

**Table 3.25 SCF dipole moments (a.u.) for the ten-electron series and the standard basis sets**

| Basis set     | NH <sub>3</sub>    | H <sub>2</sub> O   | 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 <sup>a</sup> | 0.785 <sup>b</sup> | 0.764 <sup>c</sup> |
| Experiment    | 0.579              | 0.728              | 0.716              |

<sup>a</sup> A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.* **52**: 4133 (1970).

<sup>b</sup> B. J. Rosenberg and I. Shavitt, *J. Chem. Phys.* **63**: 2162 (1975).

<sup>c</sup> 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<sup>-</sup>O<sup>+</sup>) 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<sub>3</sub>, H<sub>2</sub>O, and FH using our standard basis sets. Only at the 6-31G\* level and beyond is the proper trend H<sub>2</sub>O > FH > NH<sub>3</sub> 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 POPLÉ-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

$$|\Psi_{\text{RHF}}\rangle = |\psi_1\bar{\psi}_1 \cdots\rangle \quad (3.306)$$

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

$$|\Psi_{\text{UHF}}\rangle = |\psi_1^\alpha \bar{\psi}_1^\beta \cdots\rangle \quad (3.307)$$

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  $\mathcal{S}^2$ . 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  $\text{H}_2$ , 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  $\text{H}_2$  model. An unrestricted wave function will allow a closed-shell molecule like  $\text{H}_2$  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

$$f(1)\chi_i(1) = \varepsilon_i\chi_i(1) \quad (3.308)$$

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

$$\chi_i(\mathbf{x}) = \begin{cases} \psi_j^\alpha(\mathbf{r})\alpha(\omega) \\ \psi_j^\beta(\mathbf{r})\beta(\omega) \end{cases} \quad (3.309)$$

That is, electrons of  $\alpha$  spin are described by a set of spatial orbitals  $\{\psi_j^\alpha | j = 1, 2, \dots, K\}$ , and electrons of  $\beta$  spin are described by a different set of spatial orbitals  $\{\psi_j^\beta | j = 1, 2, \dots, K\}$ . In our previous restricted case  $\psi_j^\alpha \equiv \psi_j^\beta \equiv \psi_j$ . We are now allowing electrons of  $\alpha$  and  $\beta$  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  $\omega$ . For simplicity, we will concentrate on the equation defining  $\psi_j^\alpha$  and use the symmetry between  $\alpha$  and  $\beta$  spins to write down the corresponding equations defining  $\psi_j^\beta$ . Substituting Eq. (3.309) into Eq. (3.308) leads to

$$f(1)\psi_j^\alpha(\mathbf{r}_1)\alpha(\omega_1) = \varepsilon_i\psi_j^\alpha(\mathbf{r}_1)\alpha(\omega_1) \quad (3.310)$$

Now,  $\varepsilon_i$  is the energy of the spin orbital  $\chi_i \equiv \psi_j^\alpha\alpha$ . Since the spin orbitals for electrons of  $\alpha$  and  $\beta$  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  $\{\varepsilon_j^\beta | j = 1, 2, \dots, K\}$  for electrons of  $\beta$  spin. Thus

$$f(1)\psi_j^\alpha(\mathbf{r}_1)\alpha(\omega_1) = \varepsilon_j^\alpha\psi_j^\alpha(\mathbf{r}_1)\alpha(\omega_1) \quad (3.311)$$

If we now multiply this equation by  $\alpha^*(\omega_1)$  and integrate over spin we get

$$f^\alpha(1)\psi_j^\alpha(1) = \varepsilon_j^\alpha\psi_j^\alpha(1) \quad (3.312)$$

$$f^\beta(1)\psi_j^\beta(1) = \varepsilon_j^\beta\psi_j^\beta(1) \quad (3.313)$$

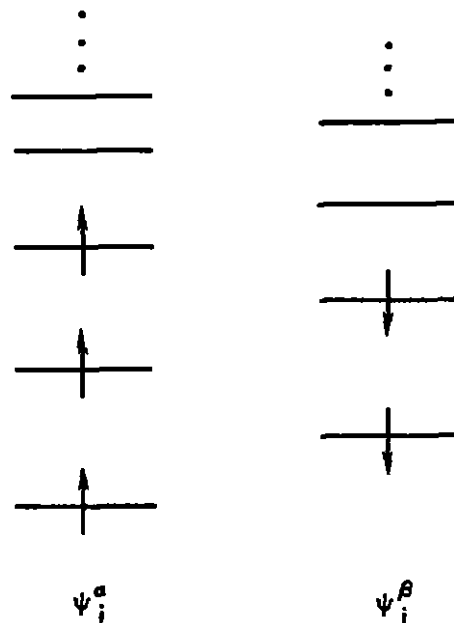
as the spatial equations defining the spatial orbitals  $\psi_j^\alpha$  and  $\psi_j^\beta$ . The spatial Fock operators  $f^\alpha(1)$  and  $f^\beta(1)$  are defined by

$$f^\alpha(\mathbf{r}_1) = \int d\omega_1 \alpha^*(\omega_1)f(\mathbf{r}_1, \omega_1)\alpha(\omega_1) \quad (3.314)$$

$$f^\beta(\mathbf{r}_1) = \int d\omega_1 \beta^*(\omega_1)f(\mathbf{r}_1, \omega_1)\beta(\omega_1) \quad (3.315)$$

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  $f^\alpha$  and  $f^\beta$ . Alternatively, we can just write down expressions for  $f^\alpha$  and  $f^\beta$  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  $\alpha$  spin. The effective interactions of an electron of  $\alpha$  spin include a coulomb and exchange interaction with all other electrons of  $\alpha$  spin plus only a coulomb interaction with electrons of  $\beta$  spin. Thus

$$f^\alpha(1) = h(1) + \sum_a^{N^\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N^\beta} J_a^\beta(1) \quad (3.316)$$

where the two sums in this equation are over the  $N^\alpha$  orbitals  $\psi_a^\alpha$  occupied by electrons of  $\alpha$  spin and the  $N^\beta$  orbitals  $\psi_a^\beta$  occupied by electrons of  $\beta$  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  $\alpha$  spin see a coulomb potential  $J_a^\alpha$  and an exchange potential  $-K_a^\alpha$  coming from each of the  $N^\alpha$  electrons of  $\alpha$  spin occupying the orbitals  $\psi_a^\alpha$ , plus a coulomb potential  $J_a^\beta$  coming from each of the  $N^\beta = N - N^\alpha$  electrons of  $\beta$  spin occupying the orbitals  $\psi_a^\beta$ . The sum over the  $N^\alpha$  orbitals  $\psi_a^\alpha$  in the above equation formally includes the interaction of an  $\alpha$  electron with itself. However, since

$$[J_a^\alpha(1) - K_a^\alpha(1)]\psi_a^\alpha(1) = 0 \quad (3.317)$$

this self-interaction is eliminated. The corresponding Fock operator for electrons of  $\beta$  spin is

$$f^\beta(1) = h(1) + \sum_a^{N^\beta} [J_a^\beta(1) - K_a^\beta(1)] + \sum_a^{N^\alpha} J_a^\alpha(1) \quad (3.318)$$

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,

$$J_a^\alpha(1) = \int d\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\alpha(\mathbf{r}_2) \quad (3.319)$$

$$\begin{aligned} K_a^\alpha(1)\psi_i^\alpha(1) &= \left[ \int d\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \psi_i^\alpha(\mathbf{r}_2) \right] \psi_a^\alpha(1) \\ &= \left[ \int d\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \mathcal{P}_{12} \psi_a^\alpha(\mathbf{r}_2) \right] \psi_i^\alpha(1) \end{aligned} \quad (3.320)$$

The definitions of  $J_a^\beta$  and  $K_a^\beta$  are strictly analogous to the above.

From the definitions (3.316) and (3.318) of the two Fock operators  $f^\alpha$  and  $f^\beta$ , we can see that the two integro-differential eigenvalue equations (3.312) and (3.313) are coupled and cannot be solved independently. That is,  $f^\alpha$  depends on the occupied  $\beta$  orbitals,  $\psi_a^\beta$ , through  $J_a^\beta$ , and  $f^\beta$  depends on the occupied  $\alpha$  orbitals,  $\psi_a^\alpha$ , through  $J_a^\alpha$ . The two equations must thus be solved by a simultaneous iterative process.

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**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

$$f^\alpha(1) = h(1) + \sum_a^{N^\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N^\beta} J_a^\beta(1)$$


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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  $\psi_i^\alpha$  or  $\psi_i^\beta$  is the expectation value

$$h_{ii}^\alpha = (\psi_i^\alpha | h | \psi_i^\alpha) \quad \text{or} \quad h_{ii}^\beta = (\psi_i^\beta | h | \psi_i^\beta) \quad (3.321)$$

The Coulomb interaction of an electron in  $\psi_i^\alpha$  with one in  $\psi_j^\beta$  is

$$J_{ij}^{\alpha\beta} = J_{ji}^{\beta\alpha} = (\psi_i^\alpha | J_j^\beta | \psi_i^\alpha) = (\psi_j^\beta | J_i^\alpha | \psi_j^\beta) = (\psi_i^\alpha \psi_i^\alpha | \psi_j^\beta \psi_j^\beta) \quad (3.322)$$

The corresponding coulomb interactions between electrons of the same spin are

$$J_{ij}^{\alpha\alpha} = (\psi_i^\alpha | J_j^\alpha | \psi_i^\alpha) = (\psi_j^\alpha | J_i^\alpha | \psi_j^\alpha) = (\psi_i^\alpha \psi_i^\alpha | \psi_j^\alpha \psi_j^\alpha) \quad (3.323)$$

and

$$J_{ij}^{\beta\beta} = (\psi_i^\beta | J_j^\beta | \psi_i^\beta) = (\psi_j^\beta | J_i^\beta | \psi_j^\beta) = (\psi_i^\beta \psi_i^\beta | \psi_j^\beta \psi_j^\beta) \quad (3.324)$$

The exchange interactions between electrons of parallel spin are

$$K_{ij}^{\alpha\alpha} = (\psi_i^\alpha | K_j^\alpha | \psi_i^\alpha) = (\psi_j^\alpha | K_i^\alpha | \psi_j^\alpha) = (\psi_i^\alpha \psi_j^\alpha | \psi_j^\alpha \psi_i^\alpha) \quad (3.325)$$

and

$$K_{ij}^{\beta\beta} = (\psi_i^\beta | K_j^\beta | \psi_i^\beta) = (\psi_j^\beta | K_i^\beta | \psi_j^\beta) = (\psi_i^\beta \psi_j^\beta | \psi_j^\beta \psi_i^\beta) \quad (3.326)$$

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,

$$E_0 = \sum_a^{N^\alpha} h_{aa}^\alpha + \sum_a^{N^\beta} h_{aa}^\beta + \frac{1}{2} \sum_a^{N^\alpha} \sum_b^{N^\alpha} (J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \frac{1}{2} \sum_a^{N^\beta} \sum_b^{N^\beta} (J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}) + \sum_a^{N^\alpha} \sum_b^{N^\beta} J_{ab}^{\alpha\beta} \quad (3.327)$$

The summations with upper limit  $N^\alpha$  are summations over the occupied orbitals  $\psi_a^\alpha$  or  $\psi_b^\alpha$ . A similar convention holds for orbitals occupied by electron of  $\beta$  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,<sup>12</sup> just as we did when deriving Roothaan's equations. We thus introduce our set of basis functions  $\{\phi_\mu | \mu = 1, 2, \dots, K\}$  and

expand the unrestricted molecular orbitals in this basis, •

$$\psi_i^\alpha = \sum_{\mu=1}^K C_{\mu i}^\alpha \phi_\mu \quad i = 1, 2, \dots, K \quad (3.328)$$

$$\psi_i^\beta = \sum_{\mu=1}^K C_{\mu i}^\beta \phi_\mu \quad i = 1, 2, \dots, K \quad (3.329)$$

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  $\psi_j^\alpha$  into the  $\alpha$  Hartree-Fock equation (3.312) gives

$$\sum_{\nu} C_{\nu j}^\alpha f^\alpha(1) \phi_\nu(1) = \epsilon_j^\alpha \sum_{\nu} C_{\nu j}^\alpha \phi_\nu(1) \quad (3.330)$$

If we multiply this equation by  $\phi_\mu^*(1)$  and integrate over the spatial coordinates of electron-one, we get

$$\sum_{\nu} F_{\mu\nu}^\alpha C_{\nu j}^\alpha = \epsilon_j^\alpha \sum_{\nu} S_{\mu\nu} C_{\nu j}^\alpha \quad j = 1, 2, \dots, K \quad (3.331)$$

where  $\mathbf{S}$  is the overlap matrix (c.f. Eq. (3.136)) and  $\mathbf{F}^\alpha$  is the matrix representation of  $f^\alpha$  in the basis  $\{\phi_\mu\}$ ,

$$F_{\mu\nu}^\alpha = \int d\mathbf{r}_1 \phi_\mu^*(1) f^\alpha(1) \phi_\nu(1) \quad (3.332)$$

Identical results can be obtained for  $\beta$  orbitals. The algebraic equations in (3.331) and the corresponding equations for  $\beta$  orbitals can be combined into the two matrix equations,

$$\mathbf{F}^\alpha \mathbf{C}^\alpha = \mathbf{S} \mathbf{C}^\alpha \boldsymbol{\epsilon}^\alpha \quad (3.333)$$

$$\mathbf{F}^\beta \mathbf{C}^\beta = \mathbf{S} \mathbf{C}^\beta \boldsymbol{\epsilon}^\beta \quad (3.334)$$

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  $\boldsymbol{\epsilon}^\alpha$  and  $\boldsymbol{\epsilon}^\beta$  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  $\psi_i^\alpha$  and  $\psi_i^\beta$  (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  $N^\alpha$  electrons of  $\alpha$  spin, then the total charge density contributed by these electrons is

$$\rho^\alpha(\mathbf{r}) = \sum_a^{N^\alpha} |\psi_a^\alpha(\mathbf{r})|^2 \quad (3.335)$$

The corresponding charge density contributed by electrons of  $\beta$  spin is

$$\rho^\beta(\mathbf{r}) = \sum_a^{N^\beta} |\psi_a^\beta(\mathbf{r})|^2 \quad (3.336)$$

and the total charge density for electrons of either spin is the sum of these

$$\rho^T(\mathbf{r}) = \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r}) \quad (3.337)$$

Integrating this equation leads, as expected, to

$$\int d\mathbf{r} \rho^T(\mathbf{r}) = N = N^\alpha + N^\beta \quad (3.338)$$

In an unrestricted wave function, electrons of  $\alpha$  and  $\beta$  spin have different spatial distributions ( $\rho^\alpha \neq \rho^\beta$ ), and it is convenient to define a *spin density*  $\rho^S(\mathbf{r})$  by

$$\rho^S(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) \quad (3.339)$$

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  $\alpha$  spin than there is of finding an electron of  $\beta$  spin the spin density is positive. Alternatively, the spin density is negative in regions of space where electrons of  $\beta$  spin are most prevalent. The individual densities  $\rho^\alpha$  and  $\rho^\beta$  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  $2\langle \mathcal{S}_z \rangle$ .

By substituting the basis set expansions (3.328) and (3.329) of the  $\alpha$  and  $\beta$  molecular orbitals into the expressions (3.335) and (3.336) for the  $\alpha$  and  $\beta$  charge densities, one can generate matrix representations (density matrices) of the  $\alpha$  and  $\beta$  charge densities,

$$\rho^\alpha(\mathbf{r}) = \sum_a^{N^\alpha} |\psi_a^\alpha(\mathbf{r})|^2 = \sum_\mu \sum_\nu P_{\mu\nu}^\alpha \phi_\mu(\mathbf{r}) \phi_\nu^*(\mathbf{r}) \quad (3.340)$$



$$\rho^\beta(\mathbf{r}) = \sum_a^{N^\beta} |\psi_a^\beta(\mathbf{r})|^2 = \sum_\mu \sum_\nu P_{\mu\nu}^\beta \phi_\mu(\mathbf{r}) \phi_\nu^*(\mathbf{r}) \quad (3.341)$$

where the density matrix  $\mathbf{P}^\alpha$  for  $\alpha$  electrons and the density matrix  $\mathbf{P}^\beta$  for  $\beta$  electrons are defined by

$$P_{\mu\nu}^\alpha = \sum_a^{N^\alpha} C_{\mu a}^\alpha (C_{\nu a}^\alpha)^* \quad (3.342)$$

$$P_{\mu\nu}^\beta = \sum_a^{N^\beta} C_{\mu a}^\beta (C_{\nu a}^\beta)^* \quad (3.343)$$

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,

$$\mathbf{P}^T = \mathbf{P}^\alpha + \mathbf{P}^\beta \quad (3.344)$$

$$\mathbf{P}^S = \mathbf{P}^\alpha - \mathbf{P}^\beta \quad (3.345)$$

**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

$$\langle \mathcal{O}_1 \rangle = \sum_\mu \sum_\nu P_{\mu\nu}^T \langle \nu | h | \mu \rangle$$

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

$$\langle \hat{\rho}^S \rangle = \rho^S(\mathbf{R}) = \text{tr}(\mathbf{P}^S \mathbf{A})$$

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  $f^\alpha$  (Eq. (3.316)) and  $f^\beta$  (Eq. (3.318)), and use expressions (3.322) to (3.326) for matrix elements of the coulomb and exchange operators. That is,

$$\begin{aligned} F_{\mu\nu}^\alpha &= \int d\mathbf{r}_1 \phi_\mu^*(1) f^\alpha(1) \phi_\nu(1) \\ &= H_{\mu\nu}^{\text{core}} + \sum_a^{N^\alpha} [(\phi_\mu \phi_\nu | \psi_a^\alpha \psi_a^\alpha) - (\phi_\mu \psi_a^\alpha | \psi_a^\alpha \phi_\nu)] + \sum_a^{N^\beta} (\phi_\mu \phi_\nu | \psi_a^\beta \psi_a^\beta) \end{aligned} \quad (3.346)$$

$$\begin{aligned} F_{\mu\nu}^\beta &= \int d\mathbf{r}_1 \phi_\mu^*(1) f^\beta(1) \phi_\nu(1) \\ &= H_{\mu\nu}^{\text{core}} + \sum_a^{N^\beta} [(\phi_\mu \phi_\nu | \psi_a^\beta \psi_a^\beta) - (\phi_\mu \psi_a^\beta | \psi_a^\beta \phi_\nu)] + \sum_a^{N^\alpha} (\phi_\mu \phi_\nu | \psi_a^\alpha \psi_a^\alpha) \end{aligned} \quad (3.347)$$

To continue, we substitute the basis set expansions of  $\psi_a^\alpha$  and  $\psi_a^\beta$  to get

$$\begin{aligned} F_{\mu\nu}^\alpha &= H_{\mu\nu}^{\text{core}} + \sum_\lambda \sum_\sigma \sum_a^{N^\alpha} C_{\lambda a}^\alpha (C_{\sigma a}^\alpha)^* [(\mu\nu | \sigma\lambda) - (\mu\lambda | \sigma\nu)] + \sum_\lambda \sum_\sigma \sum_a^{N^\beta} C_{\lambda a}^\beta (C_{\sigma a}^\beta)^* (\mu\nu | \sigma\lambda) \\ &= H_{\mu\nu}^{\text{core}} + \sum_\lambda \sum_\sigma P_{\lambda\sigma}^\alpha [(\mu\nu | \sigma\lambda) - (\mu\lambda | \sigma\nu)] + \sum_\lambda \sum_\sigma P_{\lambda\sigma}^\beta (\mu\nu | \sigma\lambda) \\ &= H_{\mu\nu}^{\text{core}} + \sum_\lambda \sum_\sigma P_{\lambda\sigma}^T (\mu\nu | \sigma\lambda) - P_{\lambda\sigma}^\alpha (\mu\lambda | \sigma\nu) \end{aligned} \quad (3.348)$$

$$\begin{aligned} F_{\mu\nu}^\beta &= H_{\mu\nu}^{\text{core}} + \sum_\lambda \sum_\sigma \sum_a^{N^\beta} C_{\lambda a}^\beta (C_{\sigma a}^\beta)^* [(\mu\nu | \sigma\lambda) - (\mu\lambda | \sigma\nu)] + \sum_\lambda \sum_\sigma \sum_a^{N^\alpha} C_{\lambda a}^\alpha (C_{\sigma a}^\alpha)^* (\mu\nu | \sigma\lambda) \\ &= H_{\mu\nu}^{\text{core}} + \sum_\lambda \sum_\sigma P_{\lambda\sigma}^\beta [(\mu\nu | \sigma\lambda) - (\mu\lambda | \sigma\nu)] + \sum_\lambda \sum_\sigma P_{\lambda\sigma}^\alpha (\mu\nu | \sigma\lambda) \\ &= H_{\mu\nu}^{\text{core}} + \sum_\lambda \sum_\sigma P_{\lambda\sigma}^T (\mu\nu | \sigma\lambda) - P_{\lambda\sigma}^\beta (\mu\lambda | \sigma\nu) \end{aligned} \quad (3.349)$$

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  $\alpha$  and  $\beta$  density matrices rather than, as in the closed-shell case,

$$P_{\mu\nu}^\alpha = P_{\mu\nu}^\beta = \frac{1}{2} P_{\mu\nu}^T \quad (3.350)$$

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  $\alpha$  and  $\beta$  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

$$\mathbf{F}^\alpha \mathbf{C}^\alpha = \mathbf{S} \mathbf{C}^\alpha \boldsymbol{\epsilon}^\alpha \quad (3.351)$$

$$\mathbf{F}^\beta \mathbf{C}^\beta = \mathbf{S} \mathbf{C}^\beta \boldsymbol{\epsilon}^\beta \quad (3.352)$$

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  $\alpha$  equations without at the same time obtaining a self-consistent solution to the  $\beta$  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  $\mathbf{F}^{\alpha'} = \mathbf{X}^\dagger \mathbf{F}^\alpha \mathbf{X}$ , diagonalizing  $\mathbf{F}^{\alpha'}$  to get  $\mathbf{C}^{\alpha'}$ , and then forming  $\mathbf{C}^\alpha = \mathbf{X} \mathbf{C}^{\alpha'}$ , 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

$$E_0 = \frac{1}{2} \sum_{\mu} \sum_{\nu} [P_{\nu\mu}^T H_{\mu\nu}^{\text{core}} + P_{\nu\mu}^\alpha F_{\mu\nu}^\alpha + P_{\nu\mu}^\beta F_{\mu\nu}^\beta]$$

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  $N^\alpha \neq N^\beta$ , 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  $\alpha$  electrons to equal the density of  $\beta$  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  $\text{CH}_3$ . This molecule has  $D_{3h}$  symmetry, i.e., it is planar with bond angles of  $120^\circ$ . 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

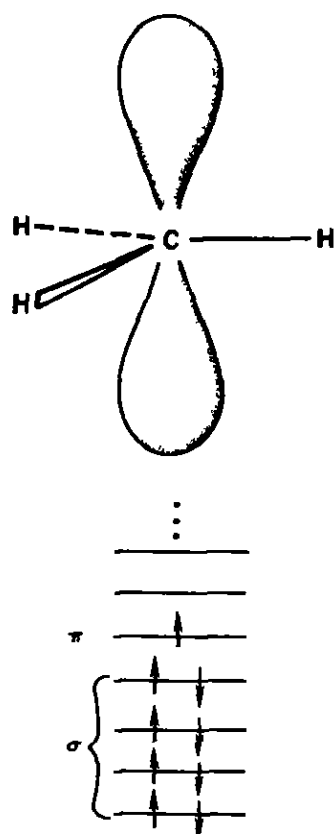


Figure 3.13 Restricted Hartree-Fock description of the planar methyl radical.

electron is in an open-shell  $\pi$  orbital, which in a minimal basis description would be a pure  $2p$  orbital on carbon. The remaining electrons are paired in  $\sigma$  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  $\pi$  orbital. Because all  $\sigma$  electrons are paired, the spin density is just

$$\rho^S(\mathbf{r}) = |\psi_\pi(\mathbf{r})|^2 \quad (3.353)$$

where  $\psi_\pi$  is the  $\pi$  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,

$$a^H(\text{Gauss}) = 1592\rho^S(\mathbf{R}_H) \quad (3.354)$$

$$a^C(\text{Gauss}) = 400.3\rho^S(\mathbf{R}_C) \quad (3.355)$$

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  $\sigma$  orbital have different interactions with the unpaired electron, i.e., the electrons of  $\alpha$  spin have a coulomb and exchange interaction with the unpaired electron while the electrons of  $\beta$  spin have only a coulomb interaction. There is thus good reason why the  $\alpha$  and  $\beta$  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  $\sigma$  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 orbital

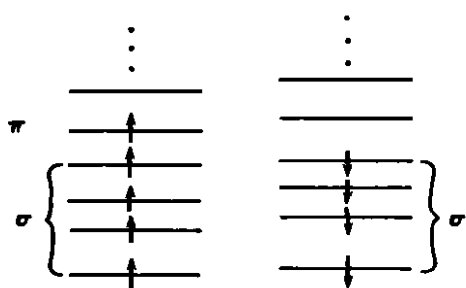
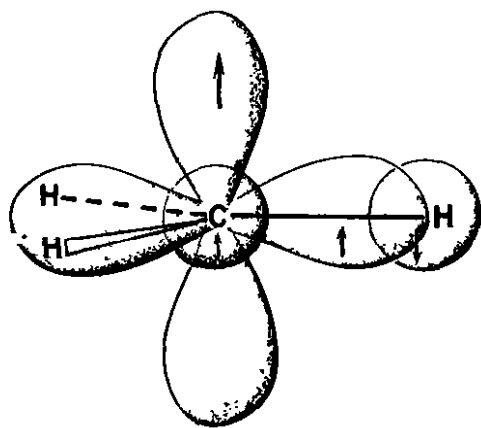


Figure 3.14 Unrestricted Hartree-Fock description of the planar methyl radical.

**Table 3.26 Unrestricted SCF spin densities and hyperfine coupling constants for the methyl radical using the standard basis sets.** A value of  $\langle \mathcal{S}^2 \rangle = 0.75$  corresponds to a pure doublet

| Basis set  | Spin density (a.u.) |         | Coupling constant (Gauss <sup>e</sup> ) |       | $\langle \mathcal{S}^2 \rangle$ |
|------------|---------------------|---------|---|-------|---------------------------------|
|            | C                   | H       | $a^C$                                   | $a^H$ |                                 |
| 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<sub>3</sub> 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  $\mathcal{S}^2$ . 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  $\langle \mathcal{S}^2 \rangle = S(S + 1) = \frac{3}{4}$ . 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  $\mathcal{S}^2$  are close to the correct value of  $\frac{3}{4}$ , showing that these contaminants are not large.

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**Exercise 3.41** Assume the unrestricted Hartree-Fock (UHF) calculations of Table 3.26 contain only the leading quartet contaminant. That is,

$$\Psi_{\text{UHF}} = c_1 {}^2\Psi + c_2 {}^4\Psi$$

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  $\langle \mathcal{S}^2 \rangle$ .

---

We have previously used Koopmans' theorem to calculate the first two ionization potentials of  $\text{N}_2$ . 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  $\text{N}_2^+$  to be lower in energy than  ${}^2\Sigma_g$  state of  $\text{N}_2^+$ . That is, the highest occupied orbital of  $\text{N}_2$  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  $\text{N}_2^+$ . Koopmans' theorem calculations assume the orbitals of these two states to be identical to those of ground state  $\text{N}_2$ . By performing separate unrestricted calculations on these two doublet states of  $\text{N}_2^+$ , 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  $\text{N}_2$  ground state from the total unrestricted energy of each of the  $\text{N}_2^+$  ions.

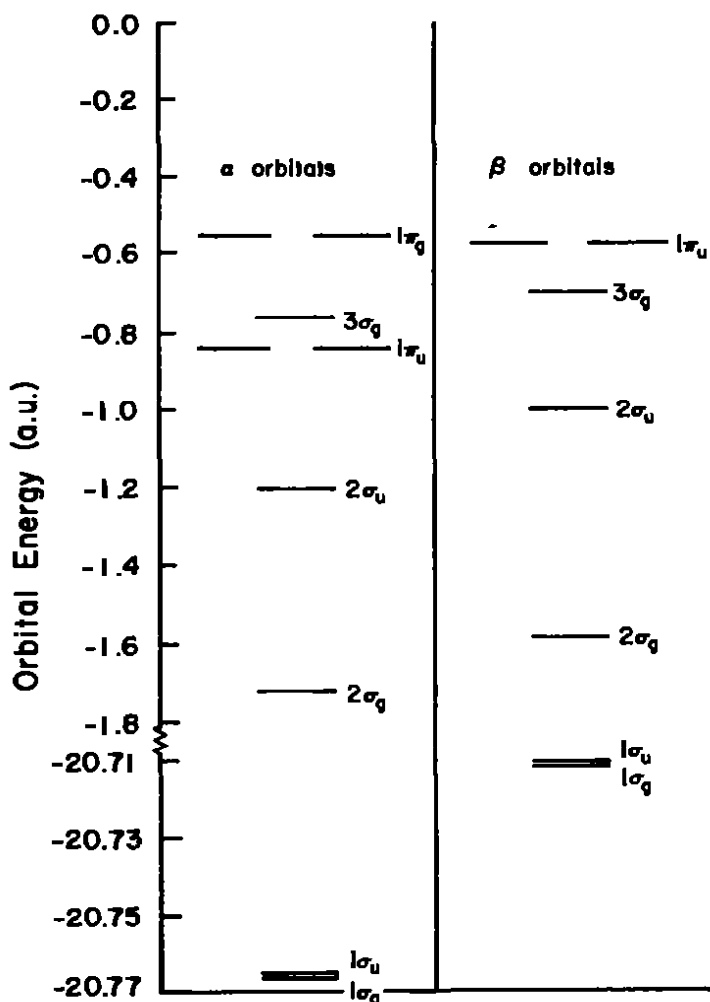
Table 3.27 shows the results of 6-31G\* calculations on the  ${}^1\Sigma_g$  state of  $\text{N}_2$  and the  ${}^2\Sigma_g$  and  ${}^2\Pi_u$  states of  $\text{N}_2^+$ . To compare with experimental vertical ionization potentials, all the calculations were performed at the equilibrium geometry ( $R = 2.074$  a.u.) of groundstate  $\text{N}_2$ . These calculations still predict that the  ${}^2\Pi_u$  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  $\alpha$  orbitals relative to the  $\beta$  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  $\alpha$  and  $\beta$  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

accommodates 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

$$\psi_1 = [2(1 + S_{12})]^{-1/2}(\phi_1 + \phi_2) \quad (3.356)$$

$$\psi_2 = [2(1 - S_{12})]^{-1/2}(\phi_1 - \phi_2) \quad (3.357)$$

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  $\psi_1^\alpha$  and  $\psi_1^\beta$  as linear combinations of the restricted symmetry determined orbitals  $\psi_1$  and  $\psi_2$ , as follows:

$$\psi_1^\alpha = \cos \theta \psi_1 + \sin \theta \psi_2 \quad (3.358)$$

$$\psi_1^\beta = \cos \theta \psi_1 - \sin \theta \psi_2 \quad (3.359)$$

The single degree of freedom here is in the angle  $\theta$ . It is sufficient to consider values of  $\theta$  between  $0^\circ$  and  $45^\circ$ . The value  $\theta = 0$  corresponds to the restricted solution  $\psi_1^\alpha = \psi_1^\beta = \psi_1$  and nonzero values of  $\theta$  correspond to unrestricted solutions  $\psi_1^\alpha \neq \psi_1^\beta$ . The unrestricted virtual orbitals are given by

$$\psi_2^\alpha = -\sin \theta \psi_1 + \cos \theta \psi_2 \quad (3.360)$$

$$\psi_2^\beta = \sin \theta \psi_1 + \cos \theta \psi_2 \quad (3.361)$$

**Exercise 3.42** Show that the set of  $\alpha$  orbitals  $\{\psi_1^\alpha, \psi_2^\alpha\}$  and the set of  $\beta$  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

$$\psi_1^\alpha = c_1\phi_1 + c_2\phi_2 \quad (3.362)$$

$$\psi_1^\beta = c_2\phi_1 + c_1\phi_2 \quad (3.363)$$

where

$$c_1 = [2(1 + S_{12})]^{-1/2} \cos \theta + [2(1 - S_{12})]^{-1/2} \sin \theta \quad (3.364)$$

$$c_2 = [2(1 + S_{12})]^{-1/2} \cos \theta - [2(1 - S_{12})]^{-1/2} \sin \theta \quad (3.365)$$

By allowing  $\psi_2$  to mix with  $\psi_1$  in the definition of the unrestricted occupied orbitals (Eqs. (3.358) and (3.359)), we allow the weights of  $\phi_1$  and  $\phi_2$  in the basis set expansions of  $\psi_1^\alpha$  and  $\psi_1^\beta$  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  $\theta$  increases from zero,  $c_1$  gets larger and  $c_2$  gets smaller or, equivalently,  $\psi_1^\alpha$  acquires a larger admixture of  $\phi_1$  and  $\psi_1^\beta$  acquires a larger admixture of  $\phi_2$ . If  $S_{12} = 0$  as is appropriate for large internuclear distances, then in the limit of  $\theta = 45^\circ$  we have  $c_1 = 1$ ,  $c_2 = 0$ , and

$$\left. \begin{array}{l} \psi_1^\alpha \equiv \phi_1 \\ \psi_1^\beta \equiv \phi_2 \end{array} \right\} \theta = 45^\circ, \quad S_{12} = 0 \quad (3.366)$$

This is the result we desire for two separate H atoms—an electron with  $\alpha$  spin in  $\phi_1$  and an electron with  $\beta$  spin in  $\phi_2$ .

We thus characterize molecular orbitals for minimal basis  $H_2$  by the single parameter  $\theta$ . At one extreme,  $\theta = 0$  corresponds to the restricted solution where the occupied molecular orbital is an equal mixture of  $\phi_1$  and  $\phi_2$ . At the other extreme,  $\theta = 45^\circ$  corresponds to an unrestricted solution for isolated hydrogen atoms. Intermediate value of  $\theta$  correspond to unrestricted solutions where  $\psi_1^\alpha$  is mainly  $\phi_1$  and  $\psi_1^\beta$  is mainly  $\phi_2$ . Figure 3.16 gives a qualitative picture of the unrestricted molecular orbitals of  $H_2$  as a function of  $\theta$ . 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 non-zero value of  $\theta$  be obtained? To investigate this question, we need to determine the energy as a function of  $\theta$ .

The electronic energy of an unrestricted single determinant wave function for  $H_2$ ,

$$|\Psi_0\rangle = |\psi_1^\alpha(1)\bar{\psi}_1^\beta(2)\rangle \quad (3.367)$$

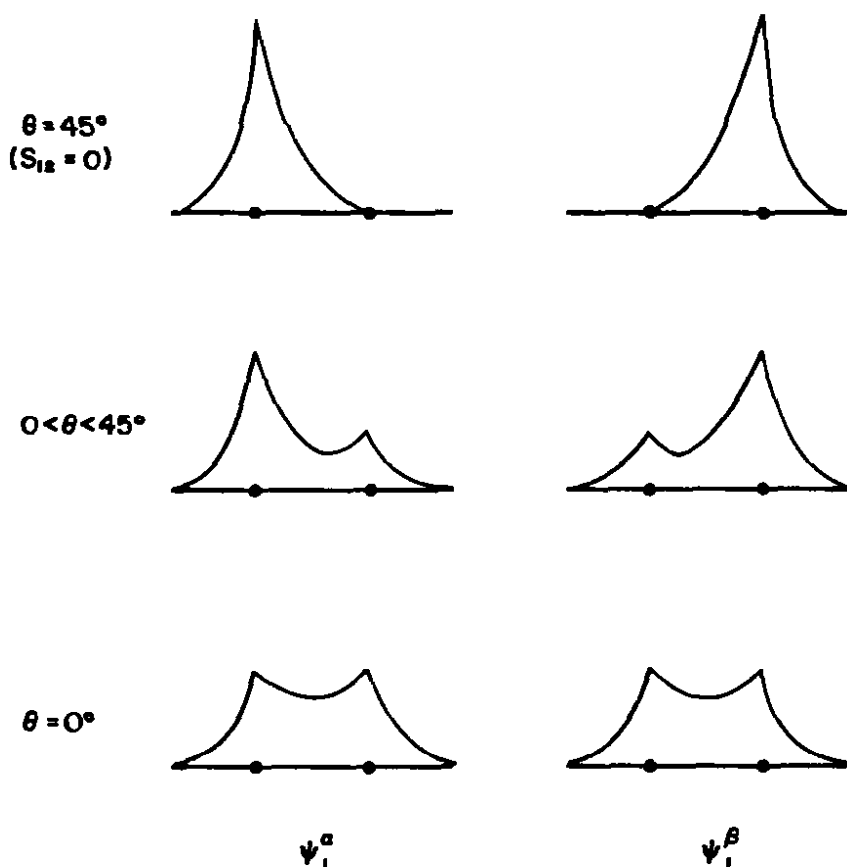


Figure 3.16 Qualitative behavior of unrestricted molecular orbitals  $\psi_1^\alpha$  and  $\psi_1^\beta$  for  $H_2$  as a function of  $\theta$ .

is just the kinetic energy and nuclear attraction of each electron, plus the coulomb repulsion between the two electrons. That is,

$$\begin{aligned} E_0 &= \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = h_{11}^\alpha + h_{11}^\beta + J_{11}^{\alpha\beta} \\ &= (\psi_1^\alpha | h | \psi_1^\alpha) + (\psi_1^\beta | h | \psi_1^\beta) + (\psi_1^\alpha \psi_1^\alpha | \psi_1^\beta \psi_1^\beta) \end{aligned} \quad (3.368)$$

Substituting the expansions (3.358) and (3.359) into this expression, we can write the electronic energy, as a function of  $\theta$ , in terms of molecular integrals of the restricted problem

$$\begin{aligned} E_0(\theta) &= 2 \cos^2 \theta h_{11} + 2 \sin^2 \theta h_{22} + \cos^4 \theta J_{11} \\ &\quad + \sin^4 \theta J_{22} + 2 \sin^2 \theta \cos^2 \theta (J_{12} - 2K_{12}) \end{aligned} \quad (3.369)$$

If  $\theta = 0$ , the unrestricted energy just reduces to the restricted energy

$$E_0(0) = 2h_{11} + J_{11} \quad (3.370)$$

The first derivative of the unrestricted energy with respect to  $\theta$  is

$$\begin{aligned} dE_0(\theta)/d\theta &= 4 \cos \theta \sin \theta [h_{22} - h_{11} + \sin^2 \theta J_{22} - \cos^2 \theta J_{11} \\ &\quad + (\cos^2 \theta - \sin^2 \theta)(J_{12} - 2K_{12})] \end{aligned} \quad (3.371)$$

To find the values of  $\theta$  which solve the Pople-Nesbet equations, i.e., to find the values of  $\theta$  which make the unrestricted energy stationary, we set

the first derivative of the unrestricted energy to zero,

$$dE_0(\theta)/d\theta = AB = 0 \quad (3.372)$$

where

$$A = 4 \cos \theta \sin \theta \quad (3.373)$$

and

$$B = h_{22} - h_{11} + \sin^2 \theta J_{22} - \cos^2 \theta J_{11} + (\cos^2 \theta - \sin^2 \theta)(J_{12} - 2K_{12}) \quad (3.374)$$

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:

$$\cos^2 \theta = \eta \quad (3.375)$$

where

$$\eta = (h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}) / (J_{11} + J_{22} - 2J_{12} + 4K_{12}) \quad (3.376)$$

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  $\eta$  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  $\theta = 39.5^\circ$ . 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),

$$\begin{aligned} d^2E_0(\theta)/d\theta^2 \Big|_{\theta=0} &= E''_0(0) = 4(h_{22} - h_{11} - J_{11} + J_{12} - 2K_{12}) \\ &= 4(\varepsilon_2 - \varepsilon_1 - J_{12} - K_{12}) \end{aligned} \quad (3.377)$$

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

$$h_{22} - h_{11} = J_{11} - J_{12} + 2K_{12} \quad (3.378)$$

then the restricted solution is a saddle point. Substituting this last saddle point condition into Eq. (3.376), we find that  $\eta = 1$  at the saddle point. Using the molecular integrals of Appendix D we can investigate the behavior of

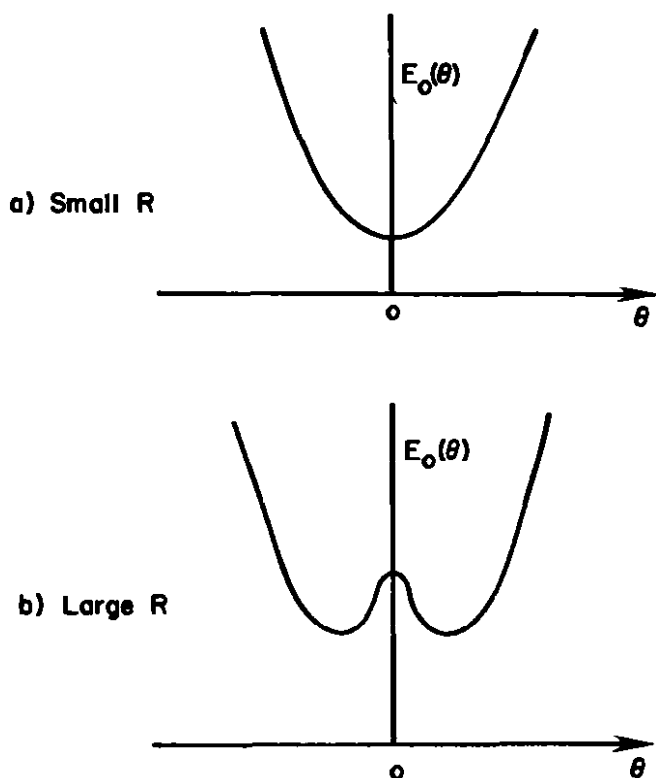


Figure 3.17 Qualitative behavior of the unrestricted energy of  $H_2$  as a function of  $\theta$  for small and large internuclear distances: a) small  $R$ ; b) large  $R$ .

$E_0''(0)$  and  $\eta$  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  $\eta$  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  $\eta$  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  $\eta$  decreases until, at a distance of approximately 2.3 a.u.,  $\eta$  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  $\eta$  can be equated to  $\cos^2 \theta$ . As the bond length becomes larger and larger,  $\theta$  gives to the limit of  $45^\circ$  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.<sup>5</sup> 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

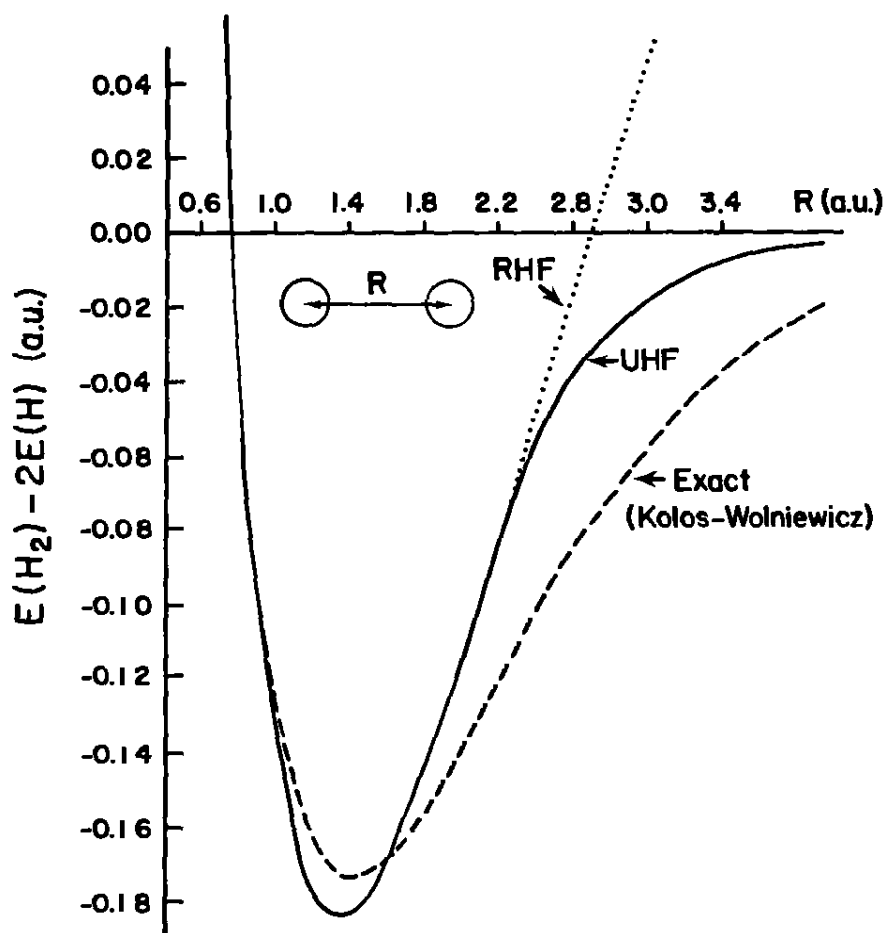


Figure 3.18 STO-3G potential curves for  $H_2$ .

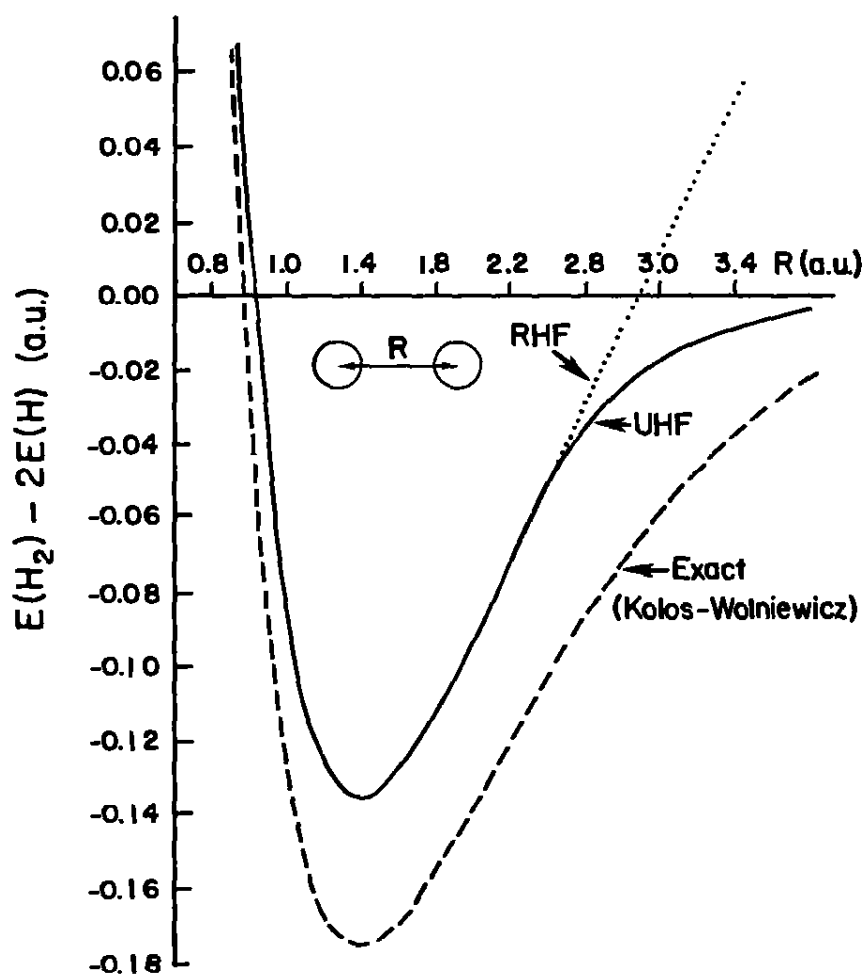


Figure 3.19 6-31G\*\* potential energy curves for  $H_2$ .

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  $R \rightarrow \infty$ , 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

$$\lim_{R \rightarrow \infty} |\Psi_0\rangle = |\phi_1(1)\bar{\phi}_2(2)\rangle \quad (3.379)$$

This, however, is not the correct form for a singlet wave function in which electrons occupy different spatial orbitals  $\phi_1$  and  $\phi_2$ . In analogy to Eq. (2.260), the singlet wave function should be

$$\lim_{R \rightarrow \infty} |\Phi_0\rangle = 2^{-1/2} [|\phi_1(1)\bar{\phi}_2(2)\rangle + |\phi_2(1)\bar{\phi}_1(2)\rangle] \quad (3.380)$$

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

$$\begin{aligned} |\Psi_0\rangle &= |\psi_1^\alpha \bar{\psi}_1^\beta\rangle = \cos^2 \theta |\psi_1 \bar{\psi}_1\rangle - \sin^2 \theta |\psi_2 \bar{\psi}_2\rangle \\ &\quad - (2)^{1/2} \cos \theta \sin \theta [|\psi_1 \bar{\psi}_2\rangle - |\psi_2 \bar{\psi}_1\rangle] / (2)^{1/2} \\ &= \cos^2 \theta |\psi_1 \bar{\psi}_1\rangle - \sin^2 \theta |\psi_2 \bar{\psi}_2\rangle \\ &\quad - (2)^{1/2} \cos \theta \sin \theta |^3\Psi_1^2\rangle \end{aligned} \quad (3.381)$$

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  $R \rightarrow \infty$  the triplet contamination increases until it represents 50% of the wave function,

$$\lim_{R \rightarrow \infty} |\Psi_0\rangle = 1/2 [|\psi_1 \bar{\psi}_1\rangle - |\psi_2 \bar{\psi}_2\rangle - (2)^{1/2} |^3\Psi_1^2\rangle] \quad (3.382)$$

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

1. J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, H. B. Schlegel, D. J. Defrees, and J. A. Pople, *Gaussian 80*, program #406, Quantum Chemistry Program Exchange, Indiana University. More recent versions, such as *Gaussian 88*, are available via Professor John Pople of Carnegie-Mellon University.
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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10. The slash here separates heavy atom (Li-Ne) basis functions from hydrogen atom basis functions.
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## FURTHER READING

- Cook, D. B., *Ab Initio Valence Calculations in Chemistry*, Wiley, New York, 1974. This book is a good source of information on the practical aspects of performing *ab initio* self-consistent-field calculations.
- Davidson, E. R. and Feller, B., Basis set selection in molecular calculations, *Chem. Rev.* **86**: 681 (1986). This article describes and compares the performance of a variety of Gaussian basis sets that are in common use.
- England, W., Salmon, L. S., and Ruedenberg, K., Localized MO's: A bridge between chemical intuition and molecular quantum mechanics, in *Topics in Current Chemistry*, Springer-Verlag, 1971; Caldwell, D. and Eyring, H., Localized orbitals in spectroscopy, *Adv. Quantum Chem.* **11**: 93 (1978). These two references discuss the invariance of Hartree-Fock orbitals to a unitary transformation, and the physical interpretation of particular