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,

$$F^\alpha_{\mu\nu} = \int d\mathbf{r}_1\ \phi^*_\mu(1) f^\alpha(1) \phi_\nu(1)$$

$$= H^{\text{core}}_{\mu\nu} + \sum_a^{N^\alpha} [(\phi_\mu\phi_\nu|\psi^\alpha_a\psi^\alpha_a) - (\phi_\mu\psi^\alpha_a|\psi^\alpha_a\phi_\nu)] + \sum_a^{N^\beta} (\phi_\mu\phi_\nu|\psi^\beta_a\psi^\beta_a) \quad (3.346)$$

$$F^\beta_{\mu\nu} = \int d\mathbf{r}_1\ \phi^*_\mu(1) f^\beta(1) \phi_\nu(1)$$

$$= H^{\text{core}}_{\mu\nu} + \sum_a^{N^\beta} [(\phi_\mu\phi_\nu|\psi^\beta_a\psi^\beta_a) - (\phi_\mu\psi^\beta_a|\psi^\beta_a\phi_\nu)] + \sum_a^{N^\alpha} (\phi_\mu\phi_\nu|\psi^\alpha_a\psi^\alpha_a) \quad (3.347)$$

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

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

$$= H^{\text{core}}_{\mu\nu} + \sum_\lambda\sum_\sigma P^\alpha_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_\lambda\sum_\sigma P^\beta_{\lambda\sigma}(\mu\nu|\sigma\lambda)$$

$$= H^{\text{core}}_{\mu\nu} + \sum_\lambda\sum_\sigma P^T_{\lambda\sigma}(\mu\nu|\sigma\lambda) - P^\alpha_{\lambda\sigma}(\mu\lambda|\sigma\nu) \quad (3.348)$$

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

$$= H^{\text{core}}_{\mu\nu} + \sum_\lambda\sum_\sigma P^\beta_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] + \sum_\lambda\sum_\sigma P^\alpha_{\lambda\sigma}(\mu\nu|\sigma\lambda)$$

$$= H^{\text{core}}_{\mu\nu} + \sum_\lambda\sum_\sigma P^T_{\lambda\sigma}(\mu\nu|\sigma\lambda) - P^\beta_{\lambda\sigma}(\mu\lambda|\sigma\nu) \quad (3.349)$$

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 $\mathbf{P}^\alpha$.