3.8.3 Unrestricted Density Matrices

We continue here with the generalization of our previous results for restricted closed-shell wave functions. If an electron is described by the molecular orbital $\psi_a^\alpha(\mathbf{r})$, then the probability of finding that electron in a volume element $d\mathbf{r}$ at $\mathbf{r}$ is $|\psi_a^\alpha(\mathbf{r})|^2\,d\mathbf{r}$. The probability distribution function (charge density) is $|\psi_a^\alpha(\mathbf{r})|^2$. If we have N^α electrons of α spin, then the total charge density contributed by these electrons is

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

The corresponding charge density contributed by electrons of β spin is

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

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

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

Integrating this equation leads, as expected, to

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

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

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

From the above definition of the spin density, it is clear that in regions of space where there is a higher probability of finding an electron of α spin than there is of finding an electron of β spin the spin density is positive. Alternatively, the spin density is negative in regions of space where electrons of β spin are most prevalent. The individual densities ρ^α and ρ^β are, of course positive everywhere. The spin density is a convenient way of describing the distribution of spins in an open-shell system.

Exercise 3.36 Use definitions (3.335) and (3.336) and Eq. (2.254) to show that the integral over all space of the spin density is $2\langle \mathscr{S}_z \rangle$.

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

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

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

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

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

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

In addition to these two density matrices, one can, of course, define, in analogy to our previous definitions, a total density matrix and a spin density matrix. That is,

$$\mathbf{P}^T = \mathbf{P}^\alpha + \mathbf{P}^\beta \tag{3.344}$$

$$\mathbf{P}^S = \mathbf{P}^\alpha - \mathbf{P}^\beta \tag{3.345}$$

Exercise 3.37 Carry through the missing steps that led to Eqs. (3.340) to (3.343).

Exercise 3.38 Show that expectation values of spin-independent sums of one-electron operators $\sum_{i=1}^{N} h(i)$ are given by

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

for any unrestricted single determinant.

Exercise 3.39 Consider the following spin-dependent operator which is a sum of one-electron operators,

$$\hat{\rho}^S = 2 \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{R}) s_z(i)$$

Use the rules for evaluating matrix elements, given in Chapter 2, to show that the expectation value of $\hat{\rho}^S$ for any unrestricted single determinant is

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

where

$$A_{\mu\nu} = \phi_\mu^*(\mathbf{R}) \phi_\nu(\mathbf{R})$$

This matrix element is important in the theory of the Fermi contact contribution to ESR and NMR coupling constants.

Having defined the unrestricted density matrices $\mathbf{P}^\alpha$, $\mathbf{P}^\beta$, $\mathbf{P}^T$, and $\mathbf{P}^S$ we will now use these definitions to give explicit form to the unrestricted Fock matrices $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$.

3.8.4 Expression for the Fock Matrices

To obtain expressions for the elements of the matrices $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$, we simply take matrix elements in the basis $\{\phi_\mu\}$ of the two Fock operators f^α (Eq. (3.316)) and f^β (Eq. (3.318)), and use expressions (3.322) to (3.326) for matrix elements of the coulomb and exchange operators. That is,

$$\begin{aligned} F^\alpha_{\mu\nu} &= \int d\mathbf{r}_1\, \phi^*_\mu(1) f^\alpha(1) \phi_\nu(1) \\ &= H^{\text{core}}_{\mu\nu} + \sum_a^{N^\alpha} [(\phi_\mu\phi_\nu|\psi^\alpha_a\psi^\alpha_a) - (\phi_\mu\psi^\alpha_a|\psi^\alpha_a\phi_\nu)] + \sum_a^{N^\beta} (\phi_\mu\phi_\nu|\psi^\beta_a\psi^\beta_a) \end{aligned} \quad (3.346)$$

$$\begin{aligned} F^\beta_{\mu\nu} &= \int d\mathbf{r}_1\, \phi^*_\mu(1) f^\beta(1) \phi_\nu(1) \\ &= H^{\text{core}}_{\mu\nu} + \sum_a^{N^\beta} [(\phi_\mu\phi_\nu|\psi^\beta_a\psi^\beta_a) - (\phi_\mu\psi^\beta_a|\psi^\beta_a\phi_\nu)] + \sum_a^{N^\alpha} (\phi_\mu\phi_\nu|\psi^\alpha_a\psi^\alpha_a) \end{aligned} \quad (3.347)$$

To continue, we substitute the basis set expansions of ψ^α_a and ψ^β_a to get

$$\begin{aligned} F^\alpha_{\mu\nu} &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma \sum_a^{N^\alpha} C^\alpha_{\lambda a}(C^\alpha_{\sigma a})^*[(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_\lambda \sum_\sigma \sum_a^{N^\beta} C^\beta_{\lambda a}(C^\beta_{\sigma a})^*(\mu\nu|\sigma\lambda) \\ &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma P^\alpha_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_\lambda \sum_\sigma P^\beta_{\lambda\sigma}(\mu\nu|\sigma\lambda) \\ &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma P^T_{\lambda\sigma}(\mu\nu|\sigma\lambda) - P^\alpha_{\lambda\sigma}(\mu\lambda|\sigma\nu) \end{aligned} \quad (3.348)$$

$$\begin{aligned} F^\beta_{\mu\nu} &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma \sum_a^{N^\beta} C^\beta_{\lambda a}(C^\beta_{\sigma a})^*[(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_\lambda \sum_\sigma \sum_a^{N^\alpha} C^\alpha_{\lambda a}(C^\alpha_{\sigma a})^*(\mu\nu|\sigma\lambda) \\ &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma P^\beta_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_\lambda \sum_\sigma P^\alpha_{\lambda\sigma}(\mu\nu|\sigma\lambda) \\ &= H^{\text{core}}_{\mu\nu} + \sum_\lambda \sum_\sigma P^T_{\lambda\sigma}(\mu\nu|\sigma\lambda) - P^\beta_{\lambda\sigma}(\mu\lambda|\sigma\nu) \end{aligned} \quad (3.349)$$

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,

$$P^\alpha_{\mu\nu} = P^\beta_{\mu\nu} = \tfrac{1}{2} P^T_{\mu\nu} \quad (3.350)$$

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 $\mathbf{P}^\alpha$.