

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

Basis set	NH ₃	H ₂ 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 ^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 NH₃, H₂O, and FH using our standard basis sets. Only at the 6-31G* level and beyond is the proper trend H₂O > FH > NH₃ 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 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

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

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 α spin are described by a set of spatial orbitals $\{\psi_j^\alpha | j = 1, 2, \dots, K\}$, and electrons of β 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 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

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

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 $\{\varepsilon_j^\beta | j = 1, 2, \dots, K\}$ for electrons of β spin. Thus

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

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

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

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

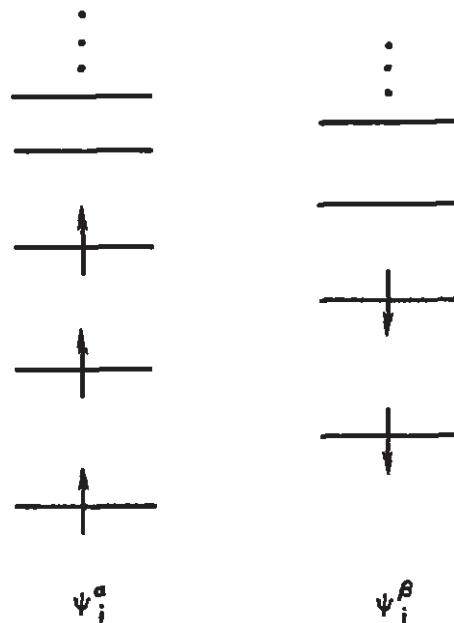
as the spatial equations defining the spatial orbitals ψ_j^α and ψ_j^β . The spatial Fock operators $f^\alpha(1)$ and $f^\beta(1)$ are defined by

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

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

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^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

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

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

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

this self-interaction is eliminated. The corresponding Fock operator for electrons of β spin is

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

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,

$$J_a^\alpha(1) = \int d\mathbf{r}_2 \psi_a^{\alpha*}(2) r_{12}^{-1} \psi_a^\alpha(2) \quad (3.319)$$

$$\begin{aligned} K_a^\alpha(1)\psi_i^\alpha(1) &= \left[\int d\mathbf{r}_2 \psi_a^{\alpha*}(2) r_{12}^{-1} \psi_i^\alpha(2) \right] \psi_a^\alpha(1) \\ &= \left[\int d\mathbf{r}_2 \psi_a^{\alpha*}(2) r_{12}^{-1} \mathcal{P}_{12} \psi_a^\alpha(2) \right] \psi_i^\alpha(1) \end{aligned} \quad (3.320)$$

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

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

The Coulomb interaction of an electron in ψ_i^α with one in ψ_j^β is

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

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^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 $\{\phi_\mu | \mu = 1, 2, \dots, K\}$ 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 ψ_j^α into the α 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}^α is the matrix representation of f^α in the basis $\{\phi_\mu\}$,

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

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,

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

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

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}^α and \mathbf{C}^β 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}^α and \mathbf{F}^β depend on both \mathbf{C}^α and \mathbf{C}^β , 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

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

The corresponding charge density contributed by electrons of β spin is

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

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 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

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

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

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,

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

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

where the density matrix \mathbf{P}^α for α electrons and the density matrix \mathbf{P}^β for β 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}^α , \mathbf{P}^β , \mathbf{P}^T , and \mathbf{P}^S we will now use these definitions to give explicit form to the unrestricted Fock matrices \mathbf{F}^α and \mathbf{F}^β .

3.8.4 Expression for the Fock Matrices

To obtain expressions for the elements of the matrices \mathbf{F}^α and \mathbf{F}^β , 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,

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

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

To continue, we substitute the basis set expansions of ψ_a^α and ψ_a^β 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 α and β 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}^α depends on \mathbf{P}^β (through the total density matrix \mathbf{P}^T) and \mathbf{F}^β similarly depends on \mathbf{P}^α .

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}^α and \mathbf{P}^β and hence \mathbf{P}^T . An obvious choice is to set these matrices to zero and use \mathbf{H}^{core} as an initial guess to both \mathbf{F}^α and \mathbf{F}^β . 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}^α and \mathbf{P}^β , at each step of the iteration, we can form \mathbf{F}^α and \mathbf{F}^β , 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}^α and \mathbf{C}^β , and then form new approximations to \mathbf{P}^α and \mathbf{P}^β . 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 $\mathbf{F}^{\alpha'} = \mathbf{X}^\dagger \mathbf{F}^\alpha \mathbf{X}$, 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 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 P^α is not equal to P^β . 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 $P^\alpha \neq P^\beta$ 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

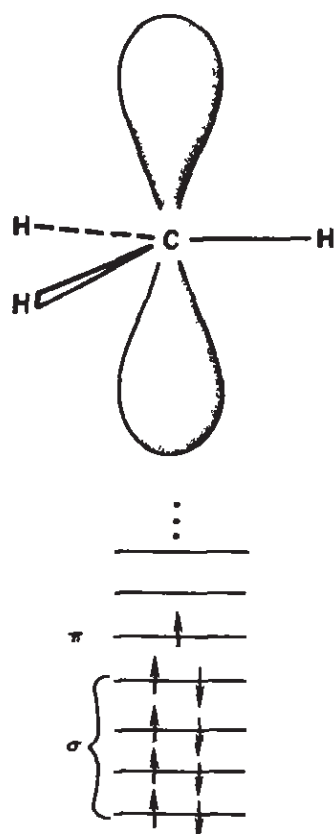


Figure 3.13 Restricted Hartree-Fock description of the planar methyl radical.