1} & (1+S_{12})^{-1} \end{pmatrix} = (1+S_{12})^{-1}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \tag{3.239}$$

If a density matrix other than the above were actually used for an initial guess in the SCF procedure and the iterations carried out, the procedure would converge to this symmetry determined solution.

Exercise 3.22 Derive the coefficients $[2(1+S_{12})]^{-1/2}$ and $[2(1-S_{12})]^{-1/2}$ in the basis function expansion of ψ_1 and ψ_2 by requiring ψ_1 and ψ_2 to be normalized.

Exercise 3.23 The coefficients of minimal basis H_2^+ are also determined by symmetry and are identical to those of minimal basis H_2. Use the above result for the coefficients to solve Eq. (3.234) for the orbital energies of minimal basis H_2^+ at $R = 1.4$ a.u. and show they are

$$\varepsilon_1 = (H_{11}^{\text{core}} + H_{12}^{\text{core}})/(1+S_{12}) = -1.2528 \text{ a.u.}$$

$$\varepsilon_2 = (H_{11}^{\text{core}} - H_{12}^{\text{core}})/(1-S_{12}) = -0.4756 \text{ a.u.}$$

Exercise 3.24 Use the general definition (3.145) of the density matrix to derive (3.239). What is the corresponding density matrix for H_2^+?

Exercise 3.25 Use the general definition (3.154) of the Fock matrix to show that the converged values of its elements for minimal basis H_2 are

$$\begin{aligned} F_{11} = F_{22} = H_{11}^{\text{core}} &+ (1+S_{12})^{-1}[\tfrac{1}{2}(\phi_1\phi_1|\phi_1\phi_1) + (\phi_1\phi_1|\phi_2\phi_2) \\ &+ (\phi_1\phi_1|\phi_1\phi_2) - \tfrac{1}{2}(\phi_1\phi_2|\phi_1\phi_2)] = -0.3655 \text{ a.u.} \end{aligned}$$

$$\begin{aligned} F_{12} = F_{21} = H_{12}^{\text{core}} &+ (1+S_{12})^{-1}[-\tfrac{1}{2}(\phi_1\phi_1|\phi_2\phi_2) + (\phi_1\phi_1|\phi_1\phi_2) \\ &+ \tfrac{3}{2}(\phi_1\phi_2|\phi_1\phi_2)] = -0.5939 \text{ a.u.} \end{aligned}$$

Exercise 3.26 Use the result of Exercise 3.23 to show that the orbital energies of minimal basis H_2, that are a solution to the Roothaan equations $\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$, are

$$\varepsilon_1 = (F_{11} + F_{12})/(1+S_{12}) = -0.5782 \text{ a.u.}$$

$$\varepsilon_2 = (F_{11} - F_{12})/(1-S_{12}) = +0.6703 \text{ a.u.}$$

Exercise 3.27 Use the general result (3.184) for the total electronic energy to show that the electronic energy of minimal basis H_2 is

$$E_0 = (F_{11} + H_{11}^{\text{core}} + F_{12} + H_{12}^{\text{core}})/(1 + S_{12}) = -1.8310 \text{ a.u.}$$

and that the total energy including nuclear repulsion is

$$E_{\text{tot}} = -1.1167 \text{ a.u.}$$

The results of the last three exercises have described the results of a minimal basis H_2 calculation in terms of integrals and matrices evaluated over members of the basis set $\{\phi_\mu\}$ rather than over members of the set of solutions $\{\psi_i\}$. That is how any actual calculation would be performed; the molecular orbitals ψ_i are not known until the calculation is completed. For a discussion of the SCF results or for use of the SCF results in subsequent treatments of correlation effects, it is convenient to transform the basic integrals in terms of the functions $\{\phi_\mu\}$ to corresponding integrals in terms of the functions $\{\psi_i\}$. Since we know the relation between the two sets of functions, i.e.,

$$\psi_i = \sum_{\mu=1}^{K} C_{\mu i}\phi_\mu \qquad i = 1, 2, \ldots, K \tag{3.240}$$

The transformations proceed as follows

$$h_{ij} = (\psi_i|h|\psi_j) = \sum_\mu \sum_\nu C_{\mu i}^* C_{\nu j} H_{\mu\nu}^{\text{core}} \tag{3.241}$$

$$(\psi_i\psi_j|\psi_k\psi_l) = \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma C_{\mu i}^* C_{\nu j} C_{\lambda k}^* C_{\sigma l}(\mu\nu|\lambda\sigma) \tag{3.242}$$

The two-index transformation of (3.241) is relatively easy and requires no more than the multiplication of $K \times K$ matrices. The four-index transformation of the two-electron integrals, however, is a very time consuming process. An optimum algorithm for performing the transformation requires the $O(K^5)$ multiplications. This is an order of K more difficult than any step in the complete SCF calculation. If the transformed two-electron integrals are not required, they certainly should not be calculated. On the other hand, most formulations for proceeding beyond the Hartree-Fock approximation, and all those considered in this book, require integrals over molecular orbitals. For our minimal basis H_2 model, the transformation is, of course, not difficult. The nonzero transformed elements of the core-Hamiltonian and two-electron integral matrix that result are

$$h_{11} = (\psi_1|h|\psi_1) = -1.2528 \text{ a.u.} \qquad h_{22} = (\psi_2|h|\psi_2) = -0.4756 \text{ a.u.}$$

$$J_{11} = (\psi_1\psi_1|\psi_1\psi_1) = 0.6746 \text{ a.u.} \qquad J_{22} = (\psi_2\psi_2|\psi_2\psi_2) = 0.6975 \text{ a.u.}$$

$$J_{12} = (\psi_1\psi_1|\psi_2\psi_2) = 0.6636 \text{ a.u.} \qquad K_{12} = (\psi_1\psi_2|\psi_2\psi_1) = 0.1813 \text{ a.u.}$$

As we've described before, h_{11} is the kinetic energy and nuclear attraction of an electron in ψ_1, h_{22} is the same for an electron in ψ_2, J_{11} is the coulomb interaction of the two electrons in ψ_1, J_{22} is the coulomb interaction of two electrons in ψ_2, J_{12} is the coulomb interaction of an electron in ψ_1 and another electron in ψ_2, and $-\mathrm{K}_{12}$ is the exchange interaction between an electron in ψ_1 and an electron with the same spin in ψ_2.

The transformed Fock matrix, $f_{ij} = (\psi_i|f|\psi_j)$ is by definition diagonal, with diagonal elements equal to the orbital energies. The closed-shell orbital energies, as derived in Exercise 3.9, are given by

$$\varepsilon_i = h_{ii} + \sum_b 2J_{ib} - K_{ib} \tag{3.243}$$

For our minimal basis model, these are

$$\varepsilon_1 = h_{11} + J_{11} = -0.5782 \text{ a.u.} \tag{3.244}$$

$$\varepsilon_2 = h_{22} + 2J_{12} - K_{12} = +0.6703 \text{ a.u.} \tag{3.245}$$

Note that $\varepsilon_2 \neq h_{22} + J_{22}$, since it is a virtual orbital and describes the energy of an electron in the $(N + 1)$-electron system, as discussed in conjunction with Koopmans' theorem. Appendix D contains the values of these orbital energies, as well as the two-electron integrals J_{11}, etc., as a function of bond length. Using the values of these integrals it will be possible, here and in later chapters, to investigate the behavior of a number of many-electron quantities for H_2, as a function of bond length.

The total electronic energy of the ground state is

$$E_0 = 2h_{11} + J_{11} = -1.8310 \text{ a.u.} \tag{3.246}$$

The total energy, including nuclear repulsion, is

$$E_{\text{tot}} = E_0 + 1/R = -1.1167 \text{ a.u.} \tag{3.247}$$

Since the energy of a hydrogen atom in this basis is -0.4666 a.u., the predicted dissociation energy of H_2 is $2(-0.4666) + 1.1167 = 0.1835$ a.u. $\equiv$ 4.99 eV. This is to be compared with the experimental dissociation energy of 4.75 eV. The agreement is remarkably good; even though the calculated energy of H_2 is much above the exact value, there is a compensating inexact treatment of the hydrogen atom.

The above dissociation energy is in good agreement with experiment, but to explore fully the dissociation question it is necessary to investigate the full potential surface. By repeating the above calculations for different values of the internuclear distance one obtains the potential curve shown in Fig. 3.5, which is to be compared with the essentially exact results of Kolos and Wolniewicz.[5] The minimal basis restricted Hartree-Fock calculation does not go to the limit of two hydrogen atoms as R goes to infinity. This result may at first be surprising. This totally incorrect behavior is not specific

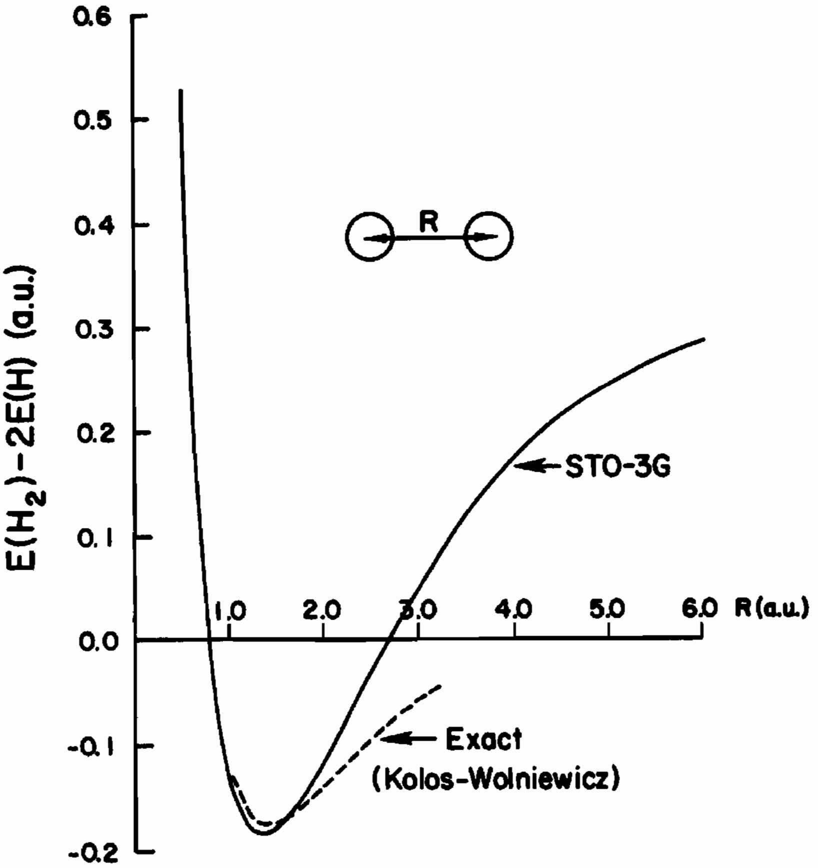


Figure 3.5 Restricted Hartree-Fock potential curve for STO-3G ($\zeta = 1.24$)H_2 compared with the accurate results of Kolos and Wolniewicz.

to H_2. If one stretches any bond for which the correct products of dissociation must be represented by open-shell wave functions, then restricted closed-shell calculations must necessarily give the wrong limit. For H_2 the products of dissociation are two localized hydrogen atoms; that is, one electron is localized near one of the protons and the other electron is localized near the other distant proton. In the restricted calculation, however, both electrons are forced to occupy the same spatial molecular orbital ψ_1. This molecular orbital is symmetry determined, having the form of (3.236). Therefore, independent of the bond length, both electrons are described by exactly the same spatial wave function and have the same probability distribution function in 3-dimensional space. Such a description is inappropriate for two separated hydrogen atoms. A restricted closed-shell Hartree-Fock calculation, which restricts electrons to occupy molecular orbitals in pairs, cannot, therefore, properly describe dissociation unless the products of dissociation are both closed-shells.

We can investigate the dissociation behavior in an analytical way by using the results of Exercises 3.25 and 3.27. As $R \to \infty$, the two-center nuclear attraction of Fig. 3.4 goes to zero and $H_{11}^{\text{core}} \to T_{11} + V_{11}^{1}$, the energy of a hydrogen atom in the basis (-0.4666). All other integrals go to zero as $R \to \infty$, except the one-center electron-electron repulsion integral $(\phi_1\phi_1|\phi_1\phi_1)$.

One therefore obtains

$$
\begin{aligned}
\lim_{R\to\infty} E_{\text{tot}}(R) &= \lim_{R\to\infty} 2H_{11}^{\text{core}} + \tfrac{1}{2}(\phi_1\phi_1|\phi_1\phi_1) \\
&= 2E(\text{H}) + \tfrac{1}{2}(\phi_1\phi_1|\phi_1\phi_1) \\
&= -0.9332 + 0.3873 \\
&= -0.5459 \text{ a.u.}
\end{aligned}
$$

The limit, rather than being twice the energy of a hydrogen atom in the same basis ($2E(\text{H})$), includes the spurious term $\frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)$. This spurious term arises because, since both electrons occupy the same spatial orbital, there remains even at infinity some electron-electron repulsion. Alternatively, the products of the dissociation are not just $2\text{H}\cdot$, but also include, incorrectly, H^- and H^+. The energy of H^- includes contributions from the electron-electron repulsion integral $(\phi_1\phi_1|\phi_1\phi_1)$. Another way of looking at this is that a molecular orbital wave function is equivalent to a valence bond wave function in which equal weight is given to covalent terms and ionic terms. Since the wave function is symmetry determined, the ionic terms remain, even on dissociation. We will return to the dissociation question when we consider unrestricted Hartree-Fock calculations.

The poor behavior of restricted closed-shell Hartree-Fock calculations upon dissociation to open-shell products does not detract from their utility in the region of equilibrium. The calculated equilibrium geometry is that at which E_{tot} is a minimum with respect to the coordinates of the nuclei. Table 3.2 shows the value of this energy for internuclear distances in the vicinity of the experimental bond length of 1.4 a.u. The calculated minimum energy occurs at 1.346 a.u. This is in error by 4% and errors of similar magnitude can be expected for equilibrium geometries of other molecules at this level of approximation.

Before leaving minimal basis H_2 (at least, temporarily), we want to use the model to illustrate exponent optimization. We have been using a standard exponent of $\zeta = 1.24$. These orbital exponents are nonlinear parameters upon which our wave function depends. By the variational principle, the best wave

Table 3.2 Energy of minimal basis STO-3G H_2 as a function of bond length

R (a.u.)	E_{tot} (a.u.)
1.32	−1.11731
1.34	−1.11750
1.36	−1.11745
1.38	−1.11719
1.40	−1.11672

$R_{\text{eq}} = 1.346$ a.u.

Table 3.3 Optimization of the Slater exponent for minimal basis STO-3G H_2 at $R = 1.4$ a.u.

ζ	E_{tot} (a.u.)
1.0	−1.08164
1.1	−1.11089
1.2	−1.11912
1.3	−1.10714

$\zeta_{\text{optimum}} = 1.19$

function of a given form is the one in which the energy has been minimized with respect to all wave function parameters. Because the orbital exponents are nonlinear parameters, however, there is no computationally easy way of determining their optimum values. Rather than go to the expense of finding their optimum values by performing many calculations with different orbital exponents it is common to choose reasonable "standard" values, such as our STO-3G value of 1.24 for the 1*s* orbitals of hydrogen. The size of the basis is increased if greater accuracy is desired. Nevertheless, it is sometimes necessary or desirable to optimize exponents if for no other reason than to determine what a "reasonable" value might be. Table 3.3 shows values of the total energy for minimal basis H_2 at $R = 1.4$ for a range of values of the 1*s* Slater exponent ζ. The optimum exponent is 1.19 at $R = 1.4$ a.u. This optimum value will change with bond length and will be different for hydrogen atoms in other molecules. One finds, however, that optimum values for a range of molecules are commonly larger than 1.0 (the exact hydrogen atom value), and the standard STO-3G value of 1.24 was chosen as representative of optimum value in a number of small molecules. The optimum value of 1.19 for H_2 means that the hydrogen molecule is in a sense "smaller" than the sum of 2 hydrogen atoms. This is common in chemical bonding—the attraction of the bonding electrons for two nuclei, rather than one, contracts the electron cloud.

3.5.3 An SCF Calculation on STO-3G HeH^+

The two-electron molecules H_2 and HeH^+ are prototypes for homonuclear and heteronuclear diatomic molecules. We have just finished describing restricted Hartree-Fock calculations on minimal basis STO-3G H_2, and we now do the same for minimal basis STO-3G HeH^+. The limitation of these minimal basis models for describing two-electron systems lies solely in the basis set. Larger basis sets would lead to correspondingly more accurate results, but the minimal basis is adequate for illustrating the points we wish to make. The extension to larger basis sets is straightforward.

Although the minimal basis sets are very small, one can describe results that are "exact" within the one-electron space spanned by these basis functions. In particular, using the minimal basis sets, we can explore any number of different computational approaches and compare the results with the "exact" results for the same basis. In later chapters we will be using the same minimal basis STO-3G H_2 and HeH^+ models to illustrate configuration interaction calculations, perturbation theory calculations, etc. The results obtained there will be compared with the "exact" results for the same basis and the Hartree-Fock calculations of this chapter.

One of the deficiencies of the minimal basis H_2 model was that, with only two basis functions, the molecular orbitals were symmetry determined and the model could not be used to illustrate the iterative nature of the SCF procedure. Because HeH^+ is heteronuclear it has less symmetry than H_2 and the molecular orbitals for the minimal basis model are not determined by symmetry. As such, restricted Hartree-Fock calculations on HeH^+ provide essentially a complete illustration of the principles involved in solving the Roothaan equations.

The singly charged helium hydride molecular ion has been known for many years from mass-spectroscopic studies. It is of interest in astrophysical problems, as the product of the β decay of HT, in scattering of protons off helium, and for a number of other reasons associated with its simplicity. There seems to be, however, little direct experimental evidence for the structure of its various electronic states. Very accurate calculations by Wolniewicz[6] show that its ground state has an equilibrium bond length of 1.4632 a.u. and an electronic binding energy of 0.0749 a.u. (2.039 eV). The ground state dissociates to a helium atom and a proton

$$\mathrm{HeH}^+(X\,^1\Sigma) \rightarrow \mathrm{He}(^1S) + \mathrm{H}^+ \tag{3.248}$$

rather than to $He^+ + H$, since the ionization potential of He (24.6 eV) is larger than the electron affinity of a proton (13.6 eV). Alternatively, the electron affinity of He^+ is larger than the electron affinity of H^+. The exact energies of the various species involved are given in Table 3.4. Since

Table 3.4 Exact energy of H and He species

Species	Energy (a.u.)
H^+	0.0
H	−0.5
He^+	−2.0
He	−2.90372[a]
HeH^+ (R = 1.4632 a.u.)	−2.97867[b]

[a] C. L. Pekeris, *Phys. Rev.* **115:** 1217 (1959).

[b] L. Wolniewicz, *J. Chem. Phys.* **43:** 1807 (1965).

the products of dissociation are closed-shells, we expect a restricted Hartree-Fock calculation to behave correctly at large bond lengths, unlike the behavior exhibited in the case of H_2.

To perform an SCF calculation, we first choose a geometry for the nuclei. We let the helium nucleus be nucleus 1 with position vector $\mathbf{R}_1$ and the hydrogen nucleus be nucleus 2 with position vector $\mathbf{R}_2$, so that $|\mathbf{R}_1 - \mathbf{R}_2| = R_{12} \equiv R$ is the internuclear distance. We will use the exact internuclear distance so that $R = 1.4632$ a.u. We then need to specify the basis set, which in our case is the STO-3G minimal basis set consisting of a 1*s* basis function on each of the two nuclei,

$$\phi_1 \simeq (\zeta_1^3/\pi)^{1/2} e^{-\zeta_1|\mathbf{r}-\mathbf{R}_1|} \tag{3.249}$$

$$\phi_2 \simeq (\zeta_2^3/\pi)^{1/2} e^{-\zeta_2|\mathbf{r}-\mathbf{R}_2|} \tag{3.250}$$

These basis functions are each a contraction of three primitive Gaussians, with the contraction coefficients of (3.221), and contraction exponents which are those of (3.221) scaled by multiplying by the square of either ζ_1 or ζ_2. It remains only to specify the Slater exponents ζ_1 for He and ζ_2 for H. The standard STO-3G exponent for H in molecular environments is $\zeta_2 = 1.24$ which is the value that we used in our minimal basis H_2 calculations. No such standard STO-3G exponent for He has been recommended, however. In choosing exponents for molecular calculations it is common to use exponents obtained by minimizing the energy of a calculation on the isolated atom using the same basis set. These are sometimes called "best atom" exponents. For H the best atom exponent is 1.0. If one performs a restricted Hartree-Fock calculation on the He atom using a basis set consisting of only one Slater orbital, $(\zeta^3/\pi)^{1/2}e^{-\zeta r}$, one finds that the best atom exponent is $27/16 = 1.6875$. The derivation of the value 27/16 is a common textbook example[7] of the variational principle. Since HeH^+ has a net positive charge, we expect, however, that the electron cloud is considerably contracted relative to that for the free atoms He and H. For illustrative purposes we will use the standard STO-3G value of $\zeta_2 = 1.24$ for H and let the standard value for He be $\zeta_1 = 1.6875 \times 1.24 = 2.0925$ which, like the value for H, is also a factor of 1.24 larger than the best atom value. Figure 3.6 shows our coordinate system and basis functions for the HeH^+ calculation. As described previously, each of the STO-3G basis functions of Fig. 3.6 or Eqs. (3.249) and (3.250) is the sum of the three primitive Gaussians.

The next step in our calculation, or most *ab initio* calculations, is the evaluation of the required integrals over the set of basis functions. Appendix A describes how the integrals can be evaluated for 1*s* Gaussian functions and gives explicit formulas for all integrals involving only 1*s* Gaussians. Appendix B gives a FORTRAN listing, and output for our HeH^+ case, of a small program which illustrates the complete steps involved in solving the Roothaan equations and which is capable of performing minimal basis

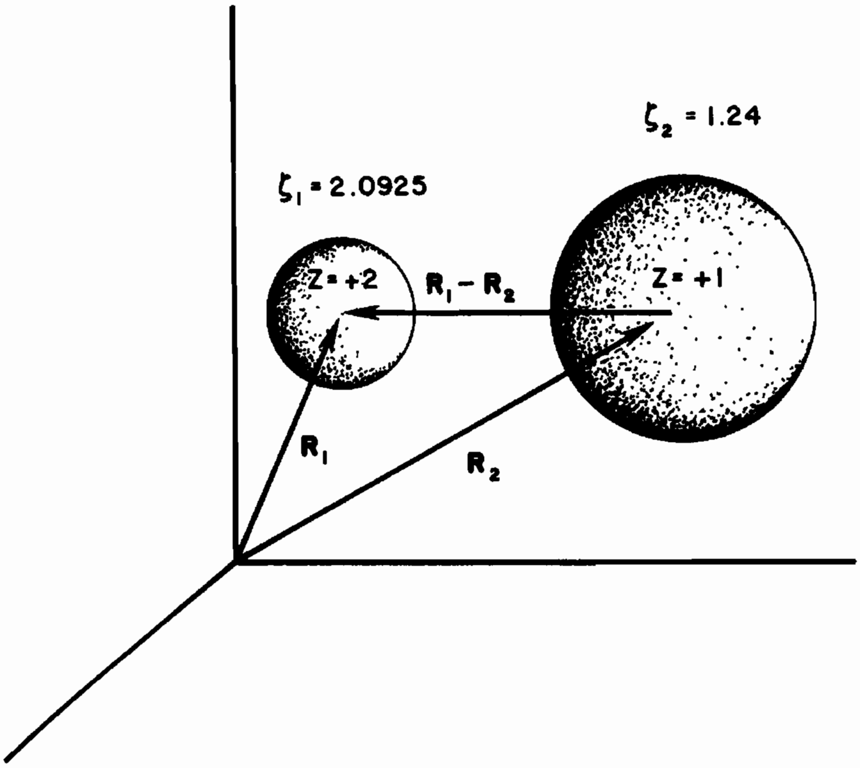


Figure 3.6 Coordinate system and basis functions for the minimal basis STO-3G HeH^+ calculation.

Gaussian calculations on any two-electron diatomic molecule. We will only give some of the results here and refer the reader to the output or program in Appendix B, when necessary. From Appendix A, the overlap of the two basis functions decreases exponentially with the internuclear distance. At the internuclear distance $R = 1.4632$ a.u. its value is $S_{12} = S_{21} = 0.4508$. This overlap is smaller than that in H_2 mainly because the He orbital is smaller and more localized than a corresponding H orbital. The overlap matrix is, therefore,

$$\mathbf{S} = \begin{pmatrix} 1.0 & 0.4508 \\ 0.4508 & 1.0 \end{pmatrix} \tag{3.251}$$

The kinetic energy matrix is

$$\mathbf{T} = \begin{pmatrix} 2.1643 & 0.1670 \\ 0.1670 & 0.7600 \end{pmatrix} \tag{3.252}$$

The T_{22} value is, of course, identical to that in H_2 since we are using the same exponent. The T_{11} value, which describes the kinetic energy of an electron in the 1s orbital around He, is much larger than that for H, reflecting the larger orbital exponent of the He orbital, which in turn reflects the larger nuclear charge of He. The smaller the average distance of electron from the nucleus, the larger is its kinetic energy.

The matrix of nuclear attraction energy to nucleus 1 (the He nucleus) is

$$\mathbf{V}^1 = \begin{pmatrix} -4.1398 & -1.1029 \\ -1.1029 & -1.2652 \end{pmatrix} \tag{3.253}$$

The one-center attraction of an electron in ϕ_1 for its own nucleus (-4.1398) is naturally larger in magnitude that the attraction of an electron in the distant function ϕ_2 for this nucleus (-1.2652). This last two-center integral becomes $-2/R$ at large internuclear distances. The off-diagonal element, the attraction for the helium nucleus of an electron described by the product distribution $\phi_1(1)\phi_2(1)$, is the quantum mechanical term responsible for chemical bonding.

The matrix of nuclear attraction energy to nucleus 2 (the H nucleus) is similar to the above, but smaller in magnitude because of the smaller nuclear charge of the proton.

$$\mathbf{V}^2 = \begin{pmatrix} -0.6772 & -0.4113 \\ -0.4113 & -1.2266 \end{pmatrix} \tag{3.254}$$

The V^2_{22} element is the same as that for H_2. The function ϕ_1 with its larger exponent is relatively localized about the He nucleus and V^2_{11} = is close to its asymptotic value of $-1/R = -0.6834$.

Having obtained the kinetic energy and nuclear attraction integrals, we can now form the core-Hamiltonian matrix

$$\mathbf{H}^{\text{core}} = \mathbf{T} + \mathbf{V}^1 + \mathbf{V}^2 = \begin{pmatrix} -2.6527 & -1.3472 \\ -1.3472 & -1.7318 \end{pmatrix} \tag{3.255}$$

As we have stated before, this is the correct Hamiltonian matrix for a single electron in the field of the nuclear point charges. The solution of a Roothaan-like equation for the core-Hamiltonian

$$\mathbf{H}^{\text{core}}\mathbf{C} = \mathbf{SC}\boldsymbol{\varepsilon} \tag{3.256}$$

would lead to the molecular orbitals and orbital energies (and, in this case, total electronic energies) for the one-electron molecule HeH^{++}. The effect of electron-electron repulsion on the molecular orbitals and orbital energies, within the single determinant approximation, is in the matrix **G** which must be added to $\mathbf{H}^{\text{core}}$ to obtain the Fock matrix **F**.

The final remaining integrals to be calculated are the two-electron repulsion integrals. Of the $2^4 = 16$ possible integrals $(\mu\nu|\lambda\sigma)$, there are only six unique integrals,

$$(\phi_1\phi_1|\phi_1\phi_1) = 1.3072 \text{ a.u.} \qquad (\phi_2\phi_2|\phi_1\phi_1) = 0.6057 \text{ a.u.}$$

$$(\phi_2\phi_1|\phi_1\phi_1) = 0.4373 \text{ a.u.} \qquad (\phi_2\phi_2|\phi_2\phi_1) = 0.3118 \text{ a.u.}$$

$$(\phi_2\phi_1|\phi_2\phi_1) = 0.1773 \text{ a.u.} \qquad (\phi_2\phi_2|\phi_2\phi_2) = 0.7746 \text{ a.u.}$$

The one-center integrals $(\phi_1\phi_1|\phi_1\phi_1)$ and $(\phi_2\phi_2|\phi_2\phi_2)$ are the repulsions between an electron in ϕ_1 (or ϕ_2) and another electron in the same orbital ϕ_1 (or ϕ_2). The average distance between two electrons in the "smaller" function ϕ_1 is less than that between two electrons in the "larger" and more diffuse function ϕ_2, and thus $(\phi_1\phi_1|\phi_1\phi_1)$ is larger than $(\phi_2\phi_2|\phi_2\phi_2)$. The two-center integral $(\phi_2\phi_2|\phi_1\phi_1)$ is the repulsion between an electron in ϕ_1 and an electron in ϕ_2. This has the asymptotic value $1/R$ as the internuclear distance becomes large. The other three integrals do not have simple classical interpretations.

We now have all the integrals needed for our SCF calculation on HeH$^+$. Prior to beginning the iterations, however, we need to derive a transformation matrix to orthonormal basis functions,

$$\phi'_\mu = \sum_\nu X_{\nu\mu}\phi_\nu \tag{3.257}$$

There are many transformations $\mathbf{X}$ that we might use to derive an orthonormal set of functions $\{\phi'_\mu\}$. The Schmidt procedure, discussed in Chapter 1, uses the following matrix

$$\mathbf{X}_{\text{Schmidt}} = \begin{pmatrix} 1 & -S_{12}/(1-S_{12}^2)^{1/2} \\ 0 & 1/(1-S_{12}^2)^{1/2} \end{pmatrix} = \begin{pmatrix} 1.0 & -0.5050 \\ 0.0 & 1.1203 \end{pmatrix} \tag{3.258}$$

Exercise 3.28 Show that the above transformation produces orthonormal basis functions.

Two other orthonormalization procedures, that we have previously described, require diagonalizing the overlap matrix. Diagonalizing a 2 × 2 matrix can be accomplished by the methods outlined in Subsection 1.1.6. For the overlap matrix, the eigenvalues are simply $s_1 = 1 + S_{12} = 1.4508$ and $s_2 = 1 - S_{12} = 0.5492$. The unitary matrix which performs the diagonalization is

$$\mathbf{U} = \begin{pmatrix} [2]^{-1/2} & [2]^{-1/2} \\ [2]^{-1/2} & -[2]^{-1/2} \end{pmatrix} \tag{3.259}$$

To derive the symmetric and canonical orthogonalization transformations we need the matrix

$$\mathbf{s}^{-1/2} = \begin{pmatrix} s_1^{-1/2} & 0 \\ 0 & s_2^{-1/2} \end{pmatrix} = \begin{pmatrix} 0.8302 & 0.0 \\ 0.0 & 1.3493 \end{pmatrix} \tag{3.260}$$

Symmetric orthogonalization then uses the transformation matrix

$$\mathbf{X}_{\text{symmetric}} = \mathbf{S}^{-1/2} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger = \begin{pmatrix} 1.0898 & -0.2596 \\ -0.2596 & 1.0898 \end{pmatrix} \tag{3.261}$$

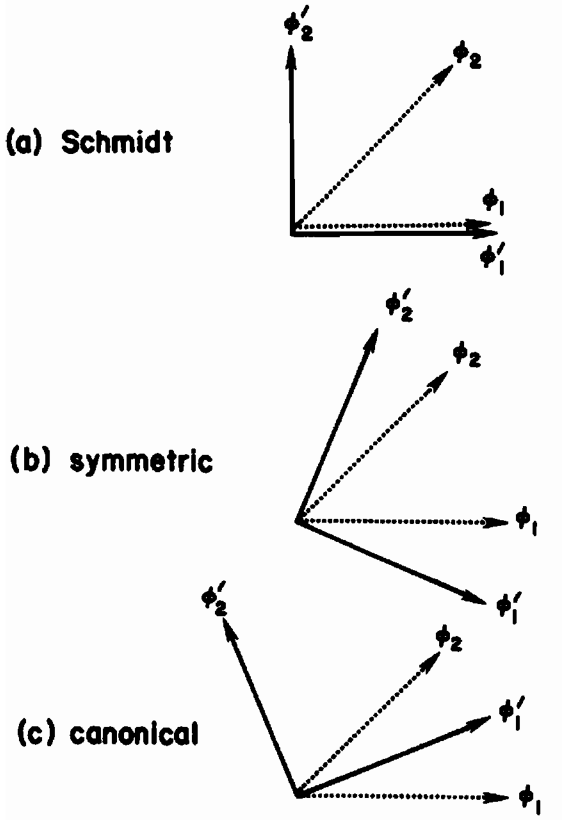


Figure 3.7 Three orthogonalization procedures: a) Schmidt; b) symmetric; c) canonical.

whereas, canonical orthogonalization uses the transformation matrix

$$\mathbf{X}_{\text{canonical}} = \mathbf{U}\mathbf{s}^{-1/2} = \begin{pmatrix} 0.5871 & 0.9541 \\ 0.5871 & -0.9541 \end{pmatrix} \tag{3.262}$$

The relationship between these three orthogonalizations is shown in Fig. 3.7. The angle θ between the original basis functions is given by $\cos\theta = S_{12}$. Schmidt orthogonalization leaves the first basis function alone and produces a second orthogonal to it. Symmetric orthogonalization produces two new functions, which most closely resemble the original basis functions. It does this by opening up the angle between the vectors to 90°. Canonical orthogonalization produces one vector which bisects the angle between the original vectors and a second vector orthogonal to the first. We will use canonical orthogonalization so that the transformed basis functions are

$$\phi'_1 = 0.5871\phi_1 + 0.5871\phi_2 \tag{3.263}$$

$$\phi'_2 = 0.9541\phi_1 - 0.9541\phi_2 \tag{3.264}$$

We are now ready to begin the SCF iteration procedure. We first need an initial guess at the density matrix. It is convenient to use the null matrix. This is equivalent to neglecting all electron-electron interaction (setting G equal to the null matrix) and using the core-Hamiltonian as a first guess at the Fock matrix

$$\mathbf{F} \simeq \mathbf{H}^{\text{core}} = \begin{pmatrix} -2.6527 & -1.3472 \\ -1.3472 & -1.7318 \end{pmatrix} \tag{3.265}$$

This is the easiest initial guess to obtain, but may be a poor one in more complicated situations. The next step is to transform the Fock matrix to the canonically orthonormalized basis set.

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} = \begin{pmatrix} -2.4397 & -0.5158 \\ -0.5158 & -1.5387 \end{pmatrix} \tag{3.266}$$

Diagonalizing this matrix, i.e., solving

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\boldsymbol{\varepsilon} \tag{3.267}$$

gives a unitary matrix of coefficients

$$\mathbf{C}' = \begin{pmatrix} 0.9104 & 0.4136 \\ 0.4136 & -0.9104 \end{pmatrix} \tag{3.268}$$

and two eigenvalues

$$\boldsymbol{\varepsilon} = \begin{pmatrix} -2.6741 & 0.0 \\ 0.0 & -1.3043 \end{pmatrix} \tag{3.269}$$

The coefficients of the original basis functions are then

$$\mathbf{C} = \mathbf{X}\mathbf{C}' = \begin{pmatrix} 0.9291 & -0.6259 \\ 0.1398 & 1.1115 \end{pmatrix} \tag{3.270}$$

Equations (3.270) and (3.269) gives the orbitals and orbital energies of HeH^{++}, which we are using as a first guess at the orbitals and orbital energies of HeH^{+}. Note that the lowest molecular orbital ψ_1 is composed mainly of ϕ_1 (coefficient = 0.9291) with only a little mixing of ϕ_2 (coefficient = 0.1398). With no electron-electron repulsion the electrons tend to congregate near the He nucleus with its higher nuclear charge. The effect of adding electron-electron repulsion, as we iterate further, will be to moderate this effect and "smear" the electrons out a bit, so as to decrease the electron-electron repulsion.

From (3.270) we can now form our first real guess at the density matrix

$$\mathbf{P} = \begin{pmatrix} 1.7266 & 0.2599 \\ 0.2599 & 0.0391 \end{pmatrix} \tag{3.271}$$

The diagonal elements of **P** show (only qualitatively) how most of the electron density is in the vicinity of the He rather than the H nucleus. A better appreciation of this would be obtained by a population analysis. The density matrix of (3.271) is not that of HeH^{++} (it differs by a factor of 2) but that of *two* noninteracting electrons in the field of the nuclei.

From **P** we can now form a guess at **G**,

$$\mathbf{G} = \begin{pmatrix} 1.2623 & 0.3740 \\ 0.3740 & 0.9890 \end{pmatrix} \tag{3.272}$$

and a new Fock matrix

$$\mathbf{F} = \mathbf{H}^{\text{core}} + \mathbf{G} = \begin{pmatrix} -1.3904 & -0.9732 \\ -0.9732 & -0.7429 \end{pmatrix} \tag{3.273}$$

Because of the positive electron-electron interaction, represented by the positive elements of the matrix $\mathbf{G}$ of (3.272), the elements of this new Fock matrix are considerably less negative than our original core-Hamiltonian guess (3.265). We can now solve the eigenvalue problem with this latest Fock matrix to get a new guess at $\mathbf{C}$ and $\mathbf{P}$, and repeat the whole procedure until self-consistency is obtained. Appendix B contains a program for doing this, and the program output for our current example of minimal basis STO-3G HeH$^+$. This output should be followed in conjunction with our description here.

Table 3.5 shows the elements of the density matrix and the corresponding electronic energy as a function of the iteration number. As the iterations proceed, charge builds up around H and decreases around He. To provide a variational value of the energy at each iteration, the formula

$$E_0 = \frac{1}{2}\sum_{\mu}\sum_{\nu} P_{\nu\mu}(H_{\mu\nu}^{\text{core}} + F_{\mu\nu}) \tag{3.274}$$

must use the same density matrix $\mathbf{P}$ as was used to form $\mathbf{F}$. Thus the energy should be calculated immediately after forming a new $\mathbf{F}$, not immediately after forming a new $\mathbf{P}$. Table 3.5 shows the energy converging monotonically from above. Because the energy is a variational quantity, the relative error in the energy is less than that in the wave function or density matrix.

The final wave function and orbital energies are

$$\mathbf{C} = \begin{pmatrix} 0.8019 & -0.7823 \\ 0.3368 & 1.0684 \end{pmatrix} \tag{3.275}$$

$$\boldsymbol{\varepsilon} = \begin{pmatrix} -1.5975 & 0.0 \\ 0.0 & -0.0617 \end{pmatrix} \tag{3.276}$$

Table 3.5 Density matrix and electronic energy during the iterative process (STO-3G HeH$^+$)

Iteration	P_{11}	P_{12}	P_{22}	E_0 (a.u.)
1	1.7266	0.2599	0.0391	−4.141863
2	1.3342	0.5166	0.2000	−4.226492
3	1.2899	0.5384	0.2247	−4.227523
4	1.2864	0.5400	0.2267	−4.227529
5	1.2862	0.5402	0.2269	−4.227529
6	1.2861	0.5402	0.2269	−4.227529

The lowest orbital, the occupied orbital ψ_1, is a bonding orbital as evidenced by the same sign for the two coefficients. It is still composed mainly of the He function ϕ_1. The virtual orbital ψ_2 is an antibonding orbital with opposite signs for the coefficients. It has a heavier weight for the H function ϕ_2 as is necessary if it is to be orthogonal to ψ_1. Koopmans' theorem allows us to predict an ionization potential and electron affinity. The predicted ionization potential is large (1.5975 a.u. = 43.5 eV) as should be the case for a cationic species. The predicted electron affinity (0.0617 a.u. = 1.7 eV) is positive, and the calculation predicts that HeH^+ will bind an electron. This does not mean that HeH will be a stable molecule, since the dissociation products of HeH^+ (i.e., He + H^+) bind an electron much more strongly (the electron affinity of H^+ is greater than the sum of the electron affinity and the dissociation energy of HeH^+).

A Mulliken population analysis can be obtained from the diagonal elements of **PS**. Such a population analysis associates 1.53 electrons with ϕ_1 and 0.47 electrons with ϕ_2. The net charge is then $+0.47$ on He and $+0.53$ on H. The formal charge of $+1$ is thus predicted to be divided more or less equally between the two atoms. A Löwdin population analysis can be obtained from the primed matrices, that is, the matrices associated with the orthonormal basis $\{\phi'_\mu\}$. The number of electrons associated with the hydrogen orbital is

$$P'_{22} = (\mathbf{S}^{1/2}\mathbf{P}\mathbf{S}^{1/2})_{22} = 2(\mathbf{S}^{1/2}\mathbf{C})^2_{12} = 0.5273 \qquad (3.277)$$

This predicts a similar separation of charge, with net charges of $+0.53$ and $+0.47$ on the He and H, respectively. Note the reversal.

The total energy of HeH^+ is obtained by adding the nuclear repulsion $2/R$ to the electronic energy, to give -2.860662 a.u. From our basic integrals it is also possible to determine the energies of H, He^+, and He. The energy of the H atom in this basis is the same as that used in the H_2 calculation, i.e., $T_{22} + V^2_{22} = -0.4666$ a.u. The energy of the one-electron atom He^+ in the basis is similarly $T_{11} + V^1_{11} = -1.9755$ a.u. The He atom has two electrons in ϕ_1 and, in addition to the kinetic energy and attraction to the helium nucleus, the energy contains a contribution from the electron-electron repulsion of the two electrons. The He atom energy is thus $2(T_{11} + V^1_{11}) + (\phi_1\phi_1|\phi_1\phi_1)$. These energies are shown in Table 3.6 for comparison with exact results in Table 3.4.

From the results in Table 3.6 it is possible to calculate dissociation energies for the processes

$$HeH^+ \rightarrow He + H^+ \qquad \Delta E = 0.2168 \text{ a.u.} \qquad (3.278)$$

$$HeH^+ \rightarrow He^+ + H \qquad \Delta E = 0.4168 \text{ a.u.} \qquad (3.279)$$

The calculations correctly predict that HeH^+ will dissociate to the closed-shells He + H^+ rather than the open shells He^+ + H. The dissociation energy of 0.2168 a.u. = 5.90 eV is quite a bit larger than the correct value

Table 3.6 Energies for H and He species with the STO-3G basis set ($\zeta_1 = 2.0925$, $\zeta_2 = 1.24$)

Species	Energy (a.u.)
H^+	0.0
H	−0.466582
He^+	−1.975514
He	−2.643876
HeH^+ ($R = 1.4632$ a.u.)	−2.860662

of 2.04 eV. This is mainly because our He exponent of 2.0925, while reasonable for the HeH^+ molecule, is quite a bit larger than the best value of 1.6875 for the dissociation product, the He atom. The He energy is too high, relative to the HeH^+ energy.

Figure 3.8 shows the whole potential curve for our standard exponents, and also shows the essentially exact results of Wolniewicz. The calculated STO-3G equilibrium bond length is 1.3782 a.u., which is in fair agreement with the accurate results, even though the well depth is much too large. Unlike the difficulty encountered in H_2 (Fig. 3.5), the dissociation behavior

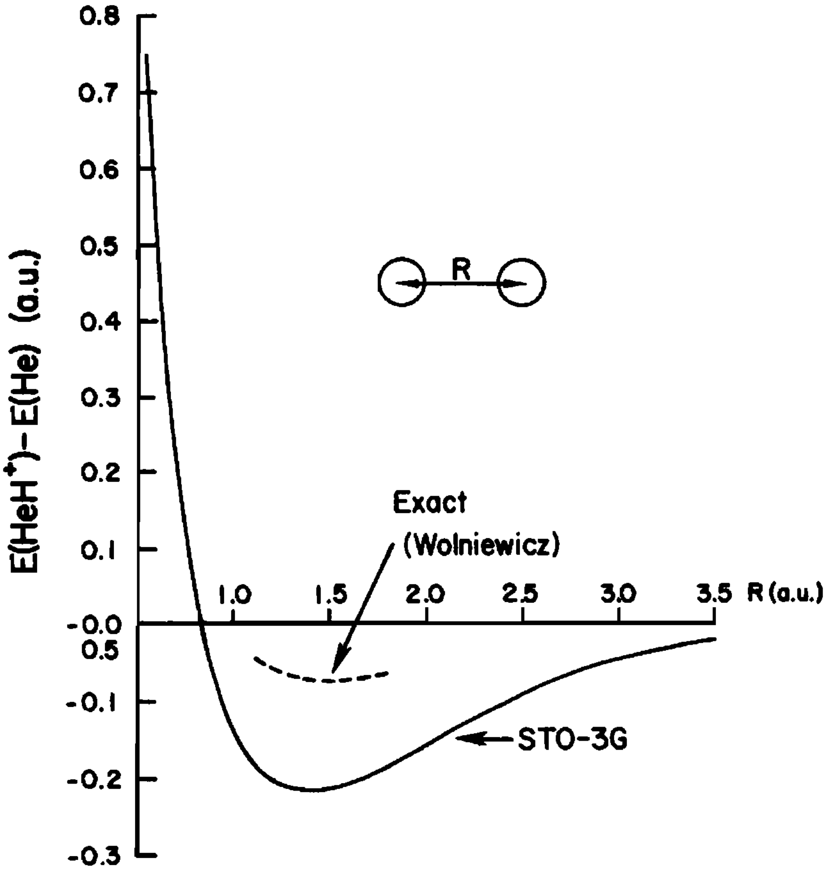


Figure 3.8 Restricted Hartree-Fock potential curve for STO-3G ($\zeta_{He} = 2.0925$, $\zeta_H = 1.24$)HeH^+ compared with the accurate results of Wolniewicz.

is correct since the products of dissociation are closed shells. We can look at this dissociation analytically as we did ~~for~~ H_2. As the bond length is stretched, the coefficient of ϕ_1 in ψ_1 increases and the coefficient of ϕ_2 in ψ_1 decreases. The electrons concentrate more and more around the He nucleus. In the limit, ψ_1 becomes just ϕ_1. The virtual orbital ψ_2, to be orthogonal to ψ_1, correspondingly becomes pure ϕ_2, that is

$$\mathbf{C}_{R\to\infty} = \begin{pmatrix} 1.0 & 0.0 \\ 0.0 & 1.0 \end{pmatrix} \tag{3.280}$$

The corresponding density matrix is

$$\mathbf{P}_{R\to\infty} = \begin{pmatrix} 2.0 & 0.0 \\ 0.0 & 0.0 \end{pmatrix} \tag{3.281}$$

The total electronic energy as $R \to \infty$ can be evaluated by setting all two-center integrals to zero. The only remaining integrals are T_{11}, T_{22}, V^1_{11}, V^2_{22}, $(\phi_1\phi_1|\phi_1\phi_1)$, and $(\phi_2\phi_2|\phi_2\phi_2)$.

Exercise 3.29 Use expression (3.184) for the electronic energy, expression (3.154) for the Fock matrix, and the asymptotic density matrix (3.281) to show that

$$E_0(R \to \infty) = 2T_{11} + 2V^1_{11} + (\phi_1\phi_1|\phi_1\phi_1)$$

This is just the proper energy of the He atom, for the minimal basis, as discussed previously in the text.

The calculations on HeH^+ described here used a standard set of exponents. A better procedure would have been to optimize exponents at each internuclear distance. If we had done so, the He exponent ζ_1 would have decreased towards the best atom value of 1.6875 as we increased R. The value of the H exponent would have decreased to zero at large R (since in the products of dissociation both electrons reside on the He, the only way the H basis function can contribute at large R is by being extremely diffuse and extending over to the region of the He nucleus). Since there are only two exponents in this problem, it would have been reasonably easy to optimize exponents, for example, just by iteratively optimizing each one in sequence. In the general problem, with many orbital exponents, finding a minimum involves searches on a many-dimensional surface with possibly many local minima. One does not routinely optimize exponents in these larger problems.

Having described restricted closed-shell Hartree-Fock calculations in conjunction with the H_2 and HeH^+ model systems, we now want to illustrate the results of more realistic calculations on polyatomic molecules. We do this not to provide a review of current calculations, but rather to illustrate the main ideas behind all calculations of the closed-shell restricted Hartree-Fock type, and to provide some feeling and intuition for how well (or how badly) such calculations compare with experiment. We will restrict our calculations to H_2, N_2, and CO and molecules in the ten-electron series CH_4, NH_3, H_2O, and FH. For each of these we will use a hierarchy of well-defined basis sets. Prior to describing the results of such calculations, however, we need to discuss the general question of polyatomic basis sets and describe the specific basis sets we will be using.

3.6 POLYATOMIC BASIS SETS

There are probably as many basis sets defined for polyatomic calculations as there are quantum chemists. The choice of a basis set is not nearly the black art, however, that it may first appear. In our sample calculations we will use a reasonably well-defined hierarchy of basis sets starting with a minimal STO-3G basis and proceeding through the 4-31G basis, which effectively doubles the number of functions, the 6-31G* basis, which adds *d*-type functions to heavy atoms C, N, O, and F and finally, the 6-31G** basis, which, in addition to *d*-type functions for heavy atoms, adds *p*-type functions to hydrogen. By performing electronic structure calculations on a small variety of molecules, using this hierarchy of basis sets, it is possible to gain some insight into the size and characteristics of a basis set needed to obtain a given level of calculational accuracy.

The above basis sets have been introduced by Pople and collaborators (see Hehre *et al.* in Further Reading at the end of this chapter) and have been used extensively, by a number of workers for calculations on a large variety of molecules. Apart from a few instances, all the calculations in this book use the STO-3G, 4-31G, 6-31G*, and 6-31G** hierarchy of basis sets. By restricting our example calculations to a very limited set of molecules and the above basis sets, we are attempting to illustrate in a systematic way how specific attributes of a basis set affect calculated quantities. We are not attempting to provide a general review of current calculations. Such a review would be out of date very quickly. While the basis sets we use are not necessarily optimum, and may themselves be out of date shortly, they do have characteristics that can be used to illustrate all basis sets.

Our purpose in this section is to explicitly define the STO-3G, 4-31G, 6-31G*, and 6-31G** basis sets that we will be using in this and subsequent chapters. In the process, however, we will describe attributes that are characteristic of most of the basis sets that are in current use, and we will introduce some of the notation and some of the mechanics of defining and choosing a basis set. In particular, we first present a general treatment of contraction.

3.6.1 Contracted Gaussian Functions

In Subsection 3.5.1, when we defined the 1*s* STO-3G basis set of our model calculations, we indicated some of the ideas pertinent to the concept of contraction. We review these briefly. There are two main considerations in the choice of a basis. The first is that one desires to use the most efficient and accurate functions possible, in the sense that the expansion

$$\psi_i = \sum_{\mu=1}^{K} C_{\mu i}\phi_\mu \tag{3.282}$$

will require the fewest possible terms for an accurate representation of the molecular orbitals ψ_i. From this consideration, Slater functions are better than Gaussian functions. The second consideration in the choice of a basis set is the speed of two-electron integral evaluation. Here Gaussian functions have the advantage. By using a basis set of *contracted Gaussian functions* one can in a sense have one's cake and eat it too. In this procedure, one lets each basis function be a fixed linear combination (contraction) of Gaussian functions (primitives). Prior to a calculation one chooses the exponents of the primitives and the contraction coefficients so as to lead to basis functions with desired qualities. The contracted basis functions might be chosen to approximate Slater functions, Hartree-Fock atomic orbitals, or any other set of functions desired. Integrals involving such basis functions reduce to sums of integrals involving the primitive Gaussian functions. Even though many primitive integrals may need to be calculated for each basis function integral, the basis function integrals will be rapidly calculated provided the method of computing primitive integrals is very fast.

To avoid confusion with a multitude of ϕ's we will use the symbol g here for a normalized Gaussian function. A contraction thus has the form.

$$\phi_\mu^{\text{CGF}}(\mathbf{r} - \mathbf{R}_A) = \sum_{p=1}^{L} d_{p\mu} g_p(\alpha_{p\mu}, \mathbf{r} - \mathbf{R}_p) \tag{3.283}$$

where $\alpha_{p\mu}$ and $d_{p\mu}$ are the contraction exponents and coefficients and L is the length of the contraction. The normalized Gaussian primitive functions are of the 1*s*, 2*p*, 3*d*, . . . type,

$$g_{1s}(\alpha, \mathbf{r}) = (8\alpha^3/\pi^3)^{1/4} e^{-\alpha r^2} \tag{3.284}$$

$$g_{2p_x}(\alpha, \mathbf{r}) = (128\alpha^5/\pi^3)^{1/4} x e^{-\alpha r^2} \tag{3.285}$$

$$g_{3d_{xy}}(\alpha, \mathbf{r}) = (2048\alpha^7/\pi^3)^{1/4} xy e^{-\alpha r^2} \tag{3.286}$$

The simplifications that occur for integral evaluation using these functions do not appear for the 2*s*, 3*p*, ... Gaussians, and so any basis function of *s* symmetry, for example a 2*s* or 3*s* Slater function, will be expanded in only 1*s* Gaussians, with similar restrictions on the other symmetry types. The origins $\mathbf{R}_P$ of the primitives in (3.283) are almost always equal to $\mathbf{R}_A$. Different origins for the primitives in a contraction are used only with Gaussian lobe basis sets. In these basis sets one approximates *s*, *p*, *d*, . . . functions as combinations of spherical 1*s* Gaussians (lobes) placed appropriately in space. For example, a 2*p* Gaussian orbital can be approximated as closely as desired by two 1*s* Gaussian lobes of opposite sign placed an infinitesimal distance apart. We will not be concerned with Gaussian lobes here.

A common way of determining contractions is from the results of atomic SCF calculations. In these atomic calculations one uses a relatively large basis of uncontracted Gaussians, optimizes all exponents, and determines the SCF coefficients of each of the derived atomic orbitals. The optimized exponents and SCF coefficients can then be used to derive suitable contraction exponents and contraction coefficients for a smaller basis set to be used in subsequent molecular calculations. Let us first illustrate this with *s*-type basis functions for hydrogen. Huzinaga[8] has determined coefficients and exponents of Gaussian expansions that minimize the energy of a hydrogen atom. With four Gaussian functions he obtains

$$\begin{aligned}\psi_{1s} = {} & 0.50907 g_{1s}(0.123317, \mathbf{r}) + 0.47449 g_{1s}(0.453757, \mathbf{r}) \\ & + 0.13424 g_{1s}(2.01330, \mathbf{r}) + 0.01906 g_{1s}(13.3615, \mathbf{r}) \qquad (3.287)\end{aligned}$$

The basis set is an uncontracted basis consisting of four functions of *s*-type symmetry, i.e., it is a (4*s*) basis. A contracted basis set derived from this would use the four Gaussian functions as primitives and contract them to reduce the number of basis functions. There are a number of ways the above four primitives might be contracted. One usually uses disjoint subsets of primitives so that no primitive appears in more than one basis function. From evidence on molecular calculations, it appears that a useful contraction scheme is one which leaves the most diffuse primitive uncontracted and contracts the remaining three primitives into one basis function, with contraction coefficients just equal to the above coefficients (SCF coefficients in the general case). That is,

$$\phi_1(\mathbf{r}) = g_{1s}(0.123317, \mathbf{r}) \qquad (3.288)$$

$$\begin{aligned}\phi_2(\mathbf{r}) &= N[0.47449 g_{1s}(0.453757, \mathbf{r}) + 0.13424 g_{1s}(2.01330, \mathbf{r}) \\ &\qquad + 0.01906 g_{1s}(13.3615, \mathbf{r})] \\ &= 0.817238 g_{1s}(0.453757, \mathbf{r}) + 0.231208 g_{1s}(2.01330, \mathbf{r}) \\ &\qquad + 0.032828 g_{1s}(13.3615, \mathbf{r}) \qquad (3.289)\end{aligned}$$

In the last equation, the contraction coefficients have been properly renormalized. This scheme leads to a contracted basis set of two *s*-type functions, i.e., a [2*s*] *contracted basis set*, coming from a (4*s*) *uncontracted basis set*. This defines a (4*s*)/[2*s*] contraction.

Huzinaga also determined relatively large uncontracted Gaussian (9*s*5*p*) basis sets, with optimized exponents, for the first-row atoms Li to Ne. Dunning[9] has suggested useful contractions of these. As an example of the procedure, consider a [3*s*2*p*] contracted basis for the oxygen atom. We are going to contract the nine primitives of *s* type into three basis functions. On inspecting the atomic SCF calculation we find that one of the nine primitives contributes strongly to both the 1*s* and 2*s* orbitals of the oxygen atom; this function is left uncontracted.

$$\phi_1(\mathbf{r}) = g_{1s}(9.5322, \mathbf{r}) \tag{3.290}$$

The two primitives, which are most diffuse, make a negligible contribution to the 1*s* atomic orbital but are the chief contributors to the 2*s* atomic orbital. They are contracted to give the second basis function,

$$\begin{aligned}\phi_2(\mathbf{r}) &= N[0.59566g_{1s}(0.9398, \mathbf{r}) + 0.52576g_{1s}(0.2846, \mathbf{r})]\\ &= 0.563459g_{1s}(0.9398, \mathbf{r}) + 0.497338g_{1s}(0.2846, \mathbf{r})\end{aligned} \tag{3.291}$$

where 0.59566 and 0.52576 are the coefficients of these primitives in the 2*s* atomic orbital of the atomic SCF calculation. The last basis function consist of the remainder of the nine primitives,

$$\begin{aligned}\phi_3(\mathbf{r}) = N[&0.14017g_{1s}(3.4136, \mathbf{r}) + 0.35555g_{1s}(27.1836, \mathbf{r})\\ &+ 0.14389g_{1s}(81.1696, \mathbf{r}) + 0.04287g_{1s}(273.188, \mathbf{r})\\ &+ 0.00897g_{1s}(1175.82, \mathbf{r}) + 0.00118g_{1s}(7816.54, \mathbf{r})]\\ = &0.241205g_{1s}(3.4136, \mathbf{r}) + 0.611832g_{1s}(27.1836, \mathbf{r})\\ &+ 0.247606g_{1s}(81.1696, \mathbf{r}) + 0.073771g_{1s}(273.188, \mathbf{r})\\ &+ 0.015436g_{1s}(1175.82, \mathbf{r}) + 0.002031g_{1s}(7816.54, \mathbf{r})\end{aligned} \tag{3.292}$$

where 0.14017, 0.35555, etc, are the coefficients of these primitives in the 1*s* atomic orbital of the atomic SCF calculation.

In a similar way, the five primitives of *p*-type symmetry are contracted to two basis functions. Here the most diffuse *p*-function is left uncontracted,

$$\phi_1(\mathbf{r}) = g_{2p}(0.2137, \mathbf{r}) \tag{3.293}$$

and the remaining four primitives are contracted using the SCF coefficients of the 2*p* atomic orbital

$$\begin{aligned}\phi_2(\mathbf{r}) = N[&0.49376g_{2p}(0.7171, \mathbf{r}) + 0.31066g_{2p}(2.3051, \mathbf{r})\\ &+ 0.09774g_{2p}(7.9040, \mathbf{r}) + 0.01541g_{2p}(35.1832, \mathbf{r})]\\ = &0.627375g_{2p}(0.71706, \mathbf{r}) + 0.394727g_{2p}(2.30512, \mathbf{r})\\ &+ 0.124189g_{2p}(7.90403, \mathbf{r}) + 0.019580g_{2p}(35.1835, \mathbf{r})\end{aligned} \tag{3.294}$$

This (9*s*5*p*)/[3*s*2*p*] contraction reduces the number of basis functions from 24 to 9. Remember the p_x, p_y, and p_z are included for each *p* orbital exponent. A calculation with either basis set would give almost identical results in a calculation on the oxygen atom, however. The loss of variational flexibility in molecular calculations is not extreme either. For example, a calculation on the water molecule using the fully uncontracted $(9s5p/4s)^{10}$ basis set gives an energy of −76.0133, whereas the [3*s*2*p*/2*s*] contracted basis gives an energy of −76.0080, only 0.007% above the much larger calculation. Because the cost of an SCF calculation increases with the fourth power of the number of basis functions, the reduction from 32 functions to 13 functions is impressive.

3.6.2 Minimal Basis Sets: STO-3G

A minimal basis set is a relatively inexpensive one, which can be used for calculations on quite large molecules. It is minimal in the sense of having the least number of functions per atom required to describe the occupied atomic orbitals of that atom. This is not quite accurate, since one usually considers 1*s*, 2*s* and 2*p*, i.e., five functions, to constitute a minimal basis set for Li and Be, for example, even though the 2*p* orbital is not occupied in these atoms. The 2*sp* (2*s* and 2*p*), 3*sp*, 4*sp*, 3*d*, . . . , etc. shells are considered together. The minimal basis set thus consists of 1 function for H and He, 5 functions for Li to Ne, 9 functions for Na to Ar, 13 functions for K and Ca, 18 functions for Sc to Kr, . . . , etc. Because the minimal basis set is so small, it is not one which can lead to quantitatively accurate results. It does, however, contain the essentials of chemical bonding and many useful qualitative results can be obtained with it.

Because of the small number of functions in a minimal basis set, it is particularly important that these functions be of near optimum form. This immediately rules out a single Gaussian function. One would prefer to use Slater functions or functions that closely resemble the known shape of atomic orbitals. A significant advance in minimal basis calculations came with the development of computer programs like "Gaussian 70," which could reproduce the results of minimal basis Slater orbital calculations using contracted Gaussian functions. The STO-LG method uses a contraction of *L* primitive Gaussians for each basis function, where the contraction coefficients and exponents are chosen so that the basis functions approximate Slater functions. We have already discussed the 1*s* STO-3G basis set in Subsection 3.5.1.

The calculations in this book are restricted to a small number of molecules, all of which include only the first row atoms up to fluorine Although the STO-LG method has been extended to second row atoms, we will only consider its formulation, and the formulation of the other basis sets which follow, for first row atoms and, in particular, for H, C, N, O, and F. We are therefore interested in the expansion of the 1*s*, 2*s*, and 2*p* Slater functions in a set of primitive Gaussians

$$\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0) = \sum_{i=1}^{L} d_{i,1s} g_{1s}(\alpha_{i,1s}) \tag{3.295}$$

$$\phi_{2s}^{\mathrm{CGF}}(\zeta = 1.0) = \sum_{i=1}^{L} d_{i,2s} g_{1s}(\alpha_{i,2sp}) \tag{3.296}$$

$$\phi_{2p}^{\mathrm{CGF}}(\zeta = 1.0) = \sum_{i=1}^{L} d_{i,2p} g_{2p}(\alpha_{i,2sp}) \tag{3.297}$$

where the contraction coefficients (d's) and exponents (α's) are to be obtained by a least-squares fit which minimizes the integrals

$$\int d\mathbf{r}\,[\phi_{1s}^{\mathrm{SF}}(\mathbf{r}) - \phi_{1s}^{\mathrm{CGF}}(\mathbf{r})]^2$$

and

$$\int d\mathbf{r}\,[\phi_{2s}^{\mathrm{SF}}(\mathbf{r}) - \phi_{2s}^{\mathrm{CGF}}(\mathbf{r})]^2 + \int d\mathbf{r}\,[\phi_{2p}^{\mathrm{SF}}(\mathbf{r}) - \phi_{2p}^{\mathrm{CGF}}(\mathbf{r})]^2$$

One of the unique aspects of the STO-LG method and the fitting procedure is the sharing of contraction exponents in $2sp$, $3sp$, ... shells. Thus the exponents in (3.296) and (3.297) are constrained to be identical and the $2s$ and $2p$ fits are performed simultaneously as indicated by the second integral above. The reason for this constraint is that if $2s$ and $2p$ functions have the same exponents, then they have the same radial behavior, and during the radial part of the integral evaluation they can be treated as one function. That is, all integrals involving any sp shell are treated together and one radial integration is sufficient for up to $256 \equiv 4^4$ separate integrals. This grouping of basis functions by shells with shared exponents leads to considerable efficiency in integral evaluation. The general STO-LG procedure uses contraction lengths up to $L = 6$. The longer the length of the contraction, however, the more time is spent in integral evaluation. It has been empirically determined that a contraction of length 3 is sufficient to lead to calculated properties that reproduce essentially all the valence features of a Slater calculation, and STO-3G has become the *de facto* standard for minimal basis calculations. Table 3.7 gives the STO-3G contraction exponents and coefficients of Eqs. (3.295) and (3.297). In the general notation, the STO-3G contraction is $(6s3p/3s)/[2s1p/1s]$.

Once the least-squares fits to Slater functions with orbital exponents $\zeta = 1.0$ (Table 3.7) are available, fits to Slater functions with other orbital exponents can be obtained by simply multiplying the α's in (3.295) to (3.297) by ζ^2. It remains to be determined what Slater orbital exponents ζ to use in electronic structure calculations. Two possibilities might be to use "best atom" exponents ($\zeta = 1.0$ for H, for example) or to optimize exponents in each calculation. The "best atom" exponents might be rather a poor choice

Table 3.7 STO-3G contraction exponents and coefficients for $1s$, $2s$, and $2p$ basis functions

α_{1s}	d_{1s}	α_{2sp}	d_{2s}	d_{2p}
0.109818	0.444635	0.0751386	0.700115	0.391957
0.405771	0.535328	0.231031	0.399513	0.607684
2.22766	0.154329	0.994203	−0.0999672	0.155916

Table 3.8 Standard STO-3G exponents

Atom	ζ_{1s}	ζ_{2sp}
H	1.24	—
Li	2.69	0.75
Be	3.68	1.10
B	4.68	1.45
C	5.67	1.72
N	6.67	1.95
O	7.66	2.25
F	8.65	2.55

for molecular environments, and optimization of nonlinear exponents is not practical for large molecules, where the dimension of the space to be searched is very large. A compromise is to use a set of standard exponents which are the average values of exponents optimized for a set of small molecules. The recommended STO-3G exponents are shown in Table 3.8.

The STO-LG basis is not the only possible minimal basis of course. Stewart,[11] for example, has determined fits of contracted Gaussian functions to individual Slater functions, without the constraint of sharing exponents in a shell. Rather than use Slater functions or fits to Slater functions, a reasonable choice is contracted basis functions which closely approximate the individually determined Hartree-Fock atomic orbitals of the atom. Calculations suggest, however, that Slater functions with near optimum exponents are better than these Hartree-Fock atomic orbitals for a minimal basis; orbitals in molecules may be rather different than those in the constituent atoms.

3.6.3 Double Zeta Basis Sets: 4-31G

A minimal basis set has rather limited variational flexibility particularly if exponents are not optimized. The first step in improving upon the minimal basis set involves using two functions for each of the minimal basis functions—a double zeta basis set. The best orbital exponents of the two functions are commonly slightly above and slightly below the optimal exponent of the minimal basis function. This allows effective expansion or "contraction" of the basis functions by variation of linear parameters rather than nonlinear exponents. The SCF procedure will weight either the coefficient of the dense or diffuse component according to whether the molecular environment requires the effective orbital to be expanded or "contracted." In addition, an extra degree of anisotropy is allowed relative to an STO-3G basis since, for example, *p* orbitals in different directions can have effectively different sizes.

The 4-31G basis set is not exactly a double zeta basis since only the valence functions are doubled and a single function is still used for each inner shell orbital. It may be termed a split valence shell basis set. The inner shells contribute little to most chemical properties and usually vary only slightly from molecule to molecule. Not splitting the inner shell functions has some effect on the total energy, but little effect on dipole moments, valence ionization potentials, charge densities, dissociation energies, and most other calculated quantities of chemical interest. The 4-31G basis thus consists of 2 functions for H and He, 9 functions for Li to Ne, 13 functions for Na to Ar, . . . , etc. For hydrogen the contractions are

$$\phi'_{1s}(\mathbf{r}) = \sum_{i=1}^{3} d'_{i,1s} g_{1s}(\alpha'_{i,1s}, \mathbf{r}) \tag{3.298}$$

$$\phi''_{1s}(\mathbf{r}) = g_{1s}(\alpha''_{1s}, \mathbf{r}) \tag{3.299}$$

The outer hydrogen function ϕ''_{1s} is uncontracted and the inner hydrogen function ϕ'_{1s} is a contraction of three primitive Gaussians. Apart from small numerical differences in deriving the contraction coefficients and exponents, the above basis functions are identical to the (4*s*)/[2*s*] functions of (3.288) and (3.289). That is, the 4-31G basis is not fit to any particular functional form but is derived by choosing the form of the contraction and then minimizing the energy of an atomic calculation by varying the contraction coefficients and exponents. The 4-31G acronym implies that the valence basis functions are contractions of three primitive Gaussians (the inner function) and one primitive Gaussian (the outer function), whereas the inner shell functions are contractions of four primitive Gaussians. Hydrogen, of course, does not have inner shells.

For the atoms Li to F, the contractions are

$$\phi_{1s}(\mathbf{r}) = \sum_{i=1}^{4} d_{i,1s} g_{1s}(\alpha_{i,1s}, \mathbf{r}) \tag{3.300}$$

$$\phi'_{2s}(\mathbf{r}) = \sum_{i=1}^{3} d'_{i,2s} g_{1s}(\alpha'_{i,2sp}, \mathbf{r}) \tag{3.301}$$

$$\phi''_{2s}(\mathbf{r}) = g_{1s}(\alpha''_{2sp}, \mathbf{r}) \tag{3.302}$$

$$\phi'_{2p}(\mathbf{r}) = \sum_{i=1}^{3} d'_{i,2p} g_{2p}(\alpha'_{i,2sp}, \mathbf{r}) \tag{3.303}$$

$$\phi''_{2p}(\mathbf{r}) = g_{2p}(\alpha''_{2sp}, \mathbf{r}) \tag{3.304}$$

As in the STO-3G basis, the 2*s* and 2*p* functions share exponents for computational efficiency. Given the above functional forms, the contraction coefficients d_{1s}, d'_{2s}, d''_{2s}, d'_{2p}, and d''_{2p} and the contraction exponents α_{1s}, α'_{2sp}, and α''_{2sp} were explicitly varied until the energy of an atomic SCF calculation reached a minimum. Unlike the STO-3G basis, which was

Table 3.9 Standard 4-31G valence shell scale factors

Atom	ζ'	ζ''
H	1.20	1.15
C	1.00	1.04
N	0.99	0.98
O	0.99	0.98
F	1.00	1.00

obtained by a least-squares fit to known functions, or a general contraction scheme based on contraction of previously determined uncontracted atomic calculations, the 4-31G basis sets were determined by choosing the specific form (3.300) to (3.304) for the contractions and then optimizing all contraction parameters. That is, the basis set was obtained by contraction first, then optimization, as opposed to optimization first, then contraction. In our general notation, the 4-31G contraction is written as $(8s4p/4s)/[3s2p/2s]$. The basis consists of inner shell functions, inner valence functions, and outer valence functions. These are contractions of 4, 3, and 1 primitive functions, respectively.

Since the basis set is obtained from atomic calculations, it is still desirable to scale exponents for the molecular environment. This is accomplished by defining an inner valence scale factor ζ' and an outer valence scale factor ζ'' and multiplying the corresponding inner and outer α's by the square of these factors. Only the valence shells are scaled. Table 3.9 gives a set of standard 4-31G scale factors. Only those for H differ significantly from unity, although the outer carbon functions are somewhat denser than in the atom.

Exercise 3.30 A 4-31G basis for He has not been officially defined. Huzinaga,[8] however, in an SCF calculation on the He atom using four uncontracted 1s Gaussians, found the coefficients and optimum exponents of the normalized 1s orbital of He to be

α_μ	$C_{\mu i}$
0.298073	0.51380
1.242567	0.46954
5.782948	0.15457
38.47497	0.02373

Use the expression for overlaps given in Appendix A to derive the contraction parameters for a 4-31G He basis set.

3.6.4 Polarized Basis Sets: 6-31G* and 6-31G**

The next step in improving a basis set could be to go to triple zeta, quadruple zeta, etc. If one goes in this direction rather than adding functions of higher angular quantum number, the basis set would not be well balanced. In the limit of a large number of only *s* and *p* functions, one finds, for example, that the equilibrium geometry of ammonia actually becomes planar. The next step beyond double zeta usually involves adding *polarization functions*, i.e., adding *d*-type functions to the first row atoms Li-F and *p*-type functions to H. To see why these are called polarization functions, consider the hydrogen atom. The exact wave function for an isolated hydrogen atom is just the 1*s* orbital. If the hydrogen atom is placed in a uniform electric field, however, the electron cloud is attracted to the direction of the electric field, and the charge distribution about the nucleus becomes asymmetric. It is polarized. The lowest order solution to this problem is a mixture of the original 1*s* orbital and a *p*-type function, i.e., the solution can be considered to be a hybridized orbital. A hydrogen atom in a molecule experiences a similar, but nonuniform, electric field arising from its nonspherical environment. By adding polarization functions, i.e., *p*-type functions, to a basis set for H we directly accommodate this effect. In a similar way, *d*-type functions, which are not occupied in first row atoms, play the role of polarization functions for the atoms Li to F. The 6-31G* and 6-31G** basis sets closely resemble the 4-31G basis set with *d*-type basis functions added to the heavy atoms (*) or *d*-type functions added to the heavy atoms, *and p*-type functions added to hydrogen (**). It has been empirically determined that adding polarization functions to the heavy atoms is more important than adding polarization functions to hydrogen. The hierarchy of our basis sets is thus STO-3G, 4-31G, 6-31G*, and 6-31G**.

The 6-31G* and 6-31G** basis sets are formed by adding polarization function to a 6-31G basis. The form of the 6-31G contractions are identical to those of the 4-31G basis, except that the inner shell functions (1*s* only, for Li to F) become a contraction of six primitive Gaussians rather than four. The 6-31G optimization was performed from the beginning and so the valence functions are not identical to those of the 4-31G basis, but are very similar. The 6-31G and 4-31G basis sets give almost identical results for valence properties although the 6-31G basis gives lower energies, because of the improvement in the inner shell.

The *d*-type functions that are added to a 6-31G basis to form a 6-31G* basis are a single set of uncontracted 3*d* primitive Gaussians. For computational convenience there are "six 3*d* functions" per atom—$3d_{xx}$, $3d_{yy}$, $3d_{zz}$, $3d_{xy}$, $3d_{yz}$, and $3d_{zx}$. These six, the Cartesian Gaussians, are linear combinations of the usual five 3*d* functions—$3d_{xy}$, $3d_{x^2-y^2}$, $3d_{yz}$, $3d_{zx}$, and $3d_{z^2}$ and a 3*s* function $(x^2 + y^2 + z^2)$. The 6-31G* basis, in addition to adding polarization functions to a 6-31G basis, thus includes one more function of *s*-type symmetry. The contraction is thus (11*s*4*p*1*d*/4*s*)/[4*s*2*p*1*d*/2*s*] and the basis set includes 2 functions for H and 15 functions for Li to F. A standard Gaussian exponent for the six 3*d* functions of $\alpha = 0.8$ has been suggested for C, N, O, and F.

The 6-31G** basis differs from the 6-31G* basis by the addition of one set of uncontracted *p*-type Gaussian primitives for each H. A standard Gaussian exponent of $\alpha = 1.1$ has been suggested for these functions. The 6-31G** contraction is thus (11*s*4*p*1*d*/4*s*1*p*)[4*s*2*p*1*d*/2*s*1*p*] and each hydrogen now includes five basis functions.

Exercise 3.31 Determine the total number of basis functions for STO-3G, 4-31G, 6-31G*, and 6-31G** calculations on benzene.

Calculations at the 6-31G* and 6-31G** level provide, in many cases, quantitative results considerably superior to those at the lower STO-3G and 4-31G levels. Even these basis sets, however, have deficiencies that can only be remedied by going to triple zeta or quadruple zeta, adding more than one set of polarization functions, adding *f*-type functions to heavy atoms and *d*-type functions to hydrogen, improving the basis function description of the inner shell electrons, etc. As technology improves it will be possible to use more and more accurate basis sets.

3.7 SOME ILLUSTRATIVE CLOSED-SHELL CALCULATIONS

In this section, we illustrate results that are characteristic of Hartree-Fock calculations on the ground state of closed-shell molecules. Now that we have discussed polyatomic basis sets and the closed-shell restricted Hartree-Fock procedure, we are in a position to appreciate the results and the methodology of sample SCF calculations. The results of an extremely large number of SCF calculations are now available in the literature; we make no attempt to review these calculations. Instead, we apply a well-defined hierarchy of basis sets to a small set of "typical" molecules, and use these calculations to illustrate the order of accuracy expected in the general SCF calculation. By restricting our calculations to a few well-defined basis sets and a small set of molecules, we will be able to apply the various methods of later chapters, which go beyond the Hartree-Fock approximation, to the same collection of basis sets and molecules. In this way, we hope to give a more systematic illustration of the results obtained from the many computational methods of quantum chemistry than would be possible by simply reviewing selected results available in the literature. Thus our purpose here, in addition to illustrating SCF results themselves, is to display Hartree-Fock values of a small number of calculated quantities, for comparison with

Table 3.10 Standard geometries used in calculations

Molecule	Bond length (a.u.)	Bond angle
H_2	1.400	
CO	2.132	
N_2	2.074	
CH_4	2.050	109.47°
NH_3	1.913	106.67°
H_2O	1.809	104.52°
FH	1.733	

better values obtained in later chapters. In some cases, the Hartree-Fock results of this section are even qualitatively wrong, but, as we shall see later, these errors are corrected by including the effects of correlation.

The molecules we will use henceforth are H_2, isoelectronic N_2 and CO, and the ten-electron series, CH_4, NH_3, H_2O, and FH. The standard geometries at which all calculations, unless otherwise indicated, have been carried out are shown in Table 3.10. These "experimental" values are close but not always identical to values obtained in the "best" or most recent structure determination. The small set of molecules we have chosen cannot, of course, illustrate the total wealth of chemistry being approached by *ab initio* calculations. They do illustrate, however, some of the interesting quantities that can be derived from an SCF calculation. When we discuss open-shell calculations in the next section, we will introduce a few additional molecules. For the most part, however, the illustrative calculations in this book are performed on the molecules of Table 3.10.

3.7.1 Total Energies

Perhaps the primary quantity available in any *ab initio* calculation is the total energy. The total energy is the electronic energy (the output of the quantum mechanical calculation) plus the classical nuclear repulsion energy. In the SCF approximation, the electronic energy is variational and the "better" the basis set, the lower is the total energy. As the basis set becomes more and more complete the total energy approaches the Hartree-Fock limit. This limit can sometimes be estimated from large basis set calculations. By the variational principle, the Hartree-Fock-limit energy is still above the "exact" energy, which here can be taken as the energy obtained from an exact solution to the nonrelativistic Schrödinger equation in the Born-Oppenheimer approximation. In very accurate calculations on the atoms He, Be, etc., proper account must be taken of relativistic and Born-Oppenheimer corrections when comparing these "exact" energies with experimental ones. For most purposes in quantum chemistry these corrections can be assumed to be negligible and "exact" results equated to experimental results.

Tables 3.11 to 3.13 show the total energies obtained for the molecules of Table 3.10 using the four basis sets, STO-3G, 4-31G, 6-31G*, and 6-31G**. H_2 has no inner shells, or heavy atoms for *d*-type polarization functions, so the 6-31G* basis set is equivalent to the 4-31G basis set for this molecule. Similarly, N_2 and CO have no hydrogen atoms to add *p*-type polarization

Table 3.11 SCF total energies (a.u.) of H_2 with the standard basis sets

Basis set	Energy
STO-3G	−1.117
4-31G	−1.127
6-31G**	−1.131
HF-limit[a]	−1.134

[a] J. M. Schulman and D. N. Kaufman, *J. Chem. Phys.* **53**: 477 (1970).

Table 3.12 SCF total energies (a.u.) of N_2 and CO with the standard basis sets

Basis set	N_2	CO
STO-3G	−107.496	−111.225
4-31G	−108.754	−112.552
6-31G*	−108.942	−112.737
HF-limit[a]	−108.997	−112.791

[a] P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta* **28**: 213 (1973).

Table 3.13 SCF total energies (a.u.) for the ten-electron series with the standard basis sets

Basis set	CH_4	NH_3	H_2O	FH
STO-3G	−39.727	−55.454	−74.963	−98.571
4-31G	−40.140	−56.102	−75.907	−99.887
6-31G*	−40.195	−56.184	−76.011	−100.003
6-31G**	−40.202	−56.195	−76.023	−100.011
HF-limit[a]	−40.225	−56.225	−76.065	−100.071

[a] P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta* **28**: 213 (1973).

functions to, so the 6-31G** basis set is equivalent to the 6-31G* basis set. These absolute energies in themselves are rather uninteresting; chemical energetics is concerned with energy differences not absolute energies.

Exercise 3.32 Use the results of Tables 3.11 to 3.13 to calculate, for each basis set and at the Hartree-Fock limit, the energy difference for the following two reactions,

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \Delta E = ?$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta E = ?$$

Are the results consistent for different basis sets? Does Hartree-Fock theory predict these reactions to be exoergic or endoergic? The experimental hydrogenation energies (heats of reaction ΔH°) at zero degrees Kelvin are -18.604 kcal mol^{-1} (N_2) and -45.894 kcal mol^{-1} (CO), with 1 a.u. of energy equivalent to 627.51 kcal mol^{-1}.

Differences in the zero-point vibrational energies of reactants and products also contribute to reaction energies. From the experimental vibrational spectra, the $3N$-6 (or $3N$-5) zero-point energies ($h\nu_0/2$) for the relevant molecules (with degeneracies in parenthesis) are:

Molecule	$h\nu_0/2$ (kcal mol^{-1})
H_2	6.18
N_2	3.35
CO	3.08
H_2O	2.28
	5.13
	5.33
NH_3	1.35
	2.32(2)
	4.77
	4.85(2)
CH_4	1.86(3)
	2.17(2)
	4.14
	4.2(3)

Calculate the contribution of zero-point vibrations to the energy of the above two reactions. Is it a reasonable approximation to neglect the effect of zero-point vibrations?

Unfortunately, energy differences satisfy no variational principle, and it is often difficult to estimate the error in an energy difference. Provided equivalent basis sets are used for each species, the error in an energy difference will be, however, much less than the error in the corresponding absolute energies. As the last exercise shows, the SCF approximation often gives valid qualitative results for an energy change, even the energy change involved in a chemical reaction. In the general case, however, some estimate of the changes in correlation energies will be necessary for valid quantitative results.

3.7.2 Ionization Potentials

Koopmans' theorem provides the theoretical justification for interpreting Hartree-Fock orbital energies as ionization potentials and electron affinities. For the series of molecules we are using, the lowest virtual orbital always has a positive orbital energy, and thus Hartree-Fock theory predicts that none of these molecules will bind an electron to form a negative ion. Hartree-Fock almost always provides a very poor description of the electron affinity, and we will not consider the energies of virtual orbitals further.

The occupied orbital energies, on the other hand, commonly provide a reasonable first description of ionization potentials. Except for the interesting case of N_2, Koopmans' ionization potentials for our series of molecules are in reasonable agreement with experiment.

The molecule H_2 has only one occupied orbital. The negative of the energy of this occupied orbital for the various basis sets is shown in Table 3.14, and all the H_2 orbitals are shown in Fig. 3.9. A small change in the occupied orbital energy is observed in going beyond the minimal basis set, but beyond the minimal basis the orbital energy remains fixed at -0.595 Hartrees. The predicted ionization potential of $+0.595$ Hartrees is only in error by $\sim 2\%$. In Table 3.14, as well as in subsequent tables, all ionization potentials are vertical rather than adiabatic. A vertical transition is one in which the final state has the same nuclear geometry as the initial state, rather than its own equilibrium nuclear geometry (adiabatic transition). The excellent agreement between the Koopmans' value and the experimental value arises because of fortuitous cancellation of the correlation and relaxation effects, which are neglected in the Koopmans' approximation. Correlation has no effect on

Table 3.14 Ionization potential (a.u.) of H_2 obtained via Koopmans' theorem

Basic set	Ionization potential
STO-3G	0.578
4-31G	0.596
6-31G**	0.595
Near-HF-limit[a]	0.595
Experiment	0.584

[a] J. M. Schulman and D. M. Kaufman, *J. Chem. Phys.* **53**: 477 (1970).

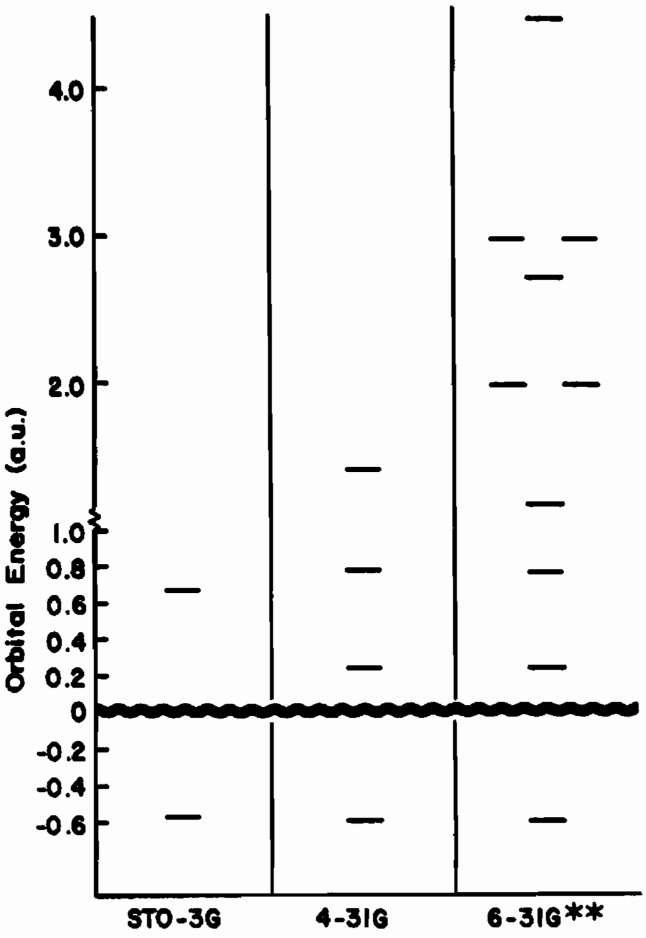


Figure 3.9 Orbital energies of H_2.

the final one-electron H_2^+ but lowers the energy of the initial H_2 state. Relaxation, on the other hand, lowers the energy of the final H_2^+ state. These two effects very nearly cancel in this example.

Table 3.15 shows the first two Koopmans' ionization potentials of CO. The highest occupied molecular orbitals of this molecule are the bonding 5σ and 1π orbitals formed mainly from linear combinations of the $2p$ orbitals

Table 3.15 The first two ionization potentials (a.u.) of CO obtained via Koopmans' theorem

	Ion symmetry	
Basis set	$^2\Sigma$	$^2\Pi$
STO-3G	0.446	0.551
4-31G	0.549	0.640
6-31G*	0.548	0.633
Near-HF-limit[a]	0.550	0.640
Experiment	0.510	0.620

[a] W. M. Huo, *J. Chem. Phys.* **43**: 624 (1965).

of the individual C and O atoms. Ionization of an electron from the 5σ orbital leads to an ion of $^2\Sigma$ symmetry while ionization of an electron from the 1π orbital leads to an ion of $^2\Pi$ symmetry. A primary question in the ionization of CO, as well as in the ionization of isoelectronic N_2, is whether the first ionization removes an electron from the 5σ or the 1π orbital. In the Hartree-Fock approximation, the equivalent question is whether the 5σ or 1π orbital is the highest lying occupied orbital.

For CO, the calculations agree with experiment in predicting that the 5σ orbital lies above the 1π orbital. The usual argument, which rationalizes this result, is that, while $2p\sigma$ orbitals on C and O interact more strongly than the corresponding $2p\pi$ orbitals on C and O and a bonding σ orbital would normally lie below a corresponding bonding π orbital, the 5σ orbital is "pushed" up by interaction with the lower 4σ antibonding orbital formed from $2s$ orbitals on C and O. In any event, the results of *ab initio* SCF calculations are in good agreement with experiment.

The molecule N_2 is isoelectronic with CO and has a similar orbital structure. Unlike CO, however, a fundamental problem arises in using Koopmans' theorem to interpret its ionization spectra. Table 3.16 compares calculated Koopmans' ionization potentials for N_2 with experiment, and Fig. 3.10 shows the calculated orbital energies. The first point to notice is that the STO-3G calculation is not in agreement with calculations using better basis sets and calculations at the Hartree-Fock limit. The STO-3G calculation predicts the $3\sigma_g$ orbital to be higher lying than the $1\pi_u$ orbital, whereas, the "correct" Hartree-Fock result is that the $1\pi_u$ orbital is the highest occupied orbital. As Fig. 3.10 shows, in homonuclear N_2, unlike heteronuclear CO, the $3\sigma_g$(5σ in CO) orbital has a different symmetry than the $2\sigma_u$(4σ in CO) orbital and, hence, the interaction which pushes these two orbitals apart is missing in N_2, but present in CO. This argument can

Table 3.16 The first two ionization potentials (a.u.) of N_2 obtained via Koopmans' theorem

	Ion symmetry	
Basis set	$^2\Sigma$	$^2\Pi$
STO-3G	0.540	0.573
4-31G	0.629	0.621
6-31G*	0.630	0.612
Near-HF-limit[a]	0.635	0.616
Experiment	0.573	0.624

[a] P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.* **44**: 1973 (1966).

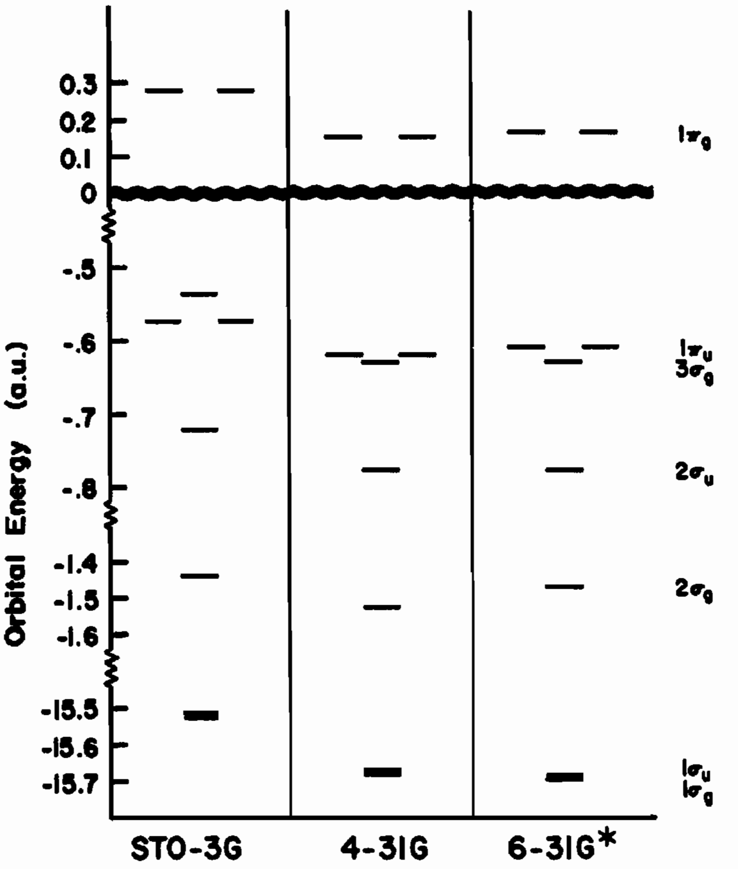


Figure 3.10 Orbital energies of N_2.

be used to rationalize why Hartree-Fock calculations predict the highest occupied orbital to be of π symmetry in N_2, but of σ symmetry in CO.

The second and most important point of Table 3.16 is that the "correct" Hartree-Fock results are in qualitative disagreement with experiment. In the molecular orbital Hartree-Fock model, the $1\pi_u$ orbital is the highest occupied orbital, yet the lowest experimental ionization potential corresponds to the production of an ion with Σ_g symmetry. This implies a breakdown of the simple orbital picture of ionization. The Hartree-Fock picture is an approximation. For the case of N_2 this approximation is not sufficiently accurate for even a qualitative understanding of the ionization phenomena. As we shall see in Chapters 4 and 7, when the single determinant Hartree-Fock model is replaced by a multideterminantal model, with its associated inclusion of correlation effects, theoretical calculations and experiment ultimately agree on the ionization spectra of N_2.

Table 3.17 shows the calculated and experimental results for the first ionization potential of molecules in the ten-electron series, CH_4, NH_3, H_2O, and FH. The largest basis set gives ionization potentials that are all slightly larger than experimental values, with the agreement becoming slightly worse as one moves to the right in the periodic table. The correct ordering FH > CH_4 > H_2O > NH_3 is reproduced, except with the minimal basis set. Figure 3.11 shows all the occupied orbitals and the first virtual orbital for this ten-electron series, using the largest 6-31G** basis set. The lowest

Table 3.17 The lowest ionization potentials (a.u.) of the ten-electron series obtained via Koopmans' theorem

Basis set	CH_4	NH_3	H_2O	FH
STO-3G	0.518	0.353	0.391	0.464
4-31G	0.543	0.414	0.500	0.628
6-31G*	0.545	0.421	0.498	0.628
6-31G**	0.543	0.421	0.497	0.627
Near-HF-limit	0.546[a]	0.428[b]	0.507[c]	0.650[d]
Experiment	0.529	0.400	0.463	0.581

[a] W. Meyer, *J. Chem. Phys.* **58**: 1017 (1973).

[b] A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.* **52**: 4133 (1970).

[c] B. J. Rosenberg and I. Shavitt, *J. Chem. Phys.* **63**: 2162 (1975).

[d] P. E. Cade and W. M. Huo, *J. Chem. Phys.* **47**: 614 (1967).

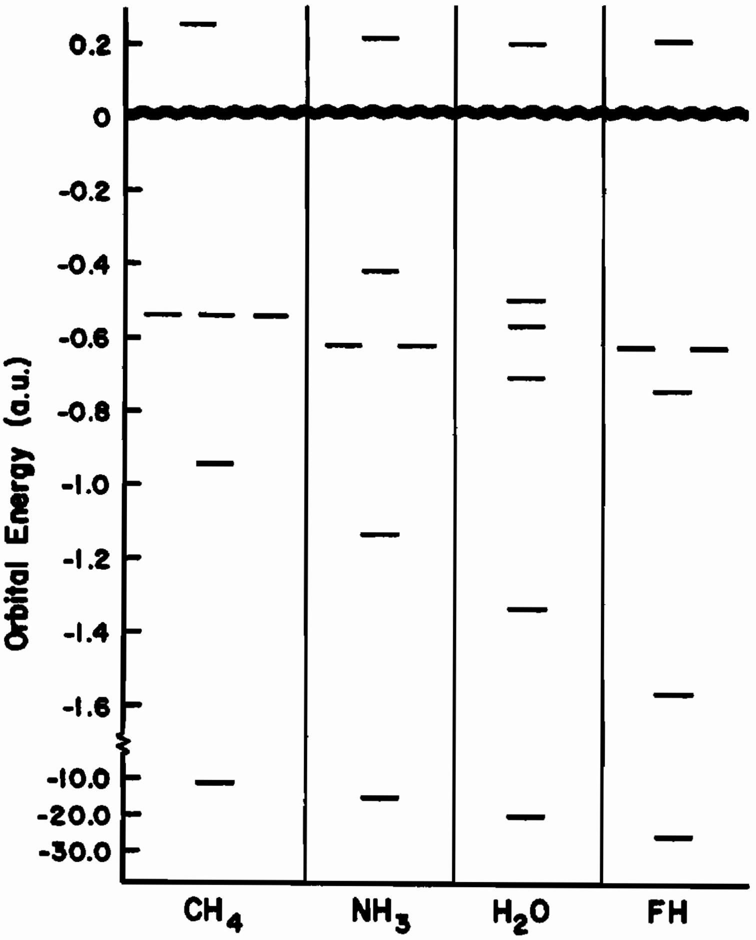


Figure 3.11 6-31G** orbital energies of the ten-electron series.

molecular orbital is essentially the 1*s* inner-shell atomic orbital of the heavy atom. The second molecular orbital is comprised mainly of the 2*s* orbital of the heavy atom, particularly as one moves to the right in the periodic table. In FH this molecular orbital is very atomic in nature and has much of the character of an inner shell. The average energy of the three highest occupied orbitals also decreases slightly as one moves to the right in the periodic table, but the individual energies of these three orbitals are determined by the symmetry of the system. That is, the reason CH_4 does not have the lowest ionization potential, in line with the trend in the rest of the series, is that the tetrahedral symmetry causes these three orbitals to be degenerate. If CH_4 was distorted from its tetrahedral symmetry, its first ionization potential would decrease.

Figure 3.12 shows all the orbital energies of H_2O, using our four standard basis sets. In this as in other examples, the occupied orbital spectrum is nearly invariant to the basis set once the basis set is of double zeta quality or better. The minimal basis set leads to ionization potentials that are significantly different from those given by better basis sets.

The Koopmans' approximation to ionization potentials provides a valuable qualitative tool for interpreting and making assignments to experimental spectra. Like any other Hartree-Fock result, however, it is not

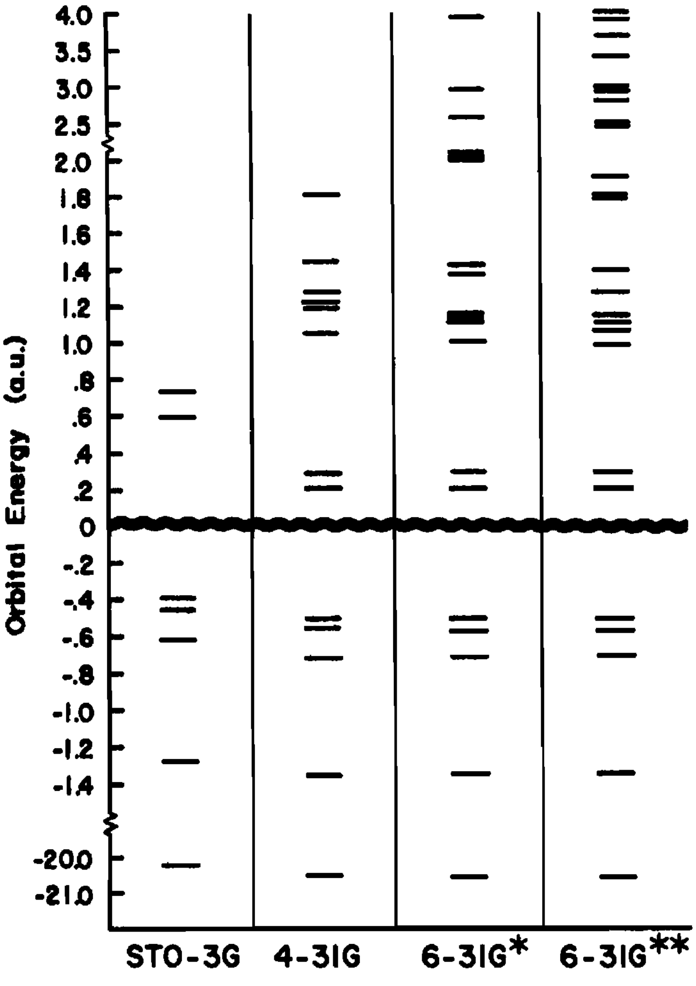


Figure 3.12 Occupied and virtual orbital energies of H_2O.

truly quantitative and, in some cases, it may even give an incorrect qualitative picture.

3.7.3 Equilibrium Geometries

Perhaps the most common use of electronic structure calculations is to predict the equilibrium geometry of molecules. In the Born-Oppenheimer approximation, the total energy, as a function of the coordinates of the nuclei, defines a potential surface. The motion of the nuclei on this potential surface defines the possible chemical reactions, the molecular vibrations, etc. The points on the potential surface of most immediate interest are the stationary points. The saddle points define transition states, and the minima define equilibrium geometries. Although one would like to know the complete details of the potential surface, this quickly becomes an impossible task as the number of nuclei and the 3N-6 degrees of freedom increase. For moderate-sized molecules, however, it may still be possible to find the potential surface minimum. This constitutes a prediction of chemical structure. In cases where the number of degrees of freedom is very large, it may be sufficient to fix certain geometric variables at their standard or expected values and optimize only the geometric variables for which little *a priori* information is available.

Since one cannot, in general, obtain a potential surface which is close to the exact Born-Oppenheimer surface, the best that can be hoped for is a potential surface which is closely parallel to the exact surface. As our discussion of minimal basis H_2 (c.f. Fig. (3.5)) has shown, the potential surface obtained from a closed shell restricted Hartree-Fock calculation will not be parallel to, nor even qualitatively resemble, the exact potential surface in regions of the surface characterizing the stretching and breaking of a bond if, as is the usual case, the dissociation products have open shells. The restricted closed-shell Hartree-Fock procedure is thus inappropriate for the general exploration of a potential surface. In most cases, however, the restricted Hartree-Fock potential surface is "reasonably" parallel to the exact surface near the region of a minimum. That is, restricted Hartree-Fock predictions of equilibrium geometries provide reasonably valid approximations to experimental values.

The problem of finding an equilibrium geometry is equivalent to the mathematical problem of nonlinear unconstrained minimization. Historically, there have been a number of different methods used for such minimizations. An inefficient, but conceptually simple, procedure is the line search. Here one varies only one variable at a time until a minimum for that variable is obtained. One cycles through all of the variables a number of times, varying each one in sequence, until the optimum values no longer change. If there is a large coupling between variables, this procedure may converge

Table 3.18 SCF equilibrium bond lengths (a.u.) of H_2

Basis set	Bond length
STO-3G	1.346
4-31G	1.380
6-31G**	1.385
Experiment	1.401

very slowly. Other procedures depend on knowing the first derivatives and possibly the second derivatives of the energy with respect to the nuclear coordinates. These are much better procedures but require an evaluation of a number of derivatives. In the past these derivatives have been calculated numerically, but there are now a number of programs that can calculate these derivatives by efficient analytical procedures and use them to generate equilibrium geometries automatically. Appendix C discusses the basic ideas behind these important developments.

Table 3.18 gives the calculated equilibrium bond lengths of H_2 with our standard basis sets. The calculated bond length of 1.385 a.u. obtained from using the 6-31G** basis set is close to the Hartree-Fock limit value. The error of 0.016 a.u. ($\sim 1\%$) in the bond length is not uncharacteristic of what can be expected from a good *ab initio* SCF calculation, although the average absolute error is more commonly $\sim$0.02–0.04 a.u.

Table 3.19 gives the calculated bond lengths for CO and N_2 and Table 3.20 the calculated bond lengths for CH_4, NH_3, H_2O, and FH. The error at the Hartree-Fock limit is somewhat larger for a distance between two heavy atoms than it is for an X-H distance. In these, as in most other molecules, bond lengths predicted by Hartree-Fock limit calculations are too

Table 3.19 SCF equilibrium bond lengths (a.u.) of N_2 and CO

Basis set	N_2	CO
STO-3G	2.143	2.166
4-31G	2.050	2.132
6-31G*	2.039	2.105
Near-HF-limit	2.013[a]	2.081[b]
Experiment	2.074	2.132

[a] P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.* **44**: 1973 (1966).

[b] W. M. Huo, *J. Chem. Phys.* **43**: 624 (1965).

Table 3.20 SCF equilibrium bond lengths (a.u.) of the ten-electron series

Basis set	CH_4	NH_3	H_2O	FH
STO-3G	2.047	1.952	1.871	1.807
4-31G	2.043	1.873	1.797	1.742
6-31G*	2.048	1.897	1.791	1.722
6-31G**	2.048	1.897	1.782	1.703
Near-HF-limit	2.048[a]	1.890[b]	1.776[c]	1.696[d]
Experiment	2.050	1.912	1.809	1.733

[a] W. Meyer, *J. Chem. Phys.* **58**: 1017 (1973).

[b] A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.* **52**: 4133 (1970).

[c] B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.* **65**: 4072 (1976).

[d] P. E. Cade and W. J. Huo, *J. Chem. Phys.* **47**: 614 (1967).

short. The average error in a bond length predicted by poorer basis sets, such as the minimal STO-3G basis set, is larger than for basis sets at the Hartree-Fock limit, and is commonly ~0.05–0.10 a.u.

Values for the calculated bond angles in NH_3 and H_2O are shown in Table 3.21. There is quite reasonable agreement (~1°–2°) at the Hartree-Fock limit. These bond angles are not particularly good at the double zeta (4-31G) level, and it appears that *d*-type functions in the basis set are necessary for a quantitative description of the angle in these molecules. If the limit is taken of adding only *s*- and *p*-type functions to a basis set for NH_3, the predicted geometry becomes planar! This illustrates the necessity of a balanced basis set.

Table 3.21 SCF equilibrium bond angles for NH_3 and H_2O

Basis set	NH_3	H_2O
STO-3G	104.2	100.0
4-31G	115.8	111.2
6-31G*	107.5	105.5
6-31G**	107.6	106.0
Near-HF-limit	107.2[a]	106.1[b]
Experiment	106.7	104.5

[a] A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.* **52**: 4133 (1970).

[b] B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.* **65**: 4072 (1976).

As with any other calculated quantity, the predictions of equilibrium geometries obtained from the *ab initio* SCF procedure cannot provide truly quantitative agreement with experiment. Nevertheless, such geometries almost always give the correct trends when comparing a series of related molecules; the *a priori* prediction of chemical structure has been one of the most successful aspects of Hartree-Fock calculations. The book by Hehre *et al.* (see Further Reading) critically evaluates the performance of SCF calculations in predicting equilibrium geometries, with many examples.

3.7.4 Population Analysis and Dipole Moments

An *ab initio* SCF calculation produces a one-electron charge density $\rho(\mathbf{r})$ describing the probability of finding an electron, i.e.,

$$\rho(\mathbf{r}) = \sum_{\mu}\sum_{\nu} P_{\mu\nu}\phi_{\mu}(\mathbf{r})\phi_{\nu}^{*}(\mathbf{r}) \tag{3.305}$$

This charge density is commonly plotted as a contour map for visual interpretation of the charge density. Alternatively, one would like to have more quantitative characterizations of the charge density. One way of doing this is to calculate the moments of the charge—dipole moment, quadrupole moment, etc. In addition, chemists would like to ascribe portions of the charge to specific atoms in line with their intuitive notions. As we have described previously, there is no rigorous way of doing this. Nevertheless, a population analysis may sometimes be useful for interpretive purposes. As an illustration of such an analysis, Tables 3.22 and 3.23 contain the net positive charge on each of the hydrogens in the 10-electron series, from either a Mulliken or a Löwdin population analysis. In agreement with standard electronegativity arguments, the hydrogen atom becomes more positively charged as one goes to the right in the periodic table. Very little can be said about the absolute magnitude of these charges, however. It is particularly dangerous to compare numbers for different basis sets. For example, a 6-31G* calculation on CH_4 compared to an STO-3G calculation

Table 3.22 A Mulliken SCF population analysis for the ten-electron series. The entries are the net charges on the hydrogens

Basis set	CH_4	NH_3	H_2O	FH
STO-3G	0.06	0.16	0.18	0.21
4-31G	0.15	0.30	0.39	0.48
6-31G*	0.16	0.33	0.43	0.52
6-31G**	0.12	0.26	0.34	0.40

Table 3.23 A Löwdin SCF population analysis for the ten-electron series. The entries are the net charges on the hydrogens

Basis set	CH_4	NH_3	H_2O	FH
STO-3G	0.03	0.10	0.13	0.15
4-31G	0.10	0.20	0.28	0.36
6-31G*	0.16	0.27	0.36	0.45
6-31G**	0.11	0.18	0.23	0.27

on NH_3 would predict the CH bond in methane to be more polar than the NH bond in ammonia. Since one adds orbitals only to hydrogen atoms in going from the 6-31G* to 6-31G** basis set, the 6-31G** basis set always assigns more electrons (less positive charge) to the hydrogens than does the 6-31G* basis set. In spite of problems, a population analysis can be a useful interpretive device when used properly.

Calculations of the dipole moment of CO are shown in Table 3.24. This particular calculation has had an interesting history, since there has been considerable disagreement as to the proper sign of the dipole moment. The correct experimental result is that the negative end of the molecule is carbon, not oxygen as simple electronegativity arguments would suggest. Although a minimal basis set gives the right sign, all SCF calculations with a basis set of double zeta quality or better predict the wrong sign. The difficulty arises because of the relatively small magnitude of the dipole moment, a result of the cancellation of two large and opposite contributions. One contribution is that of net charge which, in line with electronegativity arguments, has oxygen more negative. In addition, however, there is a lone pair of electrons on carbon, directed away from the bond. This asymmetry of the charge on carbon leads to an additional contribution to the dipole moment, which is

Table 3.24 SCF dipole moment (a.u.) of CO for the standard basis sets. A positive dipole moment corresponds to C^-O^+

Basis set	Dipole moment
STO-3G	0.066
4-31G	−0.237
6-31G*	−0.131
Near-HF-limit[a]	−0.110
Experiment	0.044

[a] A. D. McLean and M. Yoshimine, *Intern. J. Quantum Chem.* **15:** 313 (1967).

Table 3.25 SCF dipole moments (a.u.) for the ten-electron series and the standard basis sets

Basis set	NH_3	H_2O	FH
STO-3G	0.703	0.679	0.507
4-31G	0.905	1.026	0.897
6-31G*	0.768	0.876	0.780
6-31G**	0.744	0.860	0.776
Near-HF-limit	0.653[a]	0.785[b]	0.764[c]
Experiment	0.579	0.728	0.716

[a] A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.* **52**: 4133 (1970).

[b] B. J. Rosenberg and I. Shavitt, *J. Chem. Phys.* **63**: 2162 (1975).

[c] P. E. Cade and W. M. Huo, *J. Chem. Phys.* **45**: 1063 (1966).

opposite to the first contribution. The cancellation, leading to a small positive (C^-O^+) dipole moment, is not reproduced with sufficient accuracy in the SCF calculations. As we shall see in the next chapter, this disagreement between theory and experiment disappears when proper account is taken of correlation effects.

Table 3.25 contains the calculated dipole moments for NH_3, H_2O, and FH using our standard basis sets. Only at the 6-31G* level and beyond is the proper trend $H_2O > FH > NH_3$ reproduced. At the Hartree-Fock limit the calculated dipole moments are somewhat too large, but the trend is well reproduced. The 6-31G** basis set still appears to be inadequate for accurate calculation of dipole moments, since the values obtained with it are still rather distant from Hartree-Fock-limit values.

3.8 UNRESTRICTED OPEN-SHELL HARTREE-FOCK: THE POPLE-NESBET EQUATIONS

At the beginning of this chapter we derived and discussed formal properties of the Hartree-Fock equations independent of any particular form for the spin orbitals. We then introduced a set of restricted spin orbitals and have since been concerned solely with restricted closed-shell calculations of the type

$$|\Psi_{\mathrm{RHF}}\rangle = |\psi_1\bar{\psi}_1\cdots\rangle \tag{3.306}$$

Obviously, not all molecules, nor all states of closed-shell molecules, can be described by pairs of electrons in closed-shell orbitals, and we now need to generalize the previous closed-shell formalism to accommodate situations in which a molecule has one or more open-shell (unpaired) electrons. That is, we need to consider unrestricted wave functions of the type

$$|\Psi_{\text{UHF}}\rangle = |\psi_1^\alpha \bar{\psi}_1^\beta \cdots\rangle \tag{3.307}$$

In the previous chapter we gave a preliminary description of open-shell determinants (Section 2.5); we now obtain the SCF equations for unrestricted calculations.

In dealing with open-shell problems, there are two common approaches: the restricted open-shell, and the unrestricted open-shell Hartree-Fock procedures. In the restricted open-shell formalism, all electrons, except those that are explicitly required to occupy open-shell orbitals, occupy closed-shell orbitals. The advantage of this procedure is that the wave functions one obtains are eigenfunctions of the spin operator $\mathscr{S}^2$. The disadvantage is that the constraint of occupying orbitals in pairs raises the variational energy. In addition, the spatial equations defining the closed- and open-shell orbitals of restricted open-shell Hartree-Fock theory are somewhat more involved or at least less straightforward than the spatial equations of unrestricted Hartree-Fock theory. For treating open-shells our emphasis is on unrestricted calculations—mainly for reasons of simplicity and generality.

As we have discussed previously, a restricted Hartree-Fock description is inappropriate at long bond lengths for a molecule like H_2, which dissociates to open-shell species. This problem can be solved to a certain extent by using an unrestricted wave function at long bond lengths. In addition to describing unrestricted wave functions for "true" open shells (doublets, triplets, etc.), we will spend some time in this section analyzing the "singlet" dissociation problem with our minimal basis H_2 model. An unrestricted wave function will allow a closed-shell molecule like H_2 to dissociate to open-shell atoms.

In this section, then, we first introduce a set of unrestricted spin orbitals to derive the spatial eigenvalue equations of unrestricted Hartree-Fock theory. We then introduce a basis set and generate the unrestricted Pople-Nesbet matrix equations, which are analogous to the restricted Roothaan equations. We then perform some sample calculations to illustrate solutions to the unrestricted equations. Finally, we discuss the dissociation problem and its unrestricted solution.

3.8.1 Open-Shell Hartree-Fock: Unrestricted Spin Orbitals

The general Hartree-Fock eigenvalue equation, in terms of spin orbitals, is

$$f(1)\chi_i(1) = \varepsilon_i \chi_i(1) \tag{3.308}$$

What we want to do now is to introduce the specific unrestricted form for the spin orbitals $\{\chi_i\}$ and derive, from the above general Hartree-Fock equation, the spatial equations which determine the unrestricted spatial orbitals. The procedure that we use here is quite analogous to that of Subsection 3.4.1, where we derived the spatial equations determining restricted spatial orbitals. We will not repeat all details of the derivation.

Analogous to Eq. (3.110) for restricted spin orbitals, an unrestricted set of spin orbitals has the following form

$$\chi_i(\mathbf{x}) = \begin{cases} \psi_j^\alpha(\mathbf{r})\alpha(\omega) \\ \psi_j^\beta(\mathbf{r})\beta(\omega) \end{cases} \tag{3.309}$$

That is, electrons of α spin are described by a set of spatial orbitals $\{\psi_j^\alpha | j = 1, 2, \ldots, K\}$, and electrons of β spin are described by a different set of spatial orbitals $\{\psi_j^\beta | j = 1, 2, \ldots, K\}$. In our previous restricted case $\psi_j^\alpha \equiv \psi_j^\beta \equiv \psi_j$. We are now allowing electrons of α and β spin to be described by different spatial functions.

To derive the spatial equations defining $\{\psi_j^\alpha\}$ and $\{\psi_j^\beta\}$, we need to insert Eq. (3.309) for the spin orbitals $\{\chi_i\}$ into the general Hartree-Fock equation (3.308) and integrate out the spin variable ω. For simplicity, we will concentrate on the equation defining ψ_j^α and use the symmetry between α and β spins to write down the corresponding equations defining ψ_j^β. Substituting Eq. (3.309) into Eq. (3.308) leads to

$$f(1)\psi_j^\alpha(\mathbf{r}_1)\alpha(\omega_1) = \varepsilon_i\psi_j^\alpha(\mathbf{r}_1)\alpha(\omega_1) \tag{3.310}$$

Now, ε_i is the energy of the spin orbital $\chi_i \equiv \psi_j^\alpha\alpha$. Since the spin orbitals for electrons of α and β spin have different spatial parts, their energies will also be different. In the above case $\varepsilon_i \equiv \varepsilon_j^\alpha$. There will be a corresponding set of orbital energies $\{\varepsilon_j^\beta | j = 1, 2, \ldots, K\}$ for electrons of β spin. Thus

$$f(1)\psi_j^\alpha(\mathbf{r}_1)\alpha(\omega_1) = \varepsilon_j^\alpha\psi_j^\alpha(\mathbf{r}_1)\alpha(\omega_1) \tag{3.311}$$

If we now multiply this equation by $\alpha^*(\omega_1)$ and integrate over spin we get

$$f^\alpha(1)\psi_j^\alpha(1) = \varepsilon_j^\alpha\psi_j^\alpha(1) \tag{3.312}$$

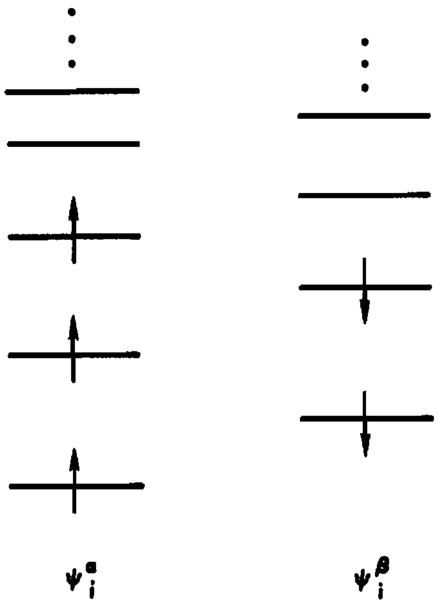
$$f^\beta(1)\psi_j^\beta(1) = \varepsilon_j^\beta\psi_j^\beta(1) \tag{3.313}$$

as the spatial equations defining the spatial orbitals ψ_j^α and ψ_j^β. The spatial Fock operators $f^\alpha(1)$ and $f^\beta(1)$ are defined by

$$f^\alpha(\mathbf{r}_1) = \int d\omega_1\ \alpha^*(\omega_1)f(\mathbf{r}_1, \omega_1)\alpha(\omega_1) \tag{3.314}$$

$$f^\beta(\mathbf{r}_1) = \int d\omega_1\ \beta^*(\omega_1)f(\mathbf{r}_1, \omega_1)\beta(\omega_1) \tag{3.315}$$

We could use the spin orbital definition (3.115) of $f(\mathbf{r}_1, \omega_1)$ to perform these integrations and work out explicit formulas for f^α and f^β. Alternatively, we can just write down expressions for f^α and f^β by considering the possible interactions defined by any unrestricted determinant,



The operator $f^\alpha(1)$ is the kinetic energy, nuclear attraction, and effective potential of an electron of α spin. The effective interactions of an electron of α spin include a coulomb and exchange interaction with all other electrons of α spin plus only a coulomb interaction with electrons of β spin. Thus

$$f^\alpha(1) = h(1) + \sum_a^{N^\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N^\beta} J_a^\beta(1) \tag{3.316}$$

where the two sums in this equation are over the N^α orbitals ψ_a^α occupied by electrons of α spin and the N^β orbitals ψ_a^β occupied by electrons of β spin. The kinetic energy and nuclear attraction are independent of spin so $h(1)$ is identical to the corresponding operator of the restricted case. The electrons of α spin see a coulomb potential J_a^α and an exchange potential $-K_a^\alpha$ coming from each of the N^α electrons of α spin occupying the orbitals ψ_a^α, plus a coulomb potential J_a^β coming from each of the $N^\beta = N - N^\alpha$ electrons of β spin occupying the orbitals ψ_a^β. The sum over the N^α orbitals ψ_a^α in the above equation formally includes the interaction of an α electron with itself. However, since

$$[J_a^\alpha(1) - K_a^\alpha(1)]\psi_a^\alpha(1) = 0 \tag{3.317}$$

this self-interaction is eliminated. The corresponding Fock operator for electrons of β spin is

$$f^\beta(1) = h(1) + \sum_a^{N^\beta} [J_a^\beta(1) - K_a^\beta(1)] + \sum_a^{N^\alpha} J_a^\alpha(1) \tag{3.318}$$

The unrestricted coulomb and exchange operators are defined in analogy to our previous definitions (3.124) and (3.125) of the restricted coulomb and exchange operators. That is,

$$J_a^\alpha(1) = \int d\mathbf{r}_2\, \psi_a^{\alpha*}(2) r_{12}^{-1} \psi_a^\alpha(2) \tag{3.319}$$

$$\begin{aligned} K_a^\alpha(1)\psi_i^\alpha(1) &= \left[\int d\mathbf{r}_2\, \psi_a^{\alpha*}(2) r_{12}^{-1} \psi_i^\alpha(2)\right]\psi_a^\alpha(1) \\ &= \left[\int d\mathbf{r}_2\, \psi_a^{\alpha*}(2) r_{12}^{-1} \mathscr{P}_{12} \psi_a^\alpha(2)\right]\psi_i^\alpha(1) \end{aligned} \tag{3.320}$$

The definitions of J_a^β and K_a^β are strictly analogous to the above.

From the definitions (3.316) and (3.318) of the two Fock operators f^α and f^β, we can see that the two integro-differential eigenvalue equations (3.312) and (3.313) are coupled and cannot be solved independently. That is, f^α depends on the occupied β orbitals, ψ_a^β, through J_a^β, and f^β depends on the occupied α orbitals, ψ_a^α, through J_a^α. The two equations must thus be solved by a simultaneous iterative process.

Exercise 3.33 Rather than use the simple technique of writing down $f^\alpha(1)$ by inspection of the possible interactions, as we have done above, use expression (3.314) for $f^\alpha(1)$ and explicitly integrate over spin and carry through the algebra, as was done in Subsection 3.4.1 for the restricted closed-shell case, to derive

$$f^\alpha(1) = h(1) + \sum_a^{N^\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N^\beta} J_a^\beta(1)$$

Now that we have derived the unrestricted Hartree-Fock equations, we can write down expressions for the unrestricted orbital energies, total unrestricted energy, etc. First, we need to define a few terms. The kinetic energy and nuclear attraction of an electron in one of the unrestricted orbitals ψ_i^α or ψ_i^β is the expectation value

$$h_{ii}^\alpha = (\psi_i^\alpha|h|\psi_i^\alpha) \quad \text{or} \quad h_{ii}^\beta = (\psi_i^\beta|h|\psi_i^\beta) \tag{3.321}$$

The Coulomb interaction of an electron in ψ_i^α with one in ψ_j^β is

$$J_{ij}^{\alpha\beta} = J_{ji}^{\beta\alpha} = (\psi_i^\alpha|J_j^\beta|\psi_i^\alpha) = (\psi_j^\beta|J_i^\alpha|\psi_j^\beta) = (\psi_i^\alpha\psi_i^\alpha|\psi_j^\beta\psi_j^\beta) \tag{3.322}$$

The corresponding coulomb interactions between electrons of the same spin are

$$J_{ij}^{\alpha\alpha} = (\psi_i^\alpha|J_j^\alpha|\psi_i^\alpha) = (\psi_j^\alpha|J_i^\alpha|\psi_j^\alpha) = (\psi_i^\alpha\psi_i^\alpha|\psi_j^\alpha\psi_j^\alpha) \tag{3.323}$$

and

$$J_{ij}^{\beta\beta} = (\psi_i^\beta|J_j^\beta|\psi_i^\beta) = (\psi_j^\beta|J_i^\beta|\psi_j^\beta) = (\psi_i^\beta\psi_i^\beta|\psi_j^\beta\psi_j^\beta) \tag{3.324}$$

The exchange interactions between electrons of parallel spin are

$$K_{ij}^{\alpha\alpha} = (\psi_i^\alpha|K_j^\alpha|\psi_i^\alpha) = (\psi_j^\alpha|K_i^\alpha|\psi_j^\alpha) = (\psi_i^\alpha\psi_j^\alpha|\psi_j^\alpha\psi_i^\alpha) \tag{3.325}$$

and

$$K_{ij}^{\beta\beta} = (\psi_i^\beta|K_j^\beta|\psi_i^\beta) = (\psi_j^\beta|K_i^\beta|\psi_j^\beta) = (\psi_i^\beta\psi_j^\beta|\psi_j^\beta\psi_i^\beta) \tag{3.326}$$

There is, of course, no exchange interaction between electrons of opposite spin.

The total unrestricted electronic energy can now be written down just by considering all the contributing energy terms,

$$E_0 = \sum_a^{N^\alpha} h_{aa}^\alpha + \sum_a^{N^\beta} h_{aa}^\beta + \frac{1}{2}\sum_a^{N^\alpha}\sum_b^{N^\alpha} (J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \frac{1}{2}\sum_a^{N^\beta}\sum_b^{N^\beta} (J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}) + \sum_a^{N^\alpha}\sum_b^{N^\beta} J_{ab}^{\alpha\beta} \tag{3.327}$$

The summations with upper limit N^α are summations over the occupied orbitals ψ_a^α or ψ_b^α. A similar convention holds for orbitals occupied by electron of β spin. The factor of $\frac{1}{2}$ in the third and fourth terms eliminates the double counting in the free summation. The self-interaction disappears since $J_{aa}^{\alpha\alpha} - K_{aa}^{\alpha\alpha} = J_{aa}^{\beta\beta} - K_{aa}^{\beta\beta} = 0$ as Eqs. (3.323) to (3.326) verify.

Exercise 3.34 The unrestricted doublet ground state of the Li atom is $|\Psi_0\rangle = |\psi_1^\alpha(1)\bar{\psi}_1^\beta(2)\psi_2^\alpha(3)\rangle$. Show that the energy of this state is $E_0 = h_{11}^\alpha + h_{11}^\beta + h_{22}^\alpha + J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha} + J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta}$.

Exercise 3.35 The unrestricted orbital energies are $\varepsilon_i^\alpha = (\psi_i^\alpha|f^\alpha|\psi_i^\alpha)$ and $\varepsilon_i^\beta = (\psi_i^\beta|f^\beta|\psi_i^\beta)$. Show that these are given by

$$\varepsilon_i^\alpha = h_{ii}^\alpha + \sum_a^{N^\alpha} (J_{ia}^{\alpha\alpha} - K_{ia}^{\alpha\alpha}) + \sum_a^{N^\beta} J_{ia}^{\alpha\beta}$$

$$\varepsilon_i^\beta = h_{ii}^\beta + \sum_a^{N^\beta} (J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta}) + \sum_a^{N^\alpha} J_{ia}^{\beta\alpha}$$

Derive an expression for E_0 in terms of the orbital energies and the coulomb and exchange energies.

3.8.2 Introduction of a Basis: The Pople-Nesbet Equations

To solve the unrestricted Hartree-Fock equations (3.312) and (3.313), we need to introduce a basis set and convert these integro differential equations to matrix equations,[12] just as we did when deriving Roothaan's equations. We thus introduce our set of basis functions $\{\phi_\mu|\mu = 1, 2, \ldots, K\}$ and expand the unrestricted molecular orbitals in this basis,

$$\psi_i^\alpha = \sum_{\mu=1}^{K} C_{\mu i}^\alpha \phi_\mu \qquad i = 1, 2, \ldots, K \tag{3.328}$$

$$\psi_i^\beta = \sum_{\mu=1}^{K} C_{\mu i}^\beta \phi_\mu \qquad i = 1, 2, \ldots, K \tag{3.329}$$

The two eigenvalue equations (3.312) and (3.313) guarantee that the sets of eigenfunctions $\{\psi_i^\alpha\}$ and $\{\psi_i^\beta\}$ individually form orthonormal sets. There is no reason, however, that a member of the set $\{\psi_i^\alpha\}$ need be orthogonal to a member of the set $\{\psi_i^\beta\}$. Even though the two sets of spatial orbitals overlap with each other, the set of $2K$ spin orbitals $\{\chi_i\}$ will form an orthonormal set, either from spatial orthogonality ($\alpha\alpha$ and $\beta\beta$ case) or spin orthogonality ($\alpha\beta$ case).

Substituting the expansion (3.328) for the orbitals ψ_j^α into the α Hartree-Fock equation (3.312) gives

$$\sum_\nu C_{\nu j}^\alpha f^\alpha(1)\phi_\nu(1) = \varepsilon_j^\alpha \sum_\nu C_{\nu j}^\alpha \phi_\nu(1) \tag{3.330}$$

If we multiply this equation by $\phi_\mu^*(1)$ and integrate over the spatial coordinates of electron-one, we get

$$\sum_\nu F_{\mu\nu}^\alpha C_{\nu j}^\alpha = \varepsilon_j^\alpha \sum_\nu S_{\mu\nu} C_{\nu j}^\alpha \qquad j = 1, 2, \ldots, K \tag{3.331}$$

where $\mathbf{S}$ is the overlap matrix (c.f. Eq. (3.136)) and $\mathbf{F}^\alpha$ is the matrix representation of f^α in the basis $\{\phi_\mu\}$,

$$F_{\mu\nu}^\alpha = \int d\mathbf{r}_1 \, \phi_\mu^*(1) f^\alpha(1) \phi_\nu(1) \tag{3.332}$$

Identical results can be obtained for β orbitals. The algebraic equations in (3.331) and the corresponding equations for β orbitals can be combined into the two matrix equations,

$$\mathbf{F}^\alpha \mathbf{C}^\alpha = \mathbf{S}\mathbf{C}^\alpha \boldsymbol{\varepsilon}^\alpha \tag{3.333}$$

$$\mathbf{F}^\beta \mathbf{C}^\beta = \mathbf{S}\mathbf{C}^\beta \boldsymbol{\varepsilon}^\beta \tag{3.334}$$

These two equations are the unrestricted generalizations of the restricted Roothaan equations (c.f. Eq. (3.139)) and were first given by Pople and Nesbet. The matrices $\boldsymbol{\varepsilon}^\alpha$ and $\boldsymbol{\varepsilon}^\beta$ are diagonal matrices of orbital energies (c.f. Eq. (3.141)). The $K \times K$ square matrices $\mathbf{C}^\alpha$ and $\mathbf{C}^\beta$ have as columns the expansion coefficients for ψ_i^α and ψ_i^β (c.f. Eq. (3.140)). These equations can be solved in a manner similar to the way Roothaan's equations are solved, except that, since $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$ depend on both $\mathbf{C}^\alpha$ and $\mathbf{C}^\beta$, the two matrix eigenvalue problems must be solved simultaneously. We will return to the solution of these equations after we have described unrestricted density matrices and the explicit form of $F_{\mu\nu}^\alpha$ and $F_{\mu\nu}^\beta$.

3.8.3 Unrestricted Density Matrices

We continue here with the generalization of our previous results for restricted closed-shell wave functions. If an electron is described by the molecular orbital $\psi_a^\alpha(\mathbf{r})$, then the probability of finding that electron in a volume element $d\mathbf{r}$ at $\mathbf{r}$ is $|\psi_a^\alpha(\mathbf{r})|^2\,d\mathbf{r}$. The probability distribution function (charge density) is $|\psi_a^\alpha(\mathbf{r})|^2$. If we have N^α electrons of α spin, then the total charge density contributed by these electrons is

$$\rho^\alpha(\mathbf{r}) = \sum_a^{N^\alpha} |\psi_a^\alpha(\mathbf{r})|^2 \tag{3.335}$$

The corresponding charge density contributed by electrons of β spin is

$$\rho^\beta(\mathbf{r}) = \sum_a^{N^\beta} |\psi_a^\beta(\mathbf{r})|^2 \tag{3.336}$$

and the total charge density for electrons of either spin is the sum of these

$$\rho^T(\mathbf{r}) = \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}) \tag{3.337}$$

Integrating this equation leads, as expected, to

$$\int d\mathbf{r}\;\rho^T(\mathbf{r}) = N = N^\alpha + N^\beta \tag{3.338}$$

In an unrestricted wave function, electrons of α and β spin have different spatial distributions ($\rho^\alpha \neq \rho^\beta$), and it is convenient to define a *spin density* $\rho^S(\mathbf{r})$ by

$$\rho^S(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) \tag{3.339}$$

From the above definition of the spin density, it is clear that in regions of space where there is a higher probability of finding an electron of α spin than there is of finding an electron of β spin the spin density is positive. Alternatively, the spin density is negative in regions of space where electrons of β spin are most prevalent. The individual densities ρ^α and ρ^β are, of course positive everywhere. The spin density is a convenient way of describing the distribution of spins in an open-shell system.

Exercise 3.36 Use definitions (3.335) and (3.336) and Eq. (2.254) to show that the integral over all space of the spin density is $2\langle \mathscr{S}_z \rangle$.

By substituting the basis set expansions (3.328) and (3.329) of the α and β molecular orbitals into the expressions (3.335) and (3.336) for the α and β charge densities, one can generate matrix representations (density matrices) of the α and β charge densities,

$$\rho^\alpha(\mathbf{r}) = \sum_a^{N^\alpha} |\psi_a^\alpha(\mathbf{r})|^2 = \sum_\mu \sum_\nu P_{\mu\nu}^\alpha \phi_\mu(\mathbf{r})\phi_\nu^*(\mathbf{r}) \tag{3.340}$$

$$\rho^\beta(\mathbf{r}) = \sum_a^{N^\beta} |\psi_a^\beta(\mathbf{r})|^2 = \sum_\mu \sum_\nu P_{\mu\nu}^\beta \phi_\mu(\mathbf{r}) \phi_\nu^*(\mathbf{r}) \tag{3.341}$$

where the density matrix $\mathbf{P}^\alpha$ for α electrons and the density matrix $\mathbf{P}^\beta$ for β electrons are defined by

$$P_{\mu\nu}^\alpha = \sum_a^{N^\alpha} C_{\mu a}^\alpha (C_{\nu a}^\alpha)^* \tag{3.342}$$

$$P_{\mu\nu}^\beta = \sum_a^{N^\beta} C_{\mu a}^\beta (C_{\nu a}^\beta)^* \tag{3.343}$$

In addition to these two density matrices, one can, of course, define, in analogy to our previous definitions, a total density matrix and a spin density matrix. That is,

$$\mathbf{P}^T = \mathbf{P}^\alpha + \mathbf{P}^\beta \tag{3.344}$$

$$\mathbf{P}^S = \mathbf{P}^\alpha - \mathbf{P}^\beta \tag{3.345}$$

Exercise 3.37 Carry through the missing steps that led to Eqs. (3.340) to (3.343).

Exercise 3.38 Show that expectation values of spin-independent sums of one-electron operators $\sum_{i=1}^N h(i)$ are given by

$$\langle \mathscr{O}_1 \rangle = \sum_\mu \sum_\nu P_{\mu\nu}^T (\nu|h|\mu)$$

for any unrestricted single determinant.

Exercise 3.39 Consider the following spin-dependent operator which is a sum of one-electron operators,

$$\hat{\rho}^S = 2 \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{R}) s_z(i)$$

Use the rules for evaluating matrix elements, given in Chapter 2, to show that the expectation value of $\hat{\rho}^S$ for any unrestricted single determinant is

$$\langle \hat{\rho}^S \rangle = \rho^S(\mathbf{R}) = \mathrm{tr}(\mathbf{P}^S \mathbf{A})$$

where

$$A_{\mu\nu} = \phi_\mu^*(\mathbf{R}) \phi_\nu(\mathbf{R})$$

This matrix element is important in the theory of the Fermi contact contribution to ESR and NMR coupling constants.

Having defined the unrestricted density matrices $\mathbf{P}^\alpha$, $\mathbf{P}^\beta$, $\mathbf{P}^T$, and $\mathbf{P}^S$ we will now use these definitions to give explicit form to the unrestricted Fock matrices $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$.

3.8.4 Expression for the Fock Matrices

To obtain expressions for the elements of the matrices $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$, we simply take matrix elements in the basis $\{\phi_\mu\}$ of the two Fock operators f^α (Eq. (3.316)) and f^β (Eq. (3.318)), and use expressions (3.322) to (3.326) for matrix elements of the coulomb and exchange operators. That is,

$$\begin{aligned} F^\alpha_{\mu\nu} &= \int d\mathbf{r}_1\ \phi^*_\mu(1) f^\alpha(1)\phi_\nu(1) \\ &= H^{\text{core}}_{\mu\nu} + \sum_a^{N^\alpha} [(\phi_\mu\phi_\nu|\psi^\alpha_a\psi^\alpha_a) - (\phi_\mu\psi^\alpha_a|\psi^\alpha_a\phi_\nu)] + \sum_a^{N^\beta} (\phi_\mu\phi_\nu|\psi^\beta_a\psi^\beta_a) \qquad (3.346) \end{aligned}$$

$$\begin{aligned} F^\beta_{\mu\nu} &= \int d\mathbf{r}_1\ \phi^*_\mu(1) f^\beta(1)\phi_\nu(1) \\ &= H^{\text{core}}_{\mu\nu} + \sum_a^{N^\beta} [(\phi_\mu\phi_\nu|\psi^\beta_a\psi^\beta_a) - (\phi_\mu\psi^\beta_a|\psi^\beta_a\phi_\nu)] + \sum_a^{N^\alpha} (\phi_\mu\phi_\nu|\psi^\alpha_a\psi^\alpha_a) \qquad (3.347) \end{aligned}$$

To continue, we substitute the basis set expansions of ψ^α_a and ψ^β_a to get

$$\begin{aligned} F^\alpha_{\mu\nu} &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma \sum_a^{N^\alpha} C^\alpha_{\lambda a}(C^\alpha_{\sigma a})^*[(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_\lambda \sum_\sigma \sum_a^{N^\beta} C^\beta_{\lambda a}(C^\beta_{\sigma a})^*(\mu\nu|\sigma\lambda) \\ &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma P^\alpha_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_\lambda \sum_\sigma P^\beta_{\lambda\sigma}(\mu\nu|\sigma\lambda) \\ &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma P^T_{\lambda\sigma}(\mu\nu|\sigma\lambda) - P^\alpha_{\lambda\sigma}(\mu\lambda|\sigma\nu) \qquad (3.348) \end{aligned}$$

$$\begin{aligned} F^\beta_{\mu\nu} &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma \sum_a^{N^\beta} C^\beta_{\lambda a}(C^\beta_{\sigma a})^*[(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_\lambda \sum_\sigma \sum_a^{N^\alpha} C^\alpha_{\lambda a}(C^\alpha_{\sigma a})^*(\mu\nu|\sigma\lambda) \\ &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma P^\beta_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_\lambda \sum_\sigma P^\alpha_{\lambda\sigma}(\mu\nu|\sigma\lambda) \\ &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma P^T_{\lambda\sigma}\ (\mu\nu|\sigma\lambda) - P^\beta_{\lambda\sigma}(\mu\lambda|\sigma\nu) \qquad (3.349) \end{aligned}$$

If one compares these expressions with the corresponding restricted closed-shell expression (3.154), one sees that the coulomb term is identical and depends on the total density matrix. The difference is only that here one has separate representations of the α and β density matrices rather than, as in the closed-shell case,

$$P^\alpha_{\mu\nu} = P^\beta_{\mu\nu} = \tfrac{1}{2} P^T_{\mu\nu} \qquad (3.350)$$

The coupling of the two sets of equations is made explicit in the above expressions, i.e., $\mathbf{F}^\alpha$ depends on $\mathbf{P}^\beta$ (through the total density matrix $\mathbf{P}^T$) and $\mathbf{F}^\beta$ similarly depends on $\mathbf{P}^\alpha$.

3.8.5 Solution of the Unrestricted SCF Equations

The procedure for solving the unrestricted SCF equations is essentially identical to that previously described for solving the Roothaan equations. An initial guess is required for the two density matrices $\mathbf{P}^{\alpha}$ and $\mathbf{P}^{\beta}$ and hence $\mathbf{P}^{T}$. An obvious choice is to set these matrices to zero and use $\mathbf{H}^{\text{core}}$ as an initial guess to both $\mathbf{F}^{\alpha}$ and $\mathbf{F}^{\beta}$. If this procedure is followed, the first iteration will produce identical orbitals for α and β spin, i.e., a restricted solution. If, however, $N^{\alpha} \neq N^{\beta}$, then all subsequent iterations will have $\mathbf{P}^{\alpha} \neq \mathbf{P}^{\beta}$ and an unrestricted solution will result.

Given approximations to $\mathbf{P}^{\alpha}$ and $\mathbf{P}^{\beta}$, at each step of the iteration, we can form $\mathbf{F}^{\alpha}$ and $\mathbf{F}^{\beta}$, solve the two generalized matrix eigenvalue problems

$$\mathbf{F}^{\alpha}\mathbf{C}^{\alpha} = \mathbf{S}\mathbf{C}^{\alpha}\boldsymbol{\varepsilon}^{\alpha} \tag{3.351}$$

$$\mathbf{F}^{\beta}\mathbf{C}^{\beta} = \mathbf{S}\mathbf{C}^{\beta}\boldsymbol{\varepsilon}^{\beta} \tag{3.352}$$

for $\mathbf{C}^{\alpha}$ and $\mathbf{C}^{\beta}$, and then form new approximations to $\mathbf{P}^{\alpha}$ and $\mathbf{P}^{\beta}$. Because of the coupling of the two equations, one cannot obtain a self-consistent solution to the α equations without at the same time obtaining a self-consistent solution to the β equations, although at any one iteration step the two matrix eigenvalue problems (3.351) and (3.352) can be solved independently; the coupling is in the formation of the Fock matrices. Solving the matrix eigenvalue problem will involve knowing a transformation matrix $\mathbf{X}$ to an orthonormal basis set, forming $\mathbf{F}^{\alpha\prime} = \mathbf{X}^{\dagger}\mathbf{F}^{\alpha}\mathbf{X}$, diagonalizing $\mathbf{F}^{\alpha\prime}$ to get $\mathbf{C}^{\alpha\prime}$, and then forming $\mathbf{C}^{\alpha} = \mathbf{X}\mathbf{C}^{\alpha\prime}$, etc., just as in the restricted closed-shell case.

Exercise 3.40 Substitute the basis set expansion of the unrestricted molecular orbitals into Eq. (3.327) for the electronic energy E_0 to show that

$$E_0 = \frac{1}{2}\sum_{\mu}\sum_{\nu}\left[P^{T}_{\nu\mu}H^{\text{core}}_{\mu\nu} + P^{\alpha}_{\nu\mu}F^{\alpha}_{\mu\nu} + P^{\beta}_{\nu\mu}F^{\beta}_{\mu\nu}\right]$$

Before going on to describe sample unrestricted calculations, an important point should be noted about solutions to the Pople-Nesbet equations for the special case $N^{\alpha} = N^{\beta}$, i.e., for the case where a molecule would normally be described by a restricted closed-shell wave function. For this case, there exists the possibility of two independent solutions to the Pople-Nesbet equations. The first solution is a restricted solution. If $\mathbf{P}^{\alpha} = \mathbf{P}^{\beta} = \frac{1}{2}\mathbf{P}$, then $\mathbf{F}^{\alpha} = \mathbf{F}^{\beta} = \mathbf{F}$ and the Pople-Nesbet equations degenerate to the Roothaan equations. *When $N^{\alpha} = N^{\beta}$, a restricted solution to the Roothaan equations is a solution to the unrestricted Pople-Nesbet equations.* This restricted solution always exists and necessarily results if an initial guess $\mathbf{P}^{\alpha} = \mathbf{P}^{\beta}$ is used. For $N^{\alpha} = N^{\beta}$, however, in addition to the restricted solution there may also exist a second unrestricted solution of lower energy. The restricted solution constrains the density of α electrons to equal the density of β electrons, but under certain conditions (which we shall consider in the last subsection of this chapter) relaxing this constraint will result in an unrestricted solution of lower energy for which $\mathbf{P}^\alpha$ is not equal to $\mathbf{P}^\beta$. *When $N^\alpha = N^\beta$, under certain conditions there exists a second solution, the unrestricted solution to the Pople-Nesbet equations.* In seeking this second solution, it is imperative that an initial guess $\mathbf{P}^\alpha \neq \mathbf{P}^\beta$ be used or the equations will necessarily yield the restricted solution. Even if an unrestricted initial guess is used, there is still the possibility that iteration will lead to the restricted solution. When two solutions exist, the initial guess will strongly determine to which solution the iterations lead.

One normally uses unrestricted wave functions to describe open-shell states of molecules for which $N^\alpha \neq N^\beta$, and the above considerations are not of concern. When, however, one uses unrestricted wave functions as a solution to the dissociation problem, as we shall subsequently do, the possibility of two solutions is of supreme importance.

3.8.6 Illustrative Unrestricted Calculations

An interesting example of the use of unrestricted wave functions occurs for the methyl radical CH_3. This molecule has D_{3h} symmetry, i.e., it is planar with bond angles of 120°. The CH internuclear distance is taken to be 2.039 a.u. The simplest description of the electronic structure of this radical is a restricted Hartree-Fock description, shown in Fig. 3.13. The unpaired

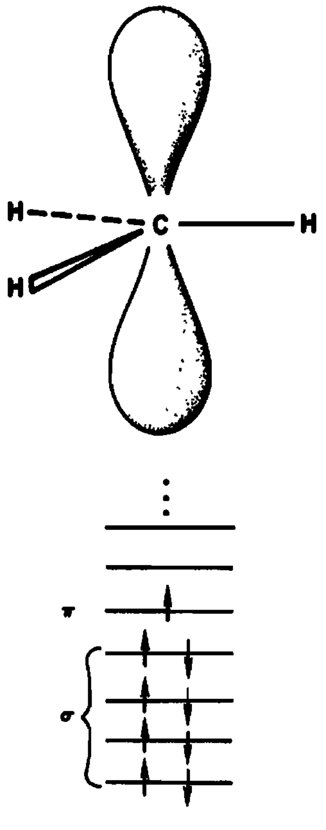


Figure 3.13 Restricted Hartree-Fock description of the planar methyl radical.

electron is in an open-shell π orbital, which in a minimal basis description would be a pure $2p$ orbital on carbon. The remaining electrons are paired in σ orbitals. In this restricted Hartree-Fock description, the spin density $\rho^s(\mathbf{r})$ is everywhere positive, except in the plane of the molecule where it is zero because of the node in the π orbital. Because all σ electrons are paired, the spin density is just

$$\rho^S(\mathbf{r}) = |\psi_\pi(\mathbf{r})|^2 \tag{3.353}$$

where ψ_π is the π molecular orbital containing the unpaired electron.

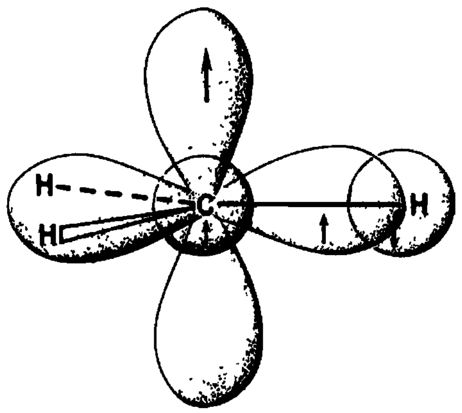
The above description, while simple, is not in agreement with experimental results. In an electron spin resonance (ESR) experiment on the methyl radical, measurements were made of a^{H} and a^{C}, the coupling constants for the hydrogen and carbon nuclei. These ESR coupling constants are a direct measure of the spin densities at the position of the respective nuclei,

$$a^{\mathrm{H}}(\text{Gauss}) = 1592\rho^S(\mathbf{R}_H) \tag{3.354}$$

$$a^{\mathrm{C}}(\text{Gauss}) = 400.3\rho^S(\mathbf{R}_C) \tag{3.355}$$

The experimental measurements of a^{H} and a^{C} give not only the magnitude but also the sign of the spin density. It is found that the spin density at the H nucleus is negative, and the spin density at the C nucleus is positive. Unfortunately, the restricted Hartree-Fock description predicts the coupling constants a^{H} and a^{C} to be both zero. If the molecule were vibrating so that part of the time the molecule had a bent C_{3v} geometry, then the restricted description would allow nonzero spin densities at the nuclei. But these spin densities and the associated coupling constants would always be positive. Thus the negative spin density at the positions of the hydrogen nuclei cannot be explained by a restricted Hartree-Fock description.

The simplest way of obtaining the correct qualitative result is to use an unrestricted Hartree-Fock description. The electrons of Fig. 3.13 that are paired in a σ orbital have different interactions with the unpaired electron, i.e., the electrons of α spin have a coulomb and exchange interaction with the unpaired electron while the electrons of β spin have only a coulomb interaction. There is thus good reason why the α and β electrons of the sigma system should have different energies and occupy different spatial orbitals. If, indeed, one does relax the constraint of paired electrons, by using the Pople-Nesbet equations, the unrestricted solution shown in Fig. 3.14 is found. This unrestricted wave function does not have the σ electrons paired and as such there will be net nonzero spin density in the sigma system, in particular, at the positions of the carbon and hydrogen nuclei. Unrestricted calculations (Table 3.26), show that the spin density is positive at the carbon nucleus and negative at the hydrogen nuclei, as also shown in the figure. This result is commonly explained by the use of two rules: an "intraatomic Hund's rule", which postulates that electrons tend to have parallel spins on the same atom, and a rule which states that the spins of electrons in orbitals



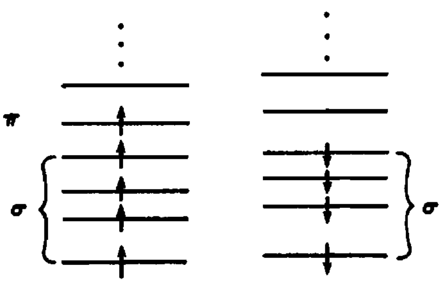


Figure 3.14 Unrestricted Hartree-Fock description of the planar methyl radical.

Table 3.26 Unrestricted SCF spin densities and hyperfine coupling constants for the methyl radical using the standard basis sets. A value of $\langle \mathscr{S}^2 \rangle = 0.75$ corresponds to a pure doublet

	Spin density (a.u.)		Coupling constant (Gauss)		
Basis set	C	H	a^C	a^H	$\langle \mathscr{S}^2 \rangle$
STO-3G	+0.2480	−0.0340	+99.3	−54.2	0.7652
4-31G	+0.2343	−0.0339	+93.8	−54.0	0.7622
6-31G*	+0.1989	−0.0303	+79.6	−48.3	0.7618
6-31G**	+0.1960	−0.0296	+78.5	−47.1	0.7614
Experiment			+38.3	−23.0	0.75

that overlap to form a chemical bond tend to be antiparallel. Negative spin density in the vicinity of the hydrogen nuclei results from application of these two rules.

Table 3.26 shows the results of *ab initio* calculations of the CH_3 hyperfine coupling constants. The correct qualitative results are obtained—a positive spin density at the carbon nucleus and a negative spin density at the hydrogen nuclei. The magnitudes of the spin densities are too large, however. They are in error by about a factor of 2 for the 6-31G** basis set. Without performing more extensive calculations, it is difficult to know whether the source of the error is in the basis sets or in the neglect of correlation. The standard basis sets we are using were derived primarily for the description of valence properties, and they may not be adequate near a nucleus. In particular, Gaussian functions are known to be poor at their origin. Also, the basis sets that we are using contain only a single function for the inner-shell of carbon.

The table also contains expectation values of $\mathscr{S}^2$. One of the deficiencies of an unrestricted calculation is that it does not produce a pure spin state. The ground state of the methyl radical is a doublet with $\langle \mathscr{S}^2 \rangle = S(S+1) = \frac{3}{4}$. The unrestricted calculations produce a doublet wave function, which is contaminated with small amounts of a quartet, sextet, etc, as discussed in Section 2.5. The expectation values of $\mathscr{S}^2$ are close to the correct value of $\frac{3}{4}$, showing that these contaminants are not large.

Exercise 3.41 Assume the unrestricted Hartree-Fock (UHF) calculations of Table 3.26 contain only the leading quartet contaminant. That is,

$$\Psi_{\mathrm{UHF}} = c_1 {}^2\Psi + c_2 {}^4\Psi$$

If the percent contamination is defined as $100c_2^2/(c_1^2 + c_2^2)$, calculate the percent contamination of each of the four calculations from the quoted value of $\langle \mathscr{S}^2 \rangle$.

We have previously used Koopmans' theorem to calculate the first two ionization potentials of N_2. As we saw at that time, calculations at the Hartree-Fock limit, or with our best (6-31G*) basis set, incorrectly predict the ${}^2\Pi_u$ state of N_2^+ to be lower in energy than ${}^2\Sigma_g$ state of N_2^+. That is, the highest occupied orbital of N_2 is calculated to be the $1\pi_u$ orbital rather than the $3\sigma_g$ orbital. There are two reasons why Koopmans' theorem might make the wrong prediction: neglect of correlation or neglect of relaxation. We can test the second alternative by explicitly performing Hartree-Fock calculations on the ${}^2\Pi_u$ and ${}^2\Sigma_g$ state of N_2^+. Koopmans' theorem calculations assume the orbitals of these two states to be identical to those of ground state N_2. By performing separate unrestricted calculations on these two doublet states of N_2^+, we will be allowing the orbitals to relax to their optimum form. The ionization potentials can then be obtained by subtracting the total restricted energy of the N_2 ground state from the total unrestricted energy of each of the N_2^+ ions.

Table 3.27 shows the results of 6-31G* calculations on the ${}^1\Sigma_g$ state of N_2 and the ${}^2\Sigma_g$ and ${}^2\Pi_u$ states of N_2^+. To compare with experimental vertical ionization potentials, all the calculations were performed at the equilibrium geometry ($R = 2.074$ a.u.) of ground state N_2. These calculations still predict that the ${}^2\Pi_\mu$ state has a lower energy than the ${}^2\Sigma_g$ state in disagreement with

Table 3.27 SCF calculations on the ground state of N_2 (restricted) and two states of N_2^+ (unrestricted) with a 6-31G* basis set. Vertical ($R_e = 2.074$ a.u.) ionization potentials are shown, and experimental values are in parenthesis

State	Total Energy (a.u.)	Ionization Potential (a.u.)
$N_2(^1\Sigma_g)$	−108.94235	
$N_2^+(^2\Pi_u)$	−108.37855	0.564 (0.624)
$N_2^+(^2\Sigma_g)$	−108.36597	0.576 (0.573)

experiment. This is therefore an indication that the qualitative disagreement of experiment with Koopmans' theorem ionization potentials for N_2 is a result of the lack of inclusion of correlation effects. Later, inclusion of correlation effects will verify this.

Our final example of *ab initio* unrestricted calculations is O_2. This molecule has unpaired spins and is paramagnetic. The first brilliant success of molecular orbital theory was the explanation of why O_2, with an even

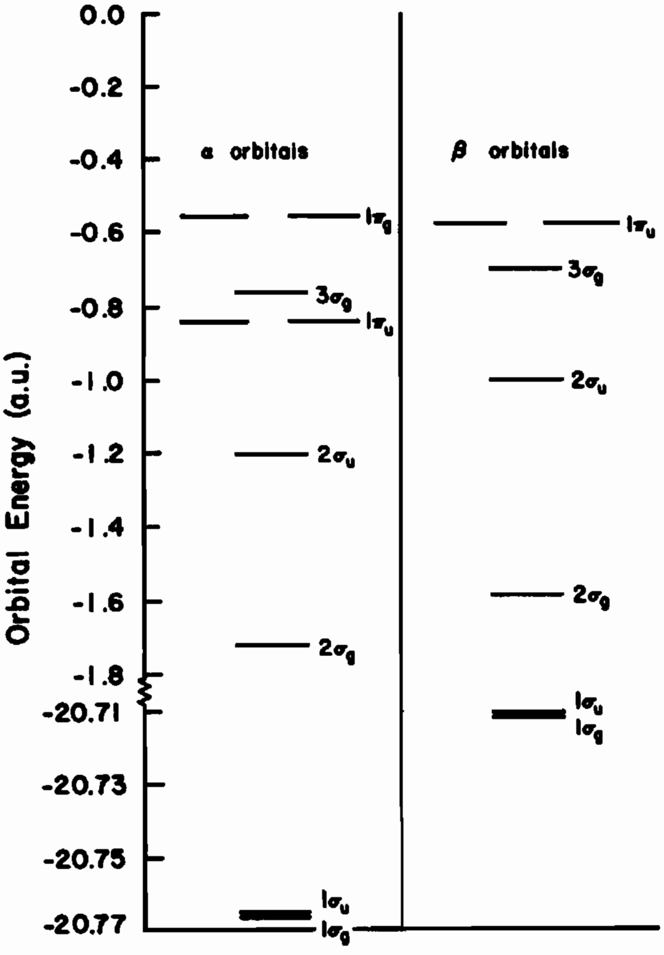


Figure 3.15 Unrestricted occupied molecular orbitals of $O_2(^3\Sigma_g^-$, $R = 2.281$ a.u.) with a 6-31G* basis set.

number of electrons, does not have all its electrons paired. The molecular orbitals of homonuclear diatomics are ordered $1\sigma_g$, $1\sigma_u$, $2\sigma_g$, $2\sigma_u$, $(3\sigma_g, 1\pi_u)$ $1\pi_g$, $3\sigma_u$. The last two electrons of O_2 go into the doubly degenerate antibonding $1\pi_g$ orbital. By Hund's rule, these two electrons go into separate $1\pi_g$ orbitals with their spins parallel so as to enjoy the negative exchange interaction. This, therefore, leads to a final ${}^3\Sigma_g^-$ state. The occupied orbitals of an unrestricted 6-31G* calculation on O_2, for a bond length of 2.281 a.u., are shown in Fig. 3.15. The "open-shell" alpha electrons in the $1\pi_g$ orbital "push" down (stabilize) the α orbitals relative to the β orbitals because of exchange interactions that are present only between electrons of the same spin. In a restricted description, all but the $1\pi_g$ orbitals would be constrained to be paired. Note how the order of the $1\pi_u$ and $3\sigma_g$ orbitals are reversed for electrons of α and β spin.

To complete our discussion of unrestricted Hartree-Fock theory, we will use our minimal basis H_2 model to investigate the description of bond dissociation by unrestricted wave functions.

3.8.7 The Dissociation Problem and Its Unrestricted Solution

The unrestricted wave function is normally used to describe open-shell states–doublets, triplets, etc., as in the examples of the last subsection. Under certain circumstances, however, it may be appropriate to use an unrestricted wave function to describe states that are normally thought of as closed-shell singlets. For the ground state of a molecule like H_2, the restricted formulation, with electrons paired, is the usual description. As we shall shortly see, it is also the only appropriate Hartree-Fock description under certain conditions. At very large bond lengths, however, one is really trying to describe two individual hydrogen atoms. A proper description will have one electron on one H atom and the other electron on the other H atom, i.e., the two electrons will have quite different spatial distributions. They should not have identical spatial distributions as is implied by a restricted wave function, which places both electrons in the same spatial orbital. It would thus appear that at equilibrium distances we want a restricted wave function, but at large bond lengths we want an unrestricted wave function. In a sense, we will be able to have our cake and eat it too. As was discussed in the previous subsection, there may exist two solutions to the unrestricted equations of Pople and Nesbet when $N^\alpha = N^\beta$. The restricted solution of Roothaan's equations is necessarily a solution to the Pople-Nesbet equations. It only remains to discover whether there is a second truly unrestricted solution that is lower in energy than the restricted solution. We shall find that for normal geometries there is not always an unrestricted solution. If, however, we stretch a bond which cleaves homolytically, like the bond in H_2 ($H_2 \rightarrow H + H$) but unlike the bond in HeH^+ ($HeH^+ \rightarrow He + H^+$), then an unrestricted solution will always exist at large bond lengths. The unrestricted solution accomodates the unpairing of electrons inherent in the breaking of the bond. To see this explicitly, we will investigate wave functions for our minimal basis model of H_2.

We could numerically solve the Pople-Nesbet equations for minimal basis STO-3G H_2, just as we have solved them for CH_3, N_2^+, and O_2. An appropriate unrestricted initial guess would be required if the iterations were to lead to an unrestricted solution rather than to the restricted solution. The transition from a restricted to an unrestricted wave function will be more transparent, however, if, rather than obtain a numerical solution to the Pople-Nesbet matrix equations, we formulate the problem in an analytical fashion.

The restricted molecular orbitals of minimal basis H_2 are symmetry determined and given by

$$\psi_1 = [2(1 + S_{12})]^{-1/2}(\phi_1 + \phi_2) \tag{3.356}$$

$$\psi_2 = [2(1 - S_{12})]^{-1/2}(\phi_1 - \phi_2) \tag{3.357}$$

Since the minimal basis model has only two basis functions with coefficients that can be varied and since molecular orbitals are constrained to be normalized, the minimal basis model has, in the general case, only one degree of freedom. An unrestricted solution, unlike the restricted solution, is not symmetry determined and a convenient way of incorporating this one degree of freedom into unrestricted calculations is to write the unrestricted occupied molecular orbitals ψ_1^α and ψ_1^β as linear combinations of the restricted symmetry determined orbitals ψ_1 and ψ_2, as follows:

$$\psi_1^\alpha = \cos\theta\psi_1 + \sin\theta\psi_2 \tag{3.358}$$

$$\psi_1^\beta = \cos\theta\psi_1 - \sin\theta\psi_2 \tag{3.359}$$

The single degree of freedom here is in the angle θ. It is sufficient to consider values of θ between 0° and 45°. The value $\theta = 0$ corresponds to the restricted solution $\psi_1^\alpha = \psi_1^\beta = \psi_1$ and nonzero values of θ correspond to unrestricted solutions $\psi_1^\alpha \neq \psi_1^\beta$. The unrestricted virtual orbitals are given by

$$\psi_2^\alpha = -\sin\theta\psi_1 + \cos\theta\psi_2 \tag{3.360}$$

$$\psi_2^\beta = \sin\theta\psi_1 + \cos\theta\psi_2 \tag{3.361}$$

Exercise 3.42 Show that the set of α orbitals $\{\psi_1^\alpha, \psi_2^\alpha\}$ and the set of β orbitals $\{\psi_1^\beta, \psi_2^\beta\}$ form separate orthonormal sets.

If we substitute the basis set expansions (3.356) and (3.357) into the previous four equations, we will obtain basis set expansions for the unrestricted molecular orbitals. The occupied molecular orbitals, which are the only ones we need consider from now on, are given by

$$\psi_1^\alpha = c_1\phi_1 + c_2\phi_2 \tag{3.362}$$

$$\psi_1^\beta = c_2\phi_1 + c_1\phi_2 \tag{3.363}$$

where

$$c_1 = [2(1 + S_{12})]^{-1/2} \cos\theta + [2(1 - S_{12})]^{-1/2} \sin\theta \tag{3.364}$$

$$c_2 = [2(1 + S_{12})]^{-1/2} \cos\theta - [2(1 - S_{12})]^{-1/2} \sin\theta \tag{3.365}$$

By allowing ψ_2 to mix with ψ_1 in the definition of the unrestricted occupied orbitals (Eqs. (3.358) and (3.359)), we allow the weights of ϕ_1 and ϕ_2 in the basis set expansions of ψ_1^α and ψ_1^β to vary as shown by Eqs. (3.362) and (3.363). If $\theta = 0$, the wave function is just the restricted wave function with $c_1 = c_2 = [2(1 + S_{12})]^{-1/2}$. As θ increases from zero, c_1 gets larger and c_2 gets smaller or, equivalently, ψ_1^α acquires a larger admixture of ϕ_1 and ψ_1^β acquires a larger admixture of ϕ_2. If $S_{12} = 0$ as is appropriate for large internuclear distances, then in the limit of $\theta = 45°$ we have $c_1 = 1$, $c_2 = 0$, and

$$\left.\begin{aligned} \psi_1^\alpha &\equiv \phi_1 \\ \psi_1^\beta &\equiv \phi_2 \end{aligned}\right\} \theta = 45°, \qquad S_{12} = 0 \tag{3.366}$$

This is the result we desire for two separate H atoms—an electron with α spin in ϕ_1 and an electron with β spin in ϕ_2.

We thus characterize molecular orbitals for minimal basis H_2 by the single parameter θ. At one extreme, $\theta = 0$ corresponds to the restricted solution where the occupied molecular orbital is an equal mixture of ϕ_1 and ϕ_2. At the other extreme, $\theta = 45°$ corresponds to an unrestricted solution for isolated hydrogen atoms. Intermediate value of θ correspond to unrestricted solutions where ψ_1^α is mainly ϕ_1 and ψ_1^β is mainly ϕ_2. Figure 3.16 gives a qualitative picture of the unrestricted molecular orbitals of H_2 as a function of θ. While we have derived this picture using the minimal basis, the figure is qualitatively correct for H_2 with any basis set.

We have seen that for the ground state of a closed-shell molecule like H_2 it appears possible to define unrestricted wave functions which have the qualitatively correct behavior that we expect for the dissociation process. It remains to relate these unrestricted wave functions to solutions of the Hartree-Fock equations. If we solve the Pople-Nesbet equations, will a nonzero value of θ be obtained? To investigate this question, we need to determine the energy as a function of θ.

The electronic energy of an unrestricted single determinant wave function for H_2,

$$|\Psi_0\rangle = |\psi_1^\alpha(1)\bar{\psi}_1^\beta(2)\rangle \tag{3.367}$$

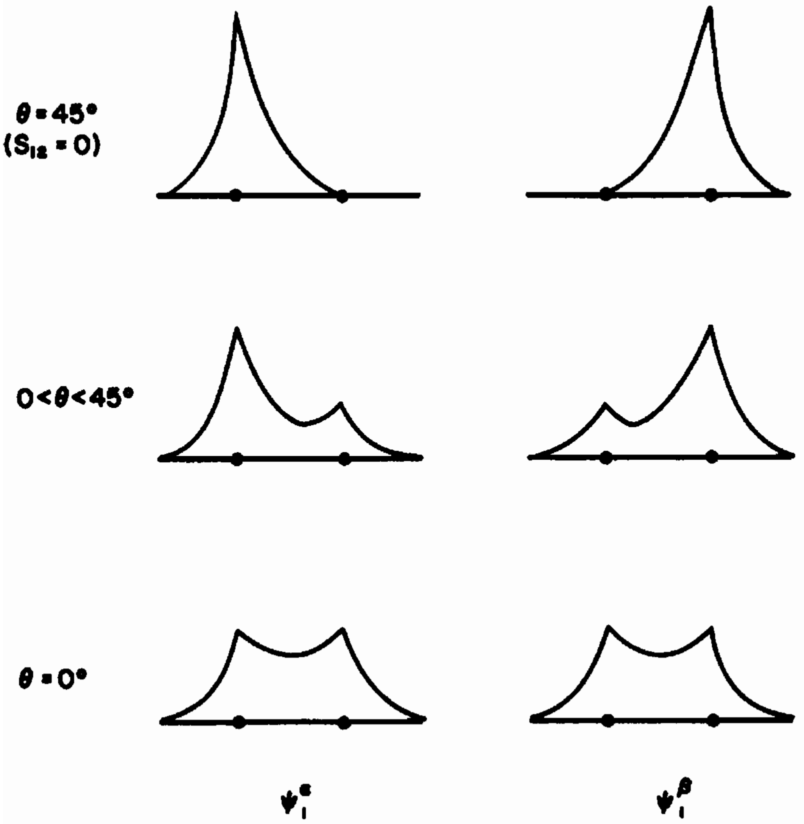


Figure 3.16 Qualitative behavior of unrestricted molecular orbitals ψ_1^α and ψ_1^β for H_2 as a function of θ.

is just the kinetic energy and nuclear attraction of each electron, plus the coulomb repulsion between the two electrons. That is,

$$\begin{aligned} E_0 &= \langle\Psi_0|\mathscr{H}|\Psi_0\rangle = h_{11}^\alpha + h_{11}^\beta + J_{11}^{\alpha\beta} \\ &= (\psi_1^\alpha|h|\psi_1^\alpha) + (\psi_1^\beta|h|\psi_1^\beta) + (\psi_1^\alpha\psi_1^\alpha|\psi_1^\beta\psi_1^\beta) \end{aligned} \tag{3.368}$$

Substituting the expansions (3.358) and (3.359) into this expression, we can write the electronic energy, as a function of θ, in terms of molecular integrals of the restricted problem

$$\begin{aligned} E_0(\theta) = 2\cos^2\theta h_{11} &+ 2\sin^2\theta h_{22} + \cos^4\theta J_{11} \\ &+ \sin^4\theta J_{22} + 2\sin^2\theta\cos^2\theta(J_{12} - 2K_{12}) \end{aligned} \tag{3.369}$$

If $\theta = 0$, the unrestricted energy just reduces to the restricted energy

$$E_0(0) = 2h_{11} + J_{11} \tag{3.370}$$

The first derivative of the unrestricted energy with respect to θ is

$$\begin{aligned} dE_0(\theta)/d\theta = 4\cos\theta\sin\theta[h_{22} - h_{11} &+ \sin^2\theta J_{22} - \cos^2\theta J_{11} \\ &+ (\cos^2\theta - \sin^2\theta)(J_{12} - 2K_{12})] \end{aligned} \tag{3.371}$$

To find the values of θ which solve the Pople-Nesbet equations, i.e., to find the values of θ which make the unrestricted energy stationary, we set the first derivative of the unrestricted energy to zero,

$$dE_0(\theta)/d\theta = AB = 0 \tag{3.372}$$

where

$$A = 4\cos\theta\sin\theta \tag{3.373}$$

and

$$B = h_{22} - h_{11} + \sin^2\theta J_{22} - \cos^2\theta J_{11} + (\cos^2\theta - \sin^2\theta)(J_{12} - 2K_{12}) \tag{3.374}$$

There are thus two ways the energy could be stationary:

1. $A = 0$. This is the restricted solution. The condition is satisfied if $\theta = 0$.
2. $B = 0$. This is the unrestricted solution. The condition is satisfied and there exists an unrestricted wave function only if there is a solution to:

   $$\cos^2\theta = \eta \tag{3.375}$$

   where

   $$\eta = (h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12})/(J_{11} + J_{22} - 2J_{12} + 4K_{12}) \tag{3.376}$$

This last equation is obtained by setting B of Equation (3.374) to zero. This equation has a solution only if the internuclear distance and basis functions, and hence the molecular integrals h_{11}, h_{22}, etc., are such that η lies between zero and one, i.e., $0 \leq \eta \leq 1$.

Exercise 3.43 Use the molecular integrals given in Appendix D to show that no unrestricted solution exists for minimal basis STO-3G H_2 at R = 1.4 a.u. Repeat the calculation for R = 4.0 a.u. and show that an unrestricted solution exists with $\theta = 39.5°$. Remember that $\varepsilon_1 = h_{11} + J_{11}$ and $\varepsilon_2 = h_{22} + 2J_{12} - K_{12}$.

To proceed with the analysis let us investigate the nature of the restricted solution ($\theta = 0$) by evaluating the second derivative of the energy (at the restricted solution),

$$\begin{aligned} d^2E_0(\theta)/d\theta^2\big]_{\theta=0} &= E_0''(0) = 4(h_{22} - h_{11} - J_{11} + J_{12} - 2K_{12}) \\ &= 4(\varepsilon_2 - \varepsilon_1 - J_{12} - K_{12}) \end{aligned} \tag{3.377}$$

The nature of the restricted solution is determined by this second derivative. If $E_0''(0) > 0$, it is an energy minimum. If $E_0''(0) < 0$, it is an energy maximum. If $E_0''(0) = 0$, i.e., if

$$h_{22} - h_{11} = J_{11} - J_{12} + 2K_{12} \tag{3.378}$$

then the restricted solution is a saddle point. Substituting this last saddle point condition into Eq. (3.376), we find that η = 1 at the saddle point. Using the molecular integrals of Appendix D we can investigate the behavior of

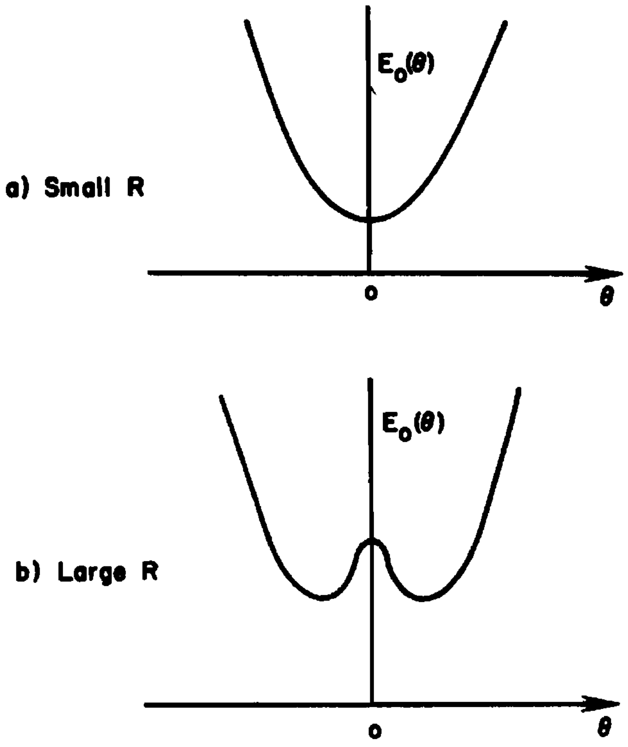


Figure 3.17 Qualitative behavior of the unrestricted energy of H_2 as a function of θ for small and large internuclear distances: a) small R; b) large R.

$E_0''(0)$ and η as a function of bond length. At short bond lengths $E_0''(0) > 0$ and $\eta > 1$. As the bond length increases both $E_0''(0)$ and η decrease monotonically, until they reach a limit at $R = \infty$ of $E_0''(0) = -1/2\ (\phi_1\phi_1|\phi_1\phi_1)$ and $\eta = 1/2$. At a transition point, which occurs in the vicinity of $R = 2.3$ a.u., the second derivative $E_0''(0)$ becomes negative and simultaneously η becomes less than 1. The behavior of the solutions is therefore as follows: At short bond lengths $\eta > 1$, the restricted solution is a true minimum, and no unrestricted solution exists. On increasing the bond length the value of η decreases until, at a distance of approximately 2.3 a.u., η becomes 1 and a saddle point occurs in the energy. This transition point defines the onset of an unrestricted solution. At a bond length beyond this, the restricted solution ($\theta = 0$) is actually a maximum in the energy as shown in Fig. 3.17. When an unrestricted solution exists ($\eta \leq 1$), the value of η can be equated to $\cos^2\theta$. As the bond length becomes larger and larger, θ gives to the limit of 45° appropriate to isolated hydrogen atoms. A potential curve for STO-3G H_2 showing the two solutions is shown in Fig. 3.18. The unrestricted energy goes smoothly to the limit of two hydrogen atoms calculated with the same basis set, i.e., $2(\phi_1|h|\phi_1)$. The restricted energy goes to a limit $1/2(\phi_1\phi_1|\phi_1\phi_1)$ above the right result. Also shown in Fig. 3.18 is the essentially exact result of Kolos and Wolniewicz.[5] The hydrogen atom energies used in the figure (-0.4666 and -0.5) are obtained with the basis sets employed in the respective methods. Thus, both curves go to zero at large R. The corresponding curves for a 6-31G** basis set are shown in Fig. 3.19.

The "correct" dissociation of H_2, which we have obtained by using an unrestricted wave function, is not free of faults. The unrestricted wave

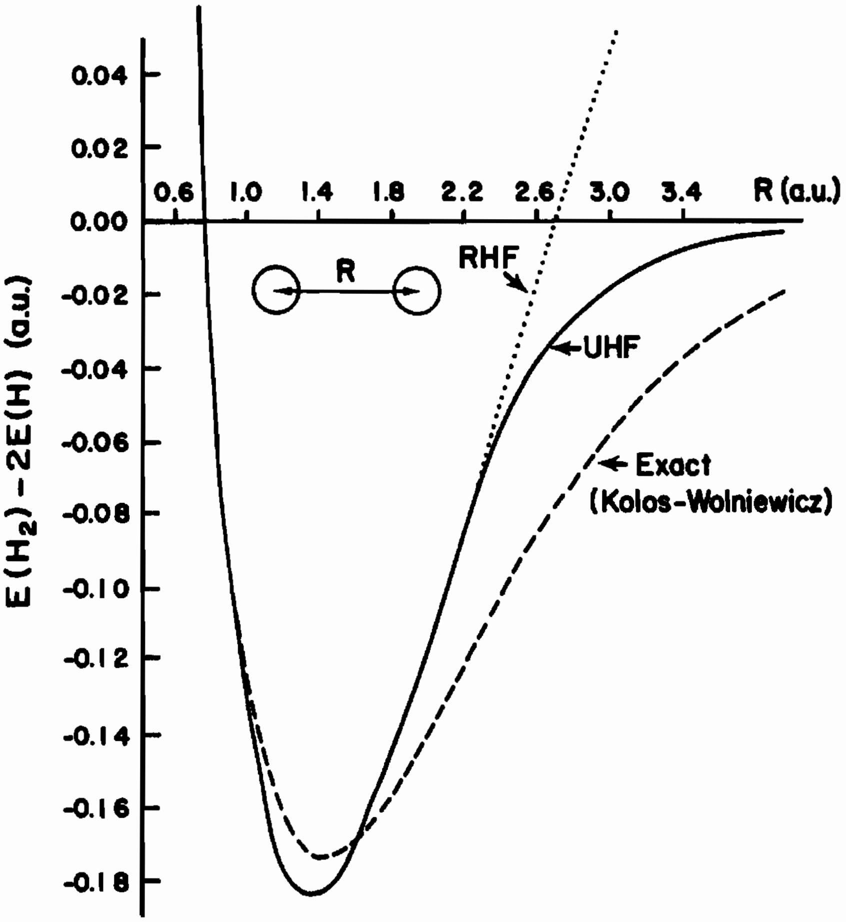


Figure 3.18 STO-3G potential curves for H_2.

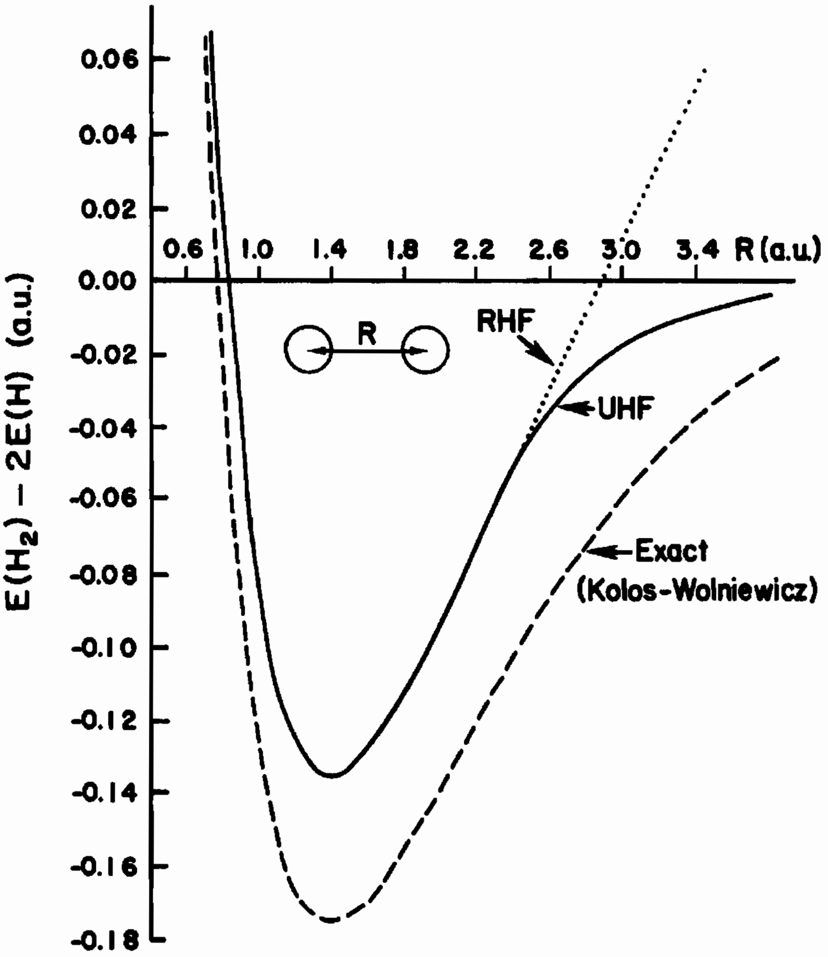


Figure 3.19 6-31G** potential energy curves for H_2.

function is not a pure singlet as one would like it to be. The energy goes to the correct limit but the total wave function does not, as we shall now see. In the limit $R \to \infty$, the molecular orbitals become $\psi_1^\alpha = \phi_1$ and $\psi_1^\beta = \phi_2$ and the unrestricted single determinant $|\Psi_0\rangle$ of Eq. (3.367) becomes

$$\lim_{R\to\infty} |\Psi_0\rangle = |\phi_1(1)\bar{\phi}_2(2)\rangle \tag{3.379}$$

This, however, is not the correct form for a singlet wave function in which electrons occupy different spatial orbitals ϕ_1 and ϕ_2. In analogy to Eq. (2.260), the singlet wave function should be

$$\lim_{R\to\infty} |\Phi_0\rangle = 2^{-1/2}[|\phi_1(1)\bar{\phi}_2(2)\rangle + |\phi_2(1)\bar{\phi}_1(2)\rangle] \tag{3.380}$$

The orbitals are correct but the total wave function is not. An alternative way of looking at this problem is obtained by substituting the expansions (3.358) and (3.359) for the unrestricted molecular orbitals into the single determinant $|\Psi_0\rangle$ and expanding the determinant

$$\begin{aligned}|\Psi_0\rangle = |\psi_1^\alpha\bar{\psi}_1^\beta\rangle &= \cos^2\theta|\psi_1\bar{\psi}_1\rangle - \sin^2\theta|\psi_2\bar{\psi}_2\rangle \\ &\quad - (2)^{1/2}\cos\theta\sin\theta[|\psi_1\bar{\psi}_2\rangle - |\psi_2\bar{\psi}_1\rangle]/(2)^{1/2} \\ &= \cos^2\theta|\psi_1\bar{\psi}_1\rangle - \sin^2\theta|\psi_2\bar{\psi}_2\rangle \\ &\quad - (2)^{1/2}\cos\theta\sin\theta|{}^3\Psi_1^2\rangle \end{aligned} \tag{3.381}$$

Here, $|{}^3\Psi_1^2\rangle$ is the singly excited triplet configuration defined in Eq. (2.261). The closed-shell determinants $|\psi_1\bar{\psi}_1\rangle$ and $|\psi_2\bar{\psi}_2\rangle$ are, of course, singlets. An unrestricted single determinant for the ground state of H_2 is thus not a pure singlet but is contaminated by a triplet. The mixing of the doubly excited determinant $|\psi_2\bar{\psi}_2\rangle$ with $|\psi_1\bar{\psi}_1\rangle$ allows the dissociation to go to the correct limit, but the triplet contaminant is required if the final wave function is to be a single determinant. As $R \to \infty$ the triplet contamination increases until it represents 50% of the wave function,

$$\lim_{R\to\infty} |\Psi_0\rangle = 1/2[|\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle - (2)^{1/2}|{}^3\Psi_1^2\rangle] \tag{3.382}$$

Although the correct dissociation energy is obtained using an unrestricted wave function, the poor wave function will limit the desirability of using, near the dissociation limit, an unrestricted single determinant as a starting point for configuration interaction or perturbation calculations.

Exercise 3.44 Derive Eq. (3.379) from Eq. (3.382).

We have only discussed the restricted Hartree-Fock dissociation problem for the minimal basis model of H_2. The ideas presented are not limited to H_2, however, and very similar effects will occur for other closed-shell systems when a bond is stretched. In H_2, the onset of unrestricted solutions occurs beyond the equilibrium distance but in the general case there may even be unrestricted solutions at the experimental geometry. By an extension of our analysis, it is possible to derive general conditions under which there exists an unrestricted solution lower in energy than the closed-shell restricted solution (Thouless, 1961).

NOTES

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2. Hartree-Fock theory in special cases, such as for restricted open-shell wave functions, involves a multideterminantal wave function. Since we will be concerned only with unrestricted open-shell wave functions, all Hartree-Fock wave functions will be single determinants.
3. In principle it is possible to use the procedures to be discussed in this section to obtain restricted closed-shell excited states, but there is no general way of keeping such calculations from converging to the ground state $|\Psi_0\rangle$ if the excited state has the same symmetry as the ground state.
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