

Modern Quantum Chemistry, Szabo & Ostlund

HW

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3 The Hartree-Fock Approximation

3.1 The HF Equations

3.1.1 The Coulomb and Exchange Operators

3.1.2 The Fock Operator

Ex 3.1

$$\begin{aligned}
 \langle \chi_i | \hat{f} | \chi_j \rangle &= \left\langle \chi_i(1) \left| h(1) + \sum_b [\mathcal{J}_b(1) - \mathcal{K}_b(1)] \right| \chi_j(1) \right\rangle \\
 &= [i|h|j] + \sum_{b \neq j} \left[\left\langle \chi_i(1) \chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_b(2) \chi_j(1) \right\rangle - \left\langle \chi_i(1) \chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_b(1) \chi_j(2) \right\rangle \right] \\
 &= [i|h|j] + \sum_{b \neq j} ([ij|bb] - [ib|bj])
 \end{aligned} \tag{3.1.1}$$

Since

$$[ij|jj] - [ij|jj] = 0 \tag{3.1.2}$$

we have

$$\begin{aligned}
 \langle \chi_i | \hat{f} | \chi_j \rangle &= \langle i | h | j \rangle + \sum_b (\langle ib | jb \rangle - \langle ib | bj \rangle) \\
 &= \langle i | h | j \rangle + \sum_b \langle ib || jb \rangle
 \end{aligned} \tag{3.1.3}$$

3.2 Derivation of the HF Equations

3.2.1 Functional Variation

3.2.2 Minimization of the Energy of a Single Determinant

Ex 3.2 Take the complex conjugate of

$$\mathcal{L}[\{\chi_\alpha\}] = E_0[\{\chi_\alpha\}] - \sum_a^N \sum_b^N \varepsilon_{ba}([a|b] - \delta_{ab}) \tag{3.2.1}$$

we have

$$\mathcal{L}[\{\chi_\alpha\}]^* = E_0[\{\chi_\alpha\}]^* - \sum_a^N \sum_b^N \varepsilon_{ba}^*([a|b]^* - \delta_{ab}^*) \tag{3.2.2}$$

i.e.

$$\mathcal{L}[\{\chi_\alpha\}] = E_0[\{\chi_\alpha\}] - \sum_a^N \sum_b^N \varepsilon_{ba}^*([b|a] - \delta_{ab}) \tag{3.2.3}$$

thus

$$\sum_a^N \sum_b^N \varepsilon_{ba}([a|b] - \delta_{ab}) = \sum_a^N \sum_b^N \varepsilon_{ba}^*([b|a] - \delta_{ab}) = \sum_b^N \sum_a^N \varepsilon_{ab}^*([a|b] - \delta_{ba}) \tag{3.2.4}$$

\therefore

$$\varepsilon_{ba} = \varepsilon_{ab}^* \tag{3.2.5}$$

Ex 3.3 \therefore

$$[\delta \chi_a | h | \chi_a] = [\chi_a | h | \delta \chi_a]^* \tag{3.2.6}$$

$$[\chi_a \delta \chi_a | \chi_b \chi_b] = [\delta \chi_a \chi_a | \chi_b \chi_b]^* \tag{3.2.7}$$

$$[\chi_a \chi_a | \chi_b \delta \chi_b] = [\chi_a \chi_a | \delta \chi_b \chi_b]^* \tag{3.2.8}$$

$$[\chi_a \chi_b | \chi_b \delta \chi_a] = [\chi_b \delta \chi_a | \chi_a \chi_b] = [\delta \chi_a \chi_b | \chi_b \chi_a]^* \tag{3.2.9}$$

$$[\chi_a \chi_b | \delta \chi_b \chi_a] = [\delta \chi_b \chi_a | \chi_a \chi_b] = [\chi_a \delta \chi_b | \chi_b \chi_a]^* \tag{3.2.10}$$

\therefore

$$\begin{aligned}\delta E_0 &= \sum_a^N [\delta \chi_a | h | \chi_a] + \frac{1}{2} \sum_a^N \sum_b^N ([\delta \chi_a \chi_a | \chi_b \chi_b] + [\chi_a \chi_a | \delta \chi_b \chi_b]) \\ &\quad - \frac{1}{2} \sum_a^N \sum_b^N ([\delta \chi_a \chi_b | \chi_b \chi_a] + [\chi_a \chi_b | \delta \chi_b \chi_a]) + \text{complex conjugates}\end{aligned}\quad (3.2.11)$$

while

$$\sum_a^N \sum_b^N [\chi_a \chi_a | \delta \chi_b \chi_b] = \sum_b^N \sum_a^N [\chi_b \chi_b | \delta \chi_a \chi_a] = \sum_a^N \sum_b^N [\delta \chi_a \chi_a | \chi_b \chi_b] \quad (3.2.12)$$

$$\sum_a^N \sum_b^N [\chi_a \chi_b | \delta \chi_b \chi_a] = \sum_b^N \sum_a^N [\chi_b \chi_a | \delta \chi_a \chi_b] = \sum_a^N \sum_b^N [\delta \chi_a \chi_b | \chi_b \chi_a] \quad (3.2.13)$$

thus

$$\delta E_0 = \sum_a^N [\delta \chi_a | h | \chi_a] + \sum_a^N \sum_b^N ([\delta \chi_a \chi_a | \chi_b \chi_b] - [\delta \chi_a \chi_b | \chi_b \chi_a]) + \text{complex conjugates} \quad (3.2.14)$$

3.2.3 The Canonical HF Equations

3.3 Interpretation of Solutions to the HF Equations

3.3.1 Orbital Energies and Koopmans' Theorem

Ex 3.4

$$f_{ij} = \langle \chi_i | f | \chi_j \rangle = \langle i | h | j \rangle + \sum_b \langle ib || jb \rangle \quad (3.3.1)$$

$$\begin{aligned}f_{ji}^* &= \langle \chi_j | f | \chi_i \rangle^* = \langle j | h | i \rangle^* + \sum_b \langle jb || ib \rangle^* \\ &= \langle i | h | j \rangle + \sum_b \langle ib || jb \rangle \\ &= f_{ij}\end{aligned}\quad (3.3.2)$$

thus the Fock operator is Hermitian.

Ex 3.5

$$\text{IP} = {}^{N-2} E - E_0$$

$$\begin{aligned}&= \sum_{a \neq c, d} \langle a | h | a \rangle + \frac{1}{2} \sum_{a \neq c, d} \sum_{b \neq c, d} \langle ab || ab \rangle - \left[\sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_a \sum_b \langle ab || ab \rangle \right] \\ &= -\langle c | h | c \rangle - \langle d | h | d \rangle - \frac{1}{2} \sum_{a \neq c, d} \langle ac || ac \rangle - \frac{1}{2} \sum_{a \neq c, d} \langle ad || ad \rangle - \frac{1}{2} \sum_{b \neq c, d} \langle cb || cb \rangle - \frac{1}{2} \sum_{b \neq c, d} \langle db || db \rangle - \langle cd || cd \rangle \\ &= -\langle c | h | c \rangle - \langle d | h | d \rangle - \sum_{a \neq c, d} \langle ac || ac \rangle - \sum_{a \neq c, d} \langle ad || ad \rangle - \langle cd || cd \rangle \\ &= -\langle c | h | c \rangle - \langle d | h | d \rangle - \left(\sum_{a \neq c} \langle ac || ac \rangle - \langle dc || dc \rangle \right) - \left(\sum_{a \neq d} \langle ad || ad \rangle - \langle cd || cd \rangle \right) - \langle cd || cd \rangle \\ &= -\varepsilon_c - \varepsilon_d + \langle cd || cd \rangle - \langle cd || dc \rangle\end{aligned}\quad (3.3.3)$$

Ex 3.6

$$\begin{aligned}
{}^N E_0 - {}^{N+1} E^r &= \sum_a \langle a | h | a \rangle + \frac{1}{2} \sum_a \sum_b \langle ab || ab \rangle \\
&\quad - \left[\sum_a \langle a | h | a \rangle + \langle r | h | r \rangle + \frac{1}{2} \sum_a \sum_b \langle ab || ab \rangle + \frac{1}{2} \sum_b \langle rb || rb \rangle + \frac{1}{2} \sum_a \langle ar || ar \rangle \right] \\
&= - \langle r | h | r \rangle - \frac{1}{2} \sum_b \langle rb || rb \rangle - \frac{1}{2} \sum_b \langle br || br \rangle \\
&= - \langle r | h | r \rangle - \sum_b \langle rb || rb \rangle
\end{aligned} \tag{3.3.4}$$

3.3.2 Brillouin's Theorem

3.3.3 The HF Hamiltonian

Ex 3.7 Suppose \mathcal{H}_0 commutes with \mathcal{P}_n ,

$$\begin{aligned}
\mathcal{H}_0 |\Psi_0\rangle &= \mathcal{H}_0 \frac{1}{\sqrt{N!}} \sum_n (-1)^{p_n} \mathcal{P}_n \left\{ \sum_i^N f(i) \chi_j(1) \cdots \chi_k(N) \right\} \\
&= \frac{1}{\sqrt{N!}} \sum_n (-1)^{p_n} \mathcal{P}_n \{ (\varepsilon_j + \cdots + \varepsilon_k) \chi_j(1) \cdots \chi_k(N) \} \\
&= \sum_a \varepsilon_a
\end{aligned} \tag{3.3.5}$$

Now we show \mathcal{H}_0 commutes with \mathcal{P}_n , for example, \mathcal{P}_{ab}

$$\mathcal{P}_{ab} \mathcal{H}_0 = \mathcal{P}_{ab} (\cdots + f(a) + \cdots + f(b) + \cdots) = (\cdots + f(b) + \cdots + f(a) + \cdots) \mathcal{P}_{ab} = \mathcal{H}_0 \mathcal{P}_{ab} \tag{3.3.6}$$

Ex 3.8

$$\mathcal{V} = \sum_i^N \sum_{j>i}^N \mathcal{O}_2 - \sum_i^N \sum_b^N [\mathcal{G}_b(i) - \mathcal{K}_b(i)] \tag{3.3.7}$$

thus

$$\begin{aligned}
\langle \Psi_0 | \mathcal{V} | \Psi_0 \rangle &= \sum_i^N \sum_{j>i}^N \langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle - \sum_i^N \sum_b^N [\langle \Psi_0 | \mathcal{G}_b(i) - \mathcal{K}_b(i) | \Psi_0 \rangle] \\
&= \frac{1}{2} \sum_a^N \sum_b^N \langle ab || ab \rangle - \sum_i^N \sum_b^N [\langle ib | ib \rangle - \langle ib | bi \rangle] \\
&= -\frac{1}{2} \sum_a^N \sum_b^N \langle ab || ab \rangle
\end{aligned} \tag{3.3.8}$$

3.4 Restricted Closed-shell HF: The Roothaan Equations

3.4.1 Closed-shell HF: Restricted Spin Orbitals

Ex 3.9

$$\begin{aligned}
\varepsilon_i &= (i|h|i) + \sum_b^N (\langle ib | ib \rangle - \langle ib | bi \rangle) \\
&= (i|h|i) + \sum_c^{N/2} (\langle ic | ic \rangle - \langle ic | ci \rangle) + \sum_{\bar{c}}^{N/2} (\langle i\bar{c} | i\bar{c} \rangle - \langle i\bar{c} | \bar{c}i \rangle)
\end{aligned} \tag{3.4.1}$$

Assume χ_j has α spin, since assuming α or β is identical

$$\begin{aligned}
\varepsilon_i &= (i|h|i) + \sum_c^{N/2} [(ic|ic) \langle \alpha | \alpha \rangle \langle \alpha | \alpha \rangle - (ic|ci) \langle \alpha | \alpha \rangle \langle \alpha | \alpha \rangle] + \sum_c^{N/2} [(ic|ic) \langle \alpha | \alpha \rangle \langle \beta | \beta \rangle - (ic|ci) \langle \alpha | \beta \rangle \langle \beta | \alpha \rangle] \\
&= (i|h|i) + \sum_c^{N/2} [2(ic|ic) - (ic|ci)] \\
&= (i|h|i) + \sum_n^{N/2} (2J_{ib} - K_{ib})
\end{aligned} \tag{3.4.2}$$

3.4.2 Introduction of a Basis: The Roothaan Equations

Ex 3.10

$$\begin{aligned}
(\mathbf{C}^\dagger \mathbf{S} \mathbf{C})_{\mu\nu} &= \sum_i \sum_j C_{\mu i}^\dagger S_{ij} C_{j\nu} \\
&= \sum_i \sum_j C_{i\mu}^* \langle \phi_i | \phi_j \rangle C_{j\nu} \\
&= \langle \phi_\mu | \phi_\nu \rangle \\
&= \delta_{\mu\nu}
\end{aligned} \tag{3.4.3}$$

thus

$$\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1} \tag{3.4.4}$$

3.4.3 The Charge Density

Ex 3.11

$$\begin{aligned}
\rho(\mathbf{r}) &= \langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \\
&= \sum_i^N \frac{1}{N!} \sum_I^{N!} \sum_J^{N!} (-1)^{p_I} (-1)^{p_J} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \hat{\mathcal{P}}_I \{ \chi_1(1) \cdots \chi_N(N) \}^* \delta(\mathbf{r}_i - \mathbf{r}) \hat{\mathcal{P}}_J \{ \chi_1(1) \cdots \chi_N(N) \}
\end{aligned} \tag{3.4.5}$$

Since $\{\chi_m\}$ are orthogonal,

$$\begin{aligned}
\rho(\mathbf{r}) &= \sum_i^N \frac{1}{N!} \sum_I^{N!} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \hat{\mathcal{P}}_I \{ \chi_1(1) \cdots \chi_N(N) \}^* \delta(\mathbf{r}_i - \mathbf{r}) \hat{\mathcal{P}}_I \{ \chi_1(1) \cdots \chi_N(N) \} \\
&= \sum_i^N \frac{1}{N!} (N-1)! \sum_s^N \int d\mathbf{x}_i \chi_s^*(\mathbf{x}_i) \delta(\mathbf{r}_i - \mathbf{r}) \chi_s(\mathbf{x}_i) \\
&= \sum_i^N \frac{1}{N} \cdot 2 \sum_s^{N/2} \int d\mathbf{r}_i \phi_s(\mathbf{r}_i) \delta(\mathbf{r}_i - \mathbf{r}) \phi_s(\mathbf{r}_i) \\
&= \sum_i^N \frac{2}{N} \sum_s^{N/2} \phi_s(\mathbf{r}) \phi_s(\mathbf{r}) \\
&= N \frac{2}{N} \sum_s^{N/2} \phi_s(\mathbf{r}) \phi_s(\mathbf{r}) \\
&= 2 \sum_s^{N/2} \phi_s(\mathbf{r}) \phi_s(\mathbf{r})
\end{aligned} \tag{3.4.6}$$

Ex 3.12 From Ex 3.10, we have

$$\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{1} \tag{3.4.7}$$

i.e.

$$\sum_i^K \sum_j^K C_{i\mu}^* S_{ij} C_{j\nu} = \delta_{\mu\nu} \quad (3.4.8)$$

thus

$$\begin{aligned} (\mathbf{PSP})_{\mu\sigma} &= \sum_{\nu}^K \sum_{\lambda}^K P_{\mu\nu} S_{\nu\lambda} P_{\lambda\sigma} \\ &= 4 \sum_{\nu}^K \sum_{\lambda}^K \sum_a^{N/2} C_{\mu a} C_{\nu a}^* S_{\nu\lambda} \sum_b^{N/2} C_{\lambda b} C_{\sigma b}^* \\ &= 4 \sum_a^{N/2} \sum_b^{N/2} C_{\mu a} \left(\sum_{\nu}^K \sum_{\lambda}^K C_{\nu a}^* S_{\nu\lambda} C_{\lambda b} \right) C_{\sigma b}^* \\ &= 4 \sum_a^{N/2} \sum_b^{N/2} C_{\mu a} \delta_{ab} C_{\sigma b}^* \\ &= 4 \sum_a^{N/2} C_{\mu a} C_{\sigma a}^* \\ &= 2P_{\mu\sigma} \end{aligned} \quad (3.4.9)$$

thus

$$\mathbf{PSP} = 2\mathbf{P} \quad (3.4.10)$$

Ex 3.13 Eq. 3.122 shows

$$f(\mathbf{r}_1) = h(\mathbf{r}_1) + \sum_a^{N/2} \int d\mathbf{r}_2 \psi_a^*(\mathbf{r}_2) (2 - \hat{\mathcal{P}}_{12}) r_{12}^{-1} \psi_a(\mathbf{r}_2) \quad (3.4.11)$$

thus

$$\begin{aligned} f(\mathbf{r}_1) &= h(\mathbf{r}_1) + \sum_a^{N/2} \int d\mathbf{r}_2 \sum_{\sigma} C_{\sigma a}^* \phi_{\sigma}^*(\mathbf{r}_2) (2 - \hat{\mathcal{P}}_{12}) r_{12}^{-1} \sum_{\lambda} C_{\lambda a} \phi_{\lambda}(\mathbf{r}_2) \\ &= h(\mathbf{r}_1) + \sum_{\sigma} \sum_{\lambda} \left(\sum_a^{N/2} C_{\sigma a}^* C_{\lambda a} \right) \int d\mathbf{r}_2 \phi_{\sigma}^*(\mathbf{r}_2) (2 - \hat{\mathcal{P}}_{12}) r_{12}^{-1} \phi_{\lambda}(\mathbf{r}_2) \\ &= h(\mathbf{r}_1) + \frac{1}{2} \sum_{\sigma, \lambda} P_{\lambda\sigma} \int d\mathbf{r}_2 \phi_{\sigma}^*(\mathbf{r}_2) (2 - \hat{\mathcal{P}}_{12}) r_{12}^{-1} \phi_{\lambda}(\mathbf{r}_2) \end{aligned} \quad (3.4.12)$$

3.4.4 Expression for the Fock Matrix

Ex 3.14 In expression $(\mu\nu|\lambda\sigma)$, there are three interchangeable pairs, i.e. $\mu \leftrightarrow \nu$, $\lambda \leftrightarrow \sigma$, and $\mu\nu \leftrightarrow \lambda\sigma$. Thus $(\mu\nu|\lambda\sigma)$ has an 8-fold symmetry. Similarly, $(\mu\mu|\lambda\sigma)$, $(\mu\nu|\mu\lambda)$, $(\mu\nu|\mu\nu)$, $(\mu\mu|\sigma\sigma)$ has 2-fold symmetry, and $(\mu\mu|\mu\nu)$, $(\mu\mu|\mu\mu)$ has 1-fold symmetry.

Therefore, the number of unique 2e integrals is

| expression | number | $K = 100$ |
|--------------------------|----------------------|-----------|
| $(\mu\nu \lambda\sigma)$ | $K(K-1)(K-2)(K-3)/8$ | 11763675 |
| $(\mu\mu \lambda\sigma)$ | $K(K-1)(K-2)/2$ | 485100 |
| $(\mu\nu \mu\lambda)$ | $K(K-1)(K-2)/2$ | 485100 |
| $(\mu\nu \mu\nu)$ | $K(K-1)/2$ | 4950 |
| $(\mu\mu \sigma\sigma)$ | $K(K-1)/2$ | 4950 |
| $(\mu\mu \mu\nu)$ | $K(K-1)$ | 9900 |
| $(\mu\mu \mu\mu)$ | K | 100 |

thus the total number is 12 753 775.

3.4.5 Orthogonalization of the Basis

Ex 3.15 \therefore

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s} \quad (3.4.13)$$

\therefore

$$\mathbf{S} \mathbf{U} = \mathbf{U} \mathbf{s} \quad (3.4.14)$$

i.e.

$$\sum_{\nu} S_{\mu\nu} U_{\nu i} = U_{\mu i} s_i \quad (3.4.15)$$

thus

$$\sum_{\mu} U_{\mu i}^* \sum_{\nu} S_{\mu\nu} U_{\nu i} = \sum_{\mu} U_{\mu i}^* U_{\mu i} s_i \quad (3.4.16)$$

$$\sum_{\mu} \sum_{\nu} U_{\mu i}^* \langle \phi_{\mu} | \phi_{\nu} \rangle U_{\nu i} = s_i \sum_{\mu} |U_{\mu i}|^2 \quad (3.4.17)$$

Suppose

$$\phi'_i = \sum_{\nu} U_{\nu i} \phi_{\nu} \quad (3.4.18)$$

thus

$$\langle \phi'_i | \phi'_i \rangle = s_i \sum_{\mu} |U_{\mu i}|^2 \quad (3.4.19)$$

\therefore

$$\langle \phi'_i | \phi'_i \rangle > 0 \quad |U_{\mu i}|^2 > 0 \quad (3.4.20)$$

\therefore

$$s_i > 0 \quad (3.4.21)$$

Ex 3.16

- (3.174)

Since (ϕ, ϕ', ψ) are row vectors

$$\psi = \phi \mathbf{C} \quad (3.4.22)$$

$$\psi = \phi' \mathbf{C}' = \phi \mathbf{X} \mathbf{C}' \quad (3.4.23)$$

we have

$$\mathbf{C} = \mathbf{X} \mathbf{C}' \quad (3.4.24)$$

i.e.

$$\mathbf{C}' = \mathbf{X}^{-1} \mathbf{C} \quad (3.4.25)$$

- (3.177)

$$\begin{aligned} F'_{\mu\nu} &= \langle \phi'_{\mu} | f | \phi'_{\nu} \rangle \\ &= \left\langle \sum_i \phi_i X_{i\mu} \left| f \right| \sum_j \phi_j X_{j\nu} \right\rangle \\ &= \sum_i \sum_j X_{i\mu}^* X_{j\nu} \langle \phi_i | f | \phi_j \rangle \\ &= \sum_i \sum_j X_{i\mu}^* F_{ij} X_{j\nu} \end{aligned} \quad (3.4.26)$$

i.e.

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} \quad (3.4.27)$$

3.4.6 The SCF Procedure

3.4.7 Expectation Values and Population Analysis

Ex 3.17 From (3.148) in the textbook, we get

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + G_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_a^{N/2} [2(\mu\nu|aa) - (\mu a|a\nu)] \quad (3.4.28)$$

thus

$$\begin{aligned} E_0 &= \sum_a^{N/2} [2h_{aa} + \sum_b^{N/2} (2J_{ab} - K_{ab})] \\ &= 2 \sum_a^{N/2} (a|h|a) + \sum_a^{N/2} \sum_b^{N/2} [2(aa|bb) - (ab|ba)] \\ &= 2 \sum_a^{N/2} \sum_\mu \sum_\nu C_{\mu a}^* C_{\nu a} (\mu|h|\nu) + \sum_a^{N/2} \sum_b^{N/2} \left[2 \sum_\mu \sum_\nu C_{\mu a}^* C_{\nu a} (\mu\nu|bb) - \sum_\mu \sum_\nu C_{\mu a}^* C_{\nu a} (\mu b|b\nu) \right] \\ &= \sum_\mu \sum_\nu P_{\nu\mu} H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_b^{N/2} \sum_\mu \sum_\nu [2P_{\nu\mu} (\mu\nu|bb) - P_{\nu\mu} (\mu b|b\nu)] \\ &= \sum_\mu \sum_\nu P_{\nu\mu} [H_{\mu\nu}^{\text{core}} + \frac{1}{2} G_{\mu\nu}] \\ &= \frac{1}{2} \sum_\mu \sum_\nu P_{\nu\mu} [H_{\mu\nu}^{\text{core}} + F_{\mu\nu}] \end{aligned} \quad (3.4.29)$$

Ex 3.18 For symmetrically orthogonalized basis,

$$\mathbf{C}' = \mathbf{S}^{1/2} \mathbf{C} \quad (3.4.30)$$

thus

$$\begin{aligned} P'_{\mu\nu} &= 2 \sum_a^{N/2} C'_{\mu a} C'^*_{\nu a} \\ &= 2 \sum_a^{N/2} \sum_i S_{\mu i}^{1/2} C_{ia} \sum_j S_{\nu j}^{1/2*} C_{ja}^* \\ &= \sum_i \sum_j S_{\mu i}^{1/2} \left(2 \sum_a^{N/2} C_{ia} C_{ja}^* \right) S_{\nu j}^{1/2*} \\ &= \sum_i \sum_j S_{\mu i}^{1/2} P_{ij} S_{\nu j}^{1/2*} \\ &= \sum_i \sum_j S_{\mu i}^{1/2} P_{ij} S_{j\nu}^{1/2} \end{aligned} \quad (3.4.31)$$

i.e.

$$\mathbf{P}' = \mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2} \quad (3.4.32)$$

thus

$$\sum_\mu (\mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2})_{\mu\mu} = \sum_\mu \mathbf{P}'_{\mu\mu} \quad (3.4.33)$$

3.5 Model Calculations on H₂ and HeH⁺

3.5.1 The 1s Minimal STO-3G Basis Set

Ex 3.19

$$\begin{aligned}
\phi_{1s}^{\text{GF}}(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_{1s}^{\text{GF}}(\alpha, \mathbf{r} - \mathbf{R}_B) &= \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2} \left(\frac{2\beta}{\pi}\right)^{3/4} e^{-\beta|\mathbf{r}-\mathbf{R}_B|^2} \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} e^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2 - \beta|\mathbf{r}-\mathbf{R}_B|^2} \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \exp\left(-\left[(\alpha + \beta)|\mathbf{r}|^2 - 2\mathbf{r} \cdot (\alpha\mathbf{R}_A + \beta\mathbf{R}_B) + \alpha|\mathbf{R}_A|^2 + \beta|\mathbf{R}_B|^2\right]\right)
\end{aligned} \tag{3.5.1}$$

Let

$$p = \alpha + \beta \quad \mathbf{R}_P = \frac{\alpha\mathbf{R}_A + \beta\mathbf{R}_B}{\alpha + \beta} \tag{3.5.2}$$

we have

$$\begin{aligned}
\phi_{1s}^{\text{GF}}(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_{1s}^{\text{GF}}(\alpha, \mathbf{r} - \mathbf{R}_B) &= \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \exp\left(-\left[p|\mathbf{r}|^2 - 2\mathbf{r} \cdot (p\mathbf{R}_P) + \alpha|\mathbf{R}_A|^2 + \beta|\mathbf{R}_B|^2\right]\right) \\
&= \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \exp\left(-\left[p|\mathbf{r} - \mathbf{R}_P|^2 - p|\mathbf{R}_P|^2 + \alpha|\mathbf{R}_A|^2 + \beta|\mathbf{R}_B|^2\right]\right) \\
&= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \left(\frac{2p}{\pi}\right)^{3/4} e^{-p|\mathbf{r}-\mathbf{R}_P|^2} \exp\left(p|\mathbf{R}_P|^2 - \alpha|\mathbf{R}_A|^2 - \beta|\mathbf{R}_B|^2\right)
\end{aligned} \tag{3.5.3}$$

Let

$$\phi_{1s}^{\text{GF}}(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_{1s}^{\text{GF}}(\alpha, \mathbf{r} - \mathbf{R}_B) = K_{AB} \left(\frac{2p}{\pi}\right)^{3/4} e^{-p|\mathbf{r}-\mathbf{R}_P|^2} \tag{3.5.4}$$

thus

$$\begin{aligned}
K_{AB} &= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\left(p|\mathbf{R}_P|^2 - \alpha|\mathbf{R}_A|^2 - \beta|\mathbf{R}_B|^2\right) \\
&= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\left(\frac{1}{p}(\alpha^2|\mathbf{R}_A|^2 + \beta^2|\mathbf{R}_B|^2 + 2\alpha\beta\mathbf{R}_A \cdot \mathbf{R}_B) - \alpha|\mathbf{R}_A|^2 - \beta|\mathbf{R}_B|^2\right) \\
&= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\left(\frac{1}{p}(\alpha^2|\mathbf{R}_A|^2 + \beta^2|\mathbf{R}_B|^2 + 2\alpha\beta\mathbf{R}_A \cdot \mathbf{R}_B - p\alpha|\mathbf{R}_A|^2 - p\beta|\mathbf{R}_B|^2)\right) \\
&= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\left(\frac{1}{p}(-\alpha\beta|\mathbf{R}_A|^2 - \alpha\beta|\mathbf{R}_B|^2 + 2\alpha\beta\mathbf{R}_A \cdot \mathbf{R}_B)\right) \\
&= \left(\frac{2\alpha\beta}{p\pi}\right)^{3/4} \exp\left(-\frac{\alpha\beta}{p}|\mathbf{R}_A - \mathbf{R}_B|^2\right)
\end{aligned} \tag{3.5.5}$$

Ex 3.20 At $r = 0$,

$$\phi_{1s}^{\text{CGF}}(\zeta = 1.0, \text{STO-1G}) = 0.267\,656 \tag{3.5.6}$$

$$\phi_{1s}^{\text{CGF}}(\zeta = 1.0, \text{STO-2G}) = 0.389\,383 \tag{3.5.7}$$

$$\phi_{1s}^{\text{CGF}}(\zeta = 1.0, \text{STO-3G}) = 0.454\,986 \tag{3.5.8}$$

while

$$\phi_{1s}^{\text{SF}}(\zeta = 1.0) = \frac{1}{\sqrt{\pi}} = 0.564\,19 \tag{3.5.9}$$

3.5.2 STO-3G H₂

Ex 3.21

$$\phi_{1s}^{\text{CGF}}(\zeta = 1.0, \text{STO-1G}) = \phi_{1s}^{\text{GF}}(0.270\,950) \quad (3.5.10)$$

Since $\alpha = \alpha_{(\zeta=1.0)} \times \zeta^2$,

$$\phi_{1s}^{\text{CGF}}(\zeta = 1.24, \text{STO-1G}) = \phi_{1s}^{\text{GF}}(0.416\,613) \quad (3.5.11)$$

thus

$$\begin{aligned} S_{12} &= K_{AB} \left(\frac{2 \cdot 2\alpha}{\pi} \right)^{3/4} \int d\mathbf{r} e^{-2\alpha|\mathbf{r}-\mathbf{R}_P|^2} \\ &= \left(\frac{2\alpha}{2\pi} \right)^{3/4} e^{-\frac{\alpha}{2}R^2} \left(\frac{2 \cdot 2\alpha}{\pi} \right)^{3/4} \int d\mathbf{r} e^{-2\alpha|\mathbf{r}-\mathbf{R}_A|^2} \\ &= \left(\frac{2\alpha}{\pi} \right)^{3/2} e^{-\frac{\alpha}{2}R^2} 4\pi \int dr r^2 e^{-2\alpha r^2} \\ &= \left(\frac{2\alpha}{\pi} \right)^{3/2} e^{-\frac{\alpha}{2}R^2} 4\pi \frac{\sqrt{\pi}}{8\sqrt{2}\alpha^{3/2}} \\ &= e^{-\frac{\alpha}{2}R^2} \end{aligned} \quad (3.5.12)$$

At $R = 1.4, \alpha = 0.416\,613$,

$$S_{12} = 0.6648 \quad (3.5.13)$$

Ex 3.22 Let

$$\psi_1 = c_1(\phi_1 + \phi_2) \quad \psi_2 = c_2(\phi_1 - \phi_2) \quad (3.5.14)$$

$$\begin{aligned} 1 &= \langle \phi_1 | \psi_1 \rangle = c_1^2(S_{11} + S_{12} + S_{21} + S_{22}) \\ &= c_1^2(2 + 2S_{12}) \end{aligned} \quad (3.5.15)$$

\therefore

$$c_1 = [2(1 + S_{12})]^{-1/2} \quad (3.5.16)$$

$$\begin{aligned} 1 &= \langle \phi_2 | \psi_2 \rangle = c_2^2(S_{11} - S_{12} - S_{21} + S_{22}) \\ &= c_2^2(2 - 2S_{12}) \end{aligned} \quad (3.5.17)$$

\therefore

$$c_2 = [2(1 - S_{12})]^{-1/2} \quad (3.5.18)$$

Ex 3.23 Suppose

$$\psi_1 = c_1(\phi_1 + \phi_2) \quad \psi_2 = c_2(\phi_1 - \phi_2) \quad (3.5.19)$$

thus

$$\mathbf{H}^{\text{core}} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\varepsilon} \quad (3.5.20)$$

$$\begin{pmatrix} H_{11}^{\text{core}} & H_{12}^{\text{core}} \\ H_{21}^{\text{core}} & H_{22}^{\text{core}} \end{pmatrix} \begin{pmatrix} c_1 & c_2 \\ c_1 & -c_2 \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} c_1 & c_2 \\ c_1 & -c_2 \end{pmatrix} \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} \quad (3.5.21)$$

$$\begin{pmatrix} (H_{11}^{\text{core}} + H_{12}^{\text{core}})c_1 & (H_{11}^{\text{core}} - H_{12}^{\text{core}})c_2 \\ (H_{21}^{\text{core}} + H_{22}^{\text{core}})c_1 & (H_{21}^{\text{core}} - H_{22}^{\text{core}})c_2 \end{pmatrix} = \begin{pmatrix} (S_{11} + S_{12})c_1\varepsilon_1 & (S_{11} - S_{12})c_2\varepsilon_2 \\ (S_{21} + S_{22})c_1\varepsilon_1 & (S_{21} - S_{22})c_2\varepsilon_2 \end{pmatrix} \quad (3.5.22)$$

\therefore

$$\begin{cases} \varepsilon_1 = (H_{11}^{\text{core}} + H_{12}^{\text{core}})/(1 + S_{12}) \\ \varepsilon_2 = (H_{11}^{\text{core}} - H_{12}^{\text{core}})/(1 - S_{12}) \end{cases} \quad (3.5.23)$$

$$\varepsilon_1 = (-1.1204 - 0.9584)/(1 + 0.6593) = -1.2528 \quad (3.5.24)$$

$$\varepsilon_2 = (-1.1204 + 0.9584)/(1 - 0.6593) = -0.4755 \quad (3.5.25)$$

Ex 3.24

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^* = 2 C_{\mu 1} C_{\nu 1}^* \quad (3.5.26)$$

\therefore

$$\begin{aligned} \mathbf{P} &= 2 \begin{pmatrix} C_{11} C_{11}^* & C_{11} C_{21}^* \\ C_{21} C_{11}^* & C_{21} C_{21}^* \end{pmatrix} \\ &= 2 \begin{pmatrix} [2(1+S_{12})]^{-1/2} [2(1+S_{12})]^{-1/2} & [2(1+S_{12})]^{-1/2} [2(1+S_{12})]^{-1/2} \\ [2(1+S_{12})]^{-1/2} [2(1+S_{12})]^{-1/2} & [2(1+S_{12})]^{-1/2} [2(1+S_{12})]^{-1/2} \end{pmatrix} \\ &= (1+S_{12})^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \end{aligned} \quad (3.5.27)$$

For H_2^+ ,

$$\mathbf{P}_{\text{H}_2^+} = \frac{1}{2} (1+S_{12})^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad (3.5.28)$$

Ex 3.25

$$\begin{aligned} F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu|\sigma\lambda) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right] \\ &= H_{\mu\nu}^{\text{core}} + (1+S_{12})^{-1} \sum_{\lambda\sigma} \left[(\mu\nu|\sigma\lambda) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right] \end{aligned} \quad (3.5.29)$$

\therefore

$$\begin{aligned} F_{11} &= H_{11}^{\text{core}} + (1+S_{12})^{-1} \left[(11|11) - \frac{1}{2} (11|11) + (11|21) - \frac{1}{2} (11|21) + (11|12) - \frac{1}{2} (12|11) + (11|22) - \frac{1}{2} (12|21) \right] \\ &= H_{11}^{\text{core}} + (1+S_{12})^{-1} \left[\frac{1}{2} (11|11) + (11|21) + (11|22) - \frac{1}{2} (12|21) \right] \end{aligned} \quad (3.5.30)$$

Ex 3.26

Ex 3.27

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

Ex 3.28

$$\begin{aligned} \mathbf{X}_{\text{Schmidt}}^\dagger \mathbf{S} \mathbf{X}_{\text{Schmidt}} &= \begin{pmatrix} 1 & 0 \\ -S_{12}/\sqrt{1-S_{12}^2} & 1/\sqrt{1-S_{12}^2} \end{pmatrix} \begin{pmatrix} 1 & S_{12} \\ S_{12} & 1 \end{pmatrix} \begin{pmatrix} 1 & -S_{12}/\sqrt{1-S_{12}^2} \\ 0 & 1/\sqrt{1-S_{12}^2} \end{pmatrix} \\ &= \begin{pmatrix} 1 & S_{12} \\ 0 & \sqrt{1-S_{12}^2} \end{pmatrix} \begin{pmatrix} 1 & -S_{12}/\sqrt{1-S_{12}^2} \\ 0 & 1/\sqrt{1-S_{12}^2} \end{pmatrix} \\ &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{aligned} \quad (3.5.31)$$

thus the Schmidt transformation produces orthonormal basis.

Ex 3.29

$$E_0(R \rightarrow \infty) = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\nu\mu}(R \rightarrow \infty) [2H_{\mu\nu}^{\text{core}} + G_{\mu\nu}] \quad (3.5.32)$$

where

$$P_{\nu\mu}(R \rightarrow \infty) = \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix} \quad (3.5.33)$$

$$\begin{aligned}
G_{\mu\nu} &= \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma}(R \rightarrow \infty) \left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu) \right] \\
&= 2 \left[(\mu\nu|\phi_1\phi_1) - \frac{1}{2}(\mu\phi_1|\phi_1\nu) \right]
\end{aligned} \tag{3.5.34}$$

thus

$$\begin{aligned}
E_0(R \rightarrow \infty) &= \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\nu\mu}(R \rightarrow \infty) [2H_{\mu\nu}^{\text{core}} + G_{\mu\nu}] \\
&= \frac{1}{2} \times 2 [2H_{11}^{\text{core}} + G_{11}] \\
&= 2(T_{11} + V_{11}^1) + 2 \left[(\phi_1\phi_1|\phi_1\phi_1) - \frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1) \right] \\
&= 2T_{11} + 2V_{11}^1 + (\phi_1\phi_1|\phi_1\phi_1)
\end{aligned} \tag{3.5.35}$$

3.6 Polyatomic Basis Sets

3.6.1 Contracted Gaussian Functions

3.6.2 Minimal Basis Sets: STO-3G

3.6.3 Double Zeta Basis Sets: 4-31G

Ex 3.30 The outer basis function

$$\phi_{1s}''(\mathbf{r}) = g_{1s}(0.298073, \mathbf{r}) \tag{3.6.1}$$

The inner basis function

$$\phi_{1s}'(\mathbf{r}) = N[0.46954g_{1s}(1.242567, \mathbf{r}) + 0.15457g_{1s}(5.782948, \mathbf{r}) + 0.02373g_{1s}(38.47497, \mathbf{r})] \tag{3.6.2}$$

Renormalize it, we get

$$N = 1.689 \tag{3.6.3}$$

thus

$$\phi_{1s}'(\mathbf{r}) = 0.79330g_{1s}(1.242567, \mathbf{r}) + 0.26115g_{1s}(5.782948, \mathbf{r}) + 0.04009g_{1s}(38.47497, \mathbf{r}) \tag{3.6.4}$$

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

Ex 3.31

| | C | H | total |
|---------------------|----|---|-------|
| STO-3G | 5 | 1 | 36 |
| 4-31G | 9 | 2 | 66 |
| 6-31G* (Cartesian) | 15 | 2 | 102 |
| 6-31G** (Cartesian) | 15 | 5 | 120 |

3.7 Some Illustrative Closed-shell Calculations

3.7.1 Total Energies

Ex 3.32

Reaction I

| basis | $\Delta E / \text{a.u.}$ | $\Delta E / (\text{kcal/mol})$ | |
|----------|--------------------------|--------------------------------|----------|
| STO-3G | -0.061 | -38.28 | exoergic |
| 4-31G | -0.069 | -43.30 | |
| 6-31G* | -0.045 | -28.24 | |
| 6-31G** | -0.055 | -34.51 | |
| HF-limit | -0.051 | -32.00 | |

Reaction II

| basis | $\Delta E/$ a.u. | $\Delta E/(\text{kcal/mol})$ | |
|----------|------------------|------------------------------|-----------|
| STO-3G | 0.186 | 116.72 | endoergic |
| 4-31G | -0.114 | -71.54 | exoergic |
| 6-31G* | -0.088 | -55.22 | |
| 6-31G** | -0.095 | -59.61 | |
| HF-limit | -0.097 | -60.87 | |

The contribution of zero-point vibrations to the energy change of reaction I would be -0.37 kcal/mol, to the energy change of reaction II would be 17.78 kcal/mol. Thus the effect of zero-point vibrations should not be ignored.

3.7.2 Ionization Potentials

3.7.3 Equilibrium Geometries

3.7.4 Population Analysis and Dipole Moments

3.8 Unrestricted Open-shell HF: The Pople-Nesbet Equations

3.8.1 Open-shell HF: Unrestricted Spin Orbitals

Ex 3.33

$$\begin{aligned}
f^\alpha(1) &= \int d\omega_1 \alpha^*(\omega_1) \left[h(1) + \sum_a \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} (1 - \hat{\mathcal{P}}_{12}) \chi_a(2) \right] \alpha(\omega_1) \\
&= h(1) + \sum_a^{N_\alpha} \left[\int d\omega_1 \alpha^*(\omega_1) \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} \chi_a(2) \alpha(\omega_1) - \int d\omega_1 \alpha^*(\omega_1) \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} \chi_a(1) \alpha(\omega_2) \right] \\
&\quad + \sum_a^{N_\beta} \left[\int d\omega_1 \alpha^*(\omega_1) \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} \chi_a(2) \alpha(\omega_1) - \int d\omega_1 \alpha^*(\omega_1) \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} \chi_a(1) \alpha(\omega_2) \right] \\
&= h(1) + \sum_a^{N_\alpha} \left[\int d\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\alpha(\mathbf{r}_2) - \int d\mathbf{r}_2 \int d\omega_2 \int d\omega_1 \alpha^*(\omega_1) \alpha^*(\omega_2) \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\alpha(\mathbf{r}_1) \alpha(\omega_1) \alpha(\omega_2) \right] \\
&\quad + \sum_a^{N_\beta} \left[\int d\mathbf{r}_2 \psi_a^{\beta*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\beta(\mathbf{r}_2) - \int d\mathbf{r}_2 \int d\omega_2 \int d\omega_1 \alpha^*(\omega_1) \beta^*(\omega_2) \psi_a^{\beta*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\beta(\mathbf{r}_1) \beta(\omega_1) \alpha(\omega_2) \right] \\
&= h(1) + \sum_a^{N_\alpha} \left[\int d\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\alpha(\mathbf{r}_2) - \int d\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\alpha(\mathbf{r}_1) \right] + \sum_a^{N_\beta} \left[\int d\mathbf{r}_2 \psi_a^{\beta*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\beta(\mathbf{r}_2) - 0 \right] \\
&= h(1) + \sum_a^{N_\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N_\beta} J_a^\beta(1) \tag{3.8.1}
\end{aligned}$$

Ex 3.34

$$\begin{aligned}
E_0 &= \sum_a h_{aa} + \frac{1}{2} \sum_a^{N_\alpha} \sum_b^{N_\alpha} (J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \sum_a^{N_\alpha} \sum_b^{N_\beta} J_{ab}^{\alpha\beta} \\
&= h_{11}^\alpha + h_{22}^\alpha + h_{11}^\alpha + J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha} + J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta} \tag{3.8.2}
\end{aligned}$$

Ex 3.35

$$\begin{aligned}
\varepsilon_i^\alpha &= (\psi_i^\alpha(1) | h(1) + \sum_a^{N_\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N_\beta} J_a^{\beta\alpha}(1) | \psi_i^\alpha(1)) \\
&= h_{ii}^\alpha + \sum_a^{N_\alpha} [J_{ia}^{\alpha\alpha} - K_{ia}^{\alpha\alpha}] + \sum_a^{N_\beta} J_{ia}^{\alpha\beta} \tag{3.8.3}
\end{aligned}$$

$$\begin{aligned}
\varepsilon_i^\beta &= (\psi_i^\beta(1)|h(1) + \sum_a^{N_\alpha} [J_a^\beta(1) - K_a^\beta(1)] + \sum_a^{N_\beta} J_a^\alpha(1)|\psi_i^\beta(1)) \\
&= h_{ii}^\beta + \sum_a^{N_\alpha} [J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta}] + \sum_a^{N_\beta} J_{ia}^{\beta\alpha}
\end{aligned} \tag{3.8.4}$$

Since

$$E_0 = \sum_a h_{aa} + \frac{1}{2} \sum_a^{N_\alpha} \sum_b^{N_\alpha} (J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \frac{1}{2} \sum_a^{N_\beta} \sum_b^{N_\beta} (J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}) + \sum_a^{N_\alpha} \sum_b^{N_\beta} J_{ab}^{\alpha\beta} \tag{3.8.5}$$

we have

$$E_0 = \sum_i^{N_\alpha} \varepsilon_i^\alpha + \sum_i^{N_\beta} \varepsilon_i^\beta - \frac{1}{2} \sum_i^{N_\alpha} \sum_a^{N_\alpha} (J_{ia}^{\alpha\alpha} - K_{ia}^{\alpha\alpha}) - \frac{1}{2} \sum_i^{N_\beta} \sum_a^{N_\beta} (J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta}) - \sum_i^{N_\beta} \sum_a^{N_\alpha} J_{ia}^{\beta\alpha} \tag{3.8.6}$$

3.8.2 Introduction of a Basis: The Pople-Nesbet Equations

3.8.3 Unrestricted Density Matrices

Ex 3.36

$$\int d\mathbf{r} \rho^S(\mathbf{r}) = \int d\mathbf{r} [\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})] \tag{3.8.7}$$

$$= N_\alpha - N_\beta \tag{3.8.8}$$

Since

$$\langle \hat{\mathcal{J}}_z \rangle = \frac{1}{2} (N_\alpha - N_\beta) \tag{3.8.9}$$

we get

$$\int d\mathbf{r} \rho^S(\mathbf{r}) = 2 \langle \hat{\mathcal{J}}_z \rangle \tag{3.8.10}$$

Ex 3.37

$$\begin{aligned}
\rho^\alpha(\mathbf{r}) &= \sum_a^{N_\alpha} \psi_a^{\alpha*}(\mathbf{r}) \psi_a^\alpha(\mathbf{r}) \\
&= \sum_a^{N_\alpha} \sum_\nu C_{\nu a}^{\alpha*} \phi_\nu^*(\mathbf{r}) \sum_\mu C_{\mu a}^\alpha \phi_\mu(\mathbf{r}) \\
&= \sum_\nu \sum_\mu \left[\sum_a^{N_\alpha} C_{\nu a}^{\alpha*} C_{\mu a}^\alpha \right] \phi_\nu^*(\mathbf{r}) \phi_\mu(\mathbf{r})
\end{aligned} \tag{3.8.11}$$

Let

$$P_{\mu\nu}^\alpha = \sum_a^{N_\alpha} C_{\nu a}^{\alpha*} C_{\mu a}^\alpha \tag{3.8.12}$$

thus

$$\rho^\alpha(\mathbf{r}) = \sum_\nu \sum_\mu P_{\mu\nu}^\alpha \phi_\mu(\mathbf{r}) \phi_\nu^*(\mathbf{r}) \tag{3.8.13}$$

The formulation for β spin is similar.

Ex 3.38

$$\begin{aligned}
\langle \mathcal{O}_1 \rangle &= \sum_i^N \langle \chi_i | h | \chi_i \rangle \\
&= \sum_i^{N_\alpha} (\psi_i^\alpha | h | \psi_i^\alpha) + \sum_i^{N_\beta} (\psi_i^\beta | h | \psi_i^\beta) \\
&= \sum_i^{N_\alpha} \sum_\nu \sum_\mu C_{\nu a}^{\alpha*} (\phi_\nu | h | \phi_\mu) C_{\mu a}^\alpha + \sum_i^{N_\beta} \sum_\nu \sum_\mu C_{\nu a}^{\beta*} (\phi_\nu | h | \phi_\mu) C_{\mu a}^\beta \\
&= \sum_\nu \sum_\mu P_{\mu\nu}^\alpha (\phi_\nu | h | \phi_\mu) + \sum_\nu \sum_\mu P_{\mu\nu}^\beta (\phi_\nu | h | \phi_\mu) \\
&= \sum_\nu \sum_\mu P_{\mu\nu}^T (\phi_\nu | h | \phi_\mu)
\end{aligned} \tag{3.8.14}$$

Ex 3.39

$$\begin{aligned}
\langle \hat{\rho}^S \rangle &= \langle \Psi_0 | \hat{\rho}^S | \Psi_0 \rangle \\
&= \frac{1}{N!} \sum_{i,j}^{N!} (-1)^{p_i} (-1)^{p_j} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \hat{\mathcal{P}}_i \{ \chi_1(1) \cdots \chi_N(N) \} \sum_m^N 2\delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \hat{\mathcal{P}}_j \{ \chi_1(1) \cdots \chi_N(N) \} \\
&= \frac{2}{N!} \sum_i^{N!} \sum_m^N \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \hat{\mathcal{P}}_i \{ \chi_1(1) \cdots \chi_N(N) \} \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \hat{\mathcal{P}}_i \{ \chi_1(1) \cdots \chi_N(N) \} \\
&= \frac{2}{N} \sum_s^N \sum_m^N \int d\mathbf{x}_m \chi_s^*(m) \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \chi_s(m) \\
&= \frac{2}{N} \sum_m^N \left[\sum_s^{N_\alpha} \int d\mathbf{r}_m \psi_s^{\alpha*}(m) \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \psi_s^\alpha(m) + \sum_s^{N_\beta} \int d\mathbf{r}_m \psi_s^{\beta*}(m) \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \psi_s^\beta(m) \right] \\
&= \frac{2}{N} \sum_m^N \left[\frac{1}{2} \sum_s^{N_\alpha} \int d\mathbf{r}_m \psi_s^{\alpha*}(m) \delta(\mathbf{r}_m - \mathbf{R}) \psi_s^\alpha(m) - \frac{1}{2} \sum_s^{N_\beta} \int d\mathbf{r}_m \psi_s^{\beta*}(m) \delta(\mathbf{r}_m - \mathbf{R}) \psi_s^\beta(m) \right] \\
&= \frac{2}{N} N \left[\frac{1}{2} \sum_s^{N_\alpha} \psi_s^{\alpha*}(\mathbf{R}) \psi_s^\alpha(\mathbf{R}) - \frac{1}{2} \sum_s^{N_\beta} \psi_s^{\beta*}(\mathbf{R}) \psi_s^\beta(\mathbf{R}) \right] \\
&= 2 \left[\frac{1}{2} \rho^\alpha(\mathbf{R}) - \frac{1}{2} \rho^\beta(\mathbf{R}) \right] \\
&= \rho^S(\mathbf{R})
\end{aligned} \tag{3.8.15}$$

where

$$\begin{aligned}
\rho^S(\mathbf{R}) &= \sum_\nu \sum_\mu P_{\nu\mu}^S \phi_\mu^*(\mathbf{R}) \phi_\nu(\mathbf{R}) \\
&= \sum_\nu (\mathbf{P}^S \mathbf{A})_{\nu\nu} \\
&= \text{tr}(\mathbf{P}^S \mathbf{A})
\end{aligned} \tag{3.8.16}$$

3.8.4 Expression for the Fock Matrices

3.8.5 Solution of the Unrestricted SCF Equations

Ex 3.40

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

$$\begin{aligned}
&= \sum_{\mu} \sum_{\nu} P_{\nu\mu}^{\alpha} H_{\mu\nu}^{\text{core}} + \sum_{\mu} \sum_{\nu} P_{\nu\mu}^{\beta} H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} P_{\nu\mu}^{\alpha} P_{\sigma\lambda}^{\alpha} [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] \\
&\quad + \frac{1}{2} \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} P_{\nu\mu}^{\beta} P_{\sigma\lambda}^{\beta} [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] + \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} P_{\nu\mu}^{\alpha} P_{\sigma\lambda}^{\beta} (\mu\nu|\lambda\sigma) \\
&= \sum_{\mu} \sum_{\nu} P_{\nu\mu}^{\alpha} \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\lambda} \sum_{\sigma} P_{\sigma\lambda}^{\alpha} [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] + \frac{1}{2} \sum_{\lambda} \sum_{\sigma} P_{\sigma\lambda}^{\beta} (\mu\nu|\lambda\sigma) \right\} \\
&\quad + \sum_{\mu} \sum_{\nu} P_{\nu\mu}^{\beta} \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\lambda} \sum_{\sigma} P_{\sigma\lambda}^{\beta} [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] + \frac{1}{2} \sum_{\lambda} \sum_{\sigma} P_{\sigma\lambda}^{\alpha} (\mu\nu|\lambda\sigma) \right\} \\
&= \sum_{\mu} \sum_{\nu} P_{\nu\mu}^{\alpha} \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\lambda} \sum_{\sigma} [P_{\sigma\lambda}^T (\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\alpha} (\mu\sigma|\lambda\nu)] \right\} \\
&\quad + \sum_{\mu} \sum_{\nu} P_{\nu\mu}^{\beta} \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\lambda} \sum_{\sigma} [P_{\sigma\lambda}^T (\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^{\beta} (\mu\sigma|\lambda\nu)] \right\}
\end{aligned} \tag{3.8.17}$$

while

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda} \sum_{\sigma} [P_{\lambda\sigma}^T (\mu\nu|\sigma\lambda) - P_{\lambda\sigma}^{\alpha} (\mu\lambda|\sigma\nu)] \tag{3.8.18}$$

$$F_{\mu\nu}^{\beta} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda} \sum_{\sigma} [P_{\lambda\sigma}^T (\mu\nu|\sigma\lambda) - P_{\lambda\sigma}^{\beta} (\mu\lambda|\sigma\nu)] \tag{3.8.19}$$

thus

$$\begin{aligned}
E_0 &= \sum_{\mu} \sum_{\nu} \left\{ P_{\nu\mu}^{\alpha} \left[\frac{1}{2} H_{\mu\nu}^{\text{core}} + \frac{1}{2} F_{\mu\nu}^{\alpha} \right] + P_{\nu\mu}^{\beta} \left[\frac{1}{2} H_{\mu\nu}^{\text{core}} + \frac{1}{2} F_{\mu\nu}^{\beta} \right] \right\} \\
&= \frac{1}{2} \sum_{\mu} \sum_{\nu} [P_{\nu\mu}^T H_{\mu\nu}^{\text{core}} + P_{\nu\mu}^{\alpha} F_{\mu\nu}^{\alpha} + P_{\nu\mu}^{\beta} F_{\mu\nu}^{\beta}]
\end{aligned} \tag{3.8.20}$$

3.8.6 Illustrative Unrestricted Calculations

Ex 3.41

$$\begin{aligned}
\langle \hat{\mathcal{J}}^2 \rangle &= \langle c_1^2 \Psi + c_2^4 \Psi \mid \hat{\mathcal{J}}^2 \mid c_1^2 \Psi + c_2^4 \Psi \rangle \\
&= \frac{3}{4} c_1^2 + \frac{15}{4} c_2^2 \\
&= \frac{3}{4} (1 - c_2^2) + \frac{15}{4} c_2^2 \\
&= \frac{3}{4} + 3c_2^2
\end{aligned} \tag{3.8.21}$$

thus

| basis | $\langle \hat{\mathcal{J}}^2 \rangle$ | c_2 | contamination/% |
|---------|---------------------------------------|---------|-----------------|
| STO-3G | 0.7652 | 0.07118 | 0.5067 |
| 4-31G | 0.7622 | 0.06377 | 0.4067 |
| 6-31G* | 0.7618 | 0.06272 | 0.3933 |
| 6-31G** | 0.7614 | 0.06164 | 0.3800 |

3.8.7 The Dissociation Problem and Its Unrestricted Solution

Ex 3.42

$$\langle \psi_1^{\alpha} \mid \psi_1^{\alpha} \rangle = \langle \cos \theta \psi_1 + \sin \theta \psi_2 \mid \cos \theta \psi_1 + \sin \theta \psi_2 \rangle = \cos^2 \theta + \sin^2 \theta = 1 \tag{3.8.22}$$

$$\langle \psi_2^{\alpha} \mid \psi_2^{\alpha} \rangle = \langle -\sin \theta \psi_1 + \cos \theta \psi_2 \mid -\sin \theta \psi_1 + \cos \theta \psi_2 \rangle = \sin^2 \theta + \cos^2 \theta = 1 \tag{3.8.23}$$

$$\langle \psi_1^{\alpha} \mid \psi_2^{\alpha} \rangle = \langle \cos \theta \psi_1 + \sin \theta \psi_2 \mid -\sin \theta \psi_1 + \cos \theta \psi_2 \rangle = -\cos \theta \sin \theta + \sin \theta \cos \theta = 0 \tag{3.8.24}$$

thus $\{\psi_1^\alpha, \psi_2^\alpha\}$ is orthonormal.

Similarly conclusion can be derived for β orbitals.

Ex 3.43 For $R = 1.4$,

$$\begin{aligned}\eta &= \frac{h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} \\ &= \frac{(\varepsilon_2 - 2J_{12} + K_{12}) - (\varepsilon_1 - J_{11}) + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} \\ &= \frac{\varepsilon_2 - \varepsilon_1 + J_{11} + J_{22} - 3J_{12} + 3K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} \\ &= \frac{0.6703 + 0.5782 + 0.6746 + 0.6975 - 3 \times 0.6636 + 3 \times 0.1813}{0.6746 + 0.6975 - 2 \times 0.6636 + 4 \times 0.1813} \text{notag} \quad (3.8.25) \\ &= 1.524 > 1 \quad (3.8.26)\end{aligned}$$

thus unrestricted solution does not exist for this case.

For $R = 4.0$,

$$\begin{aligned}\eta &= \frac{\varepsilon_2 - \varepsilon_1 + J_{11} + J_{22} - 3J_{12} + 3K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} \\ &= \frac{0.0916 + 0.2542 + 0.5026 + 0.5259 - 3 \times 0.5121 + 3 \times 0.2651}{0.5026 + 0.5259 - 2 \times 0.5121 + 4 \times 0.2651} \text{notag} \quad (3.8.27) \\ &= 0.5948 \quad (3.8.28)\end{aligned}$$

$$\theta = \arccos(\sqrt{\eta}) = 0.6900 = 39.53^\circ \quad (3.8.29)$$

Ex 3.44

$$\begin{aligned}\lim_{R \rightarrow \infty} |\Psi_0\rangle &= \frac{1}{2} \left[|\psi_1 \bar{\psi}_1\rangle - |\psi_2 \bar{\psi}_2\rangle - \sqrt{2} |^3\Psi_1^2\rangle \right] \\ &= \frac{1}{2} \left[|\psi_1 \bar{\psi}_1\rangle - |\psi_2 \bar{\psi}_2\rangle - (|\psi_1 \bar{\psi}_2\rangle - |\psi_2 \bar{\psi}_1\rangle) \right] \\ &= \frac{1}{2} \left[\frac{1}{2} |(\phi_1 + \phi_2)(\bar{\phi}_1 + \bar{\phi}_2)\rangle - \frac{1}{2} |(\phi_1 - \phi_2)(\bar{\phi}_1 - \bar{\phi}_2)\rangle - \left(\frac{1}{2} |(\phi_1 + \phi_2)(\bar{\phi}_1 - \bar{\phi}_2)\rangle - \frac{1}{2} |(\phi_1 - \phi_2)(\bar{\phi}_1 + \bar{\phi}_2)\rangle \right) \right] \\ &= \frac{1}{4} (|\phi_1 \bar{\phi}_1\rangle + |\phi_1 \bar{\phi}_2\rangle + |\phi_2 \bar{\phi}_1\rangle + |\phi_2 \bar{\phi}_2\rangle) - \frac{1}{4} (|\phi_1 \bar{\phi}_1\rangle - |\phi_1 \bar{\phi}_2\rangle - |\phi_2 \bar{\phi}_1\rangle + |\phi_2 \bar{\phi}_2\rangle) \\ &\quad - \frac{1}{4} [(|\phi_1 \bar{\phi}_1\rangle - |\phi_1 \bar{\phi}_2\rangle + |\phi_2 \bar{\phi}_1\rangle - |\phi_2 \bar{\phi}_2\rangle) - (|\phi_1 \bar{\phi}_1\rangle + |\phi_1 \bar{\phi}_2\rangle - |\phi_2 \bar{\phi}_1\rangle - |\phi_2 \bar{\phi}_2\rangle)] \\ &= \frac{1}{2} (|\phi_1 \bar{\phi}_2\rangle + |\phi_2 \bar{\phi}_1\rangle) - \frac{1}{4} (-2|\phi_1 \bar{\phi}_2\rangle + 2|\phi_2 \bar{\phi}_1\rangle) \\ &= |\phi_1 \bar{\phi}_2\rangle \quad (3.8.30)\end{aligned}$$