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

$$\left\langle \chi_i \left| \hat{f} \right| \chi_j \right\rangle = \left\langle \chi_i(1) \left| h(1) + \sum_b [\mathscr{J}_b(1) - \mathscr{K}_b(1)] \right| \chi_j(1) \right\rangle$$

$$= [i|h|j] + \sum_{b \neq j} \left[\left\langle \chi_i(1)\chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_b(2)\chi_j(1) \right\rangle - \left\langle \chi_i(1)\chi_b(2) \left| \frac{1}{r_{12}} \right| \chi_b(1)\chi_j(2) \right\rangle \right]$$

$$= [i|h|j] + \sum_{b \neq j} ([ij|bb] - [ib|bj]) \tag{3.1.1}$$

Since

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

we have

$$\left\langle \chi_i \left| \hat{f} \right| \chi_j \right\rangle = \langle i \,|\, h \,|\, j \rangle + \sum_b (\langle ib \,|\, jb \rangle - \langle ib \,|\, bj \rangle)$$

$$= \langle i \,|\, h \,|\, j \rangle + \sum_b \langle ib \,\|\, jb \rangle \tag{3.1.3}$$

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

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

we have

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

i.e.

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

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 $\because$

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

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

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

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

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

$\therefore$

$$\delta E_0 = \sum_a^N [\delta\chi_a|h|\chi_a] + \frac{1}{2}\sum_a^N \sum_b^N \left([\delta\chi_a\chi_a|\chi_b\chi_b] + [\chi_a\chi_a|\delta\chi_b\chi_b]\right)$$

$$- \frac{1}{2}\sum_a^N \sum_b^N \left([\delta\chi_a\chi_b|\chi_b\chi_a] + [\chi_a\chi_b|\delta\chi_b\chi_a]\right) + \text{complex conjugates} \tag{3.2.11}$$

while

$$\sum_a^N \sum_b^N [\chi_a\chi_a|\delta\chi_b\chi_b] = \sum_b^N \sum_a^N [\chi_b\chi_b|\delta\chi_a\chi_a] = \sum_a^N \sum_b^N [\delta\chi_a\chi_a|\chi_b\chi_b] \tag{3.2.12}$$

$$\sum_a^N \sum_b^N [\chi_a\chi_b|\delta\chi_b\chi_a] = \sum_b^N \sum_a^N [\chi_b\chi_a|\delta\chi_a\chi_b] = \sum_a^N \sum_b^N [\delta\chi_a\chi_b|\chi_b\chi_a] \tag{3.2.13}$$

thus

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

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

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

$$f_{ji}^* = \langle \chi_j | f | \chi_i \rangle^* = \langle j | h | i \rangle^* + \sum_b \langle jb \| ib \rangle^*$$

$$= \langle i | h | j \rangle + \sum_b \langle ib \| jb \rangle$$

$$= f_{ij} \tag{3.3.2}$$

thus the Fock operator is Hermitian.

Ex 3.5

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

$$= \sum_{a \neq c,d} \langle a | h | a \rangle + \frac{1}{2}\sum_{a \neq c,d}\sum_{b \neq c,d} \langle ab \| ab \rangle - \left[\sum_a \langle a | h | a \rangle + \frac{1}{2}\sum_a\sum_b \langle ab \| ab \rangle\right]$$

$$= -\langle c | h | c \rangle - \langle d | h | d \rangle - \frac{1}{2}\sum_{a \neq c,d} \langle ac \| ac \rangle - \frac{1}{2}\sum_{a \neq c,d} \langle ad \| ad \rangle - \frac{1}{2}\sum_{b \neq c,d} \langle cb \| cb \rangle - \frac{1}{2}\sum_{b \neq c,d} \langle db \| db \rangle - \langle cd \| cd \rangle$$

$$= -\langle c | h | c \rangle - \langle d | h | d \rangle - \sum_{a \neq c,d} \langle ac \| ac \rangle - \sum_{a \neq c,d} \langle ad \| ad \rangle - \langle cd \| cd \rangle$$

$$= -\langle c | h | c \rangle - \langle d | h | d \rangle - \left(\sum_{a \neq c} \langle ac \| ac \rangle - \langle dc \| dc \rangle\right) - \left(\sum_{a \neq d} \langle ad \| ad \rangle - \langle cd \| cd \rangle\right) - \langle cd \| cd \rangle$$

$$= -\varepsilon_c - \varepsilon_d + \langle cd | cd \rangle - \langle cd | dc \rangle \tag{3.3.3}$$

Ex 3.6

$$
{}^{N}E_0 - {}^{N+1}E^r = \sum_a \langle a \,|\, h \,|\, a \rangle + \frac{1}{2}\sum_a \sum_b \langle ab \,\|\, ab \rangle
$$

$$
- \left[\sum_a \langle a \,|\, h \,|\, a \rangle + \langle r \,|\, h \,|\, r \rangle + \frac{1}{2}\sum_a \sum_b \langle ab \,\|\, ab \rangle + \frac{1}{2}\sum_b \langle rb \,\|\, rb \rangle + \frac{1}{2}\sum_a \langle ar \,\|\, ar \rangle \right]
$$

$$
= -\langle r \,|\, h \,|\, r \rangle - \frac{1}{2}\sum_b \langle rb \,\|\, rb \rangle - \frac{1}{2}\sum_b \langle br \,\|\, br \rangle
$$

$$
= -\langle r \,|\, h \,|\, r \rangle - \sum_b \langle rb \,\|\, rb \rangle \tag{3.3.4}
$$

3.3.2 Brillouin's Theorem

3.3.3 The HF Hamiltonian

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

$$
\mathscr{H}_0 \,|\Psi_0\rangle = \mathscr{H}_0 \frac{1}{\sqrt{N!}} \sum_n^{N!} (-1)^{p_n} \mathscr{P}_n \left\{ \sum_i^N f(i)\chi_j(1)\cdots\chi_k(N) \right\}
$$

$$
= \frac{1}{\sqrt{N!}} \sum_n^{N!} (-1)^{p_n} \mathscr{P}_n \{ (\varepsilon_j + \cdots + \varepsilon_k)\chi_j(1)\cdots\chi_k(N) \}
$$

$$
= \sum_a \varepsilon_a \tag{3.3.5}
$$

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

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

Ex 3.8

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

thus

$$
\langle \Psi_0 \,|\, \mathscr{V} \,|\, \Psi_0 \rangle = \sum_i^N \sum_{j>i}^N \langle \Psi_0 \,|\, \mathscr{O}_2 \,|\, \Psi_0 \rangle - \sum_i^N \sum_b^N [\langle \Psi_0 \,|\, \mathscr{G}_b(i) - \mathscr{K}_b(i) \,|\, \Psi_0 \rangle]
$$

$$
= \frac{1}{2}\sum_a^N \sum_b^N \langle ab \,\|\, ab \rangle - \sum_i^N \sum_b^N [\langle ib \,|\, ib \rangle - \langle ib \,|\, bi \rangle]
$$

$$
= -\frac{1}{2}\sum_a^N \sum_b^N \langle ab \,\|\, ab \rangle \tag{3.3.8}
$$

3.4 Restricted Closed-shell HF: The Roothaan Equations

3.4.1 Closed-shell HF: Restricted Spin Orbitals

Ex 3.9

$$
\varepsilon_i = (i|h|i) + \sum_b^N (\langle ib \,|\, ib \rangle - \langle ib \,|\, bi \rangle)
$$

$$
= (i|h|i) + \sum_c^{N/2} (\langle ic \,|\, ic \rangle - \langle ic \,|\, ci \rangle) + \sum_{\bar{c}}^{N/2} (\langle i\bar{c} \,|\, i\bar{c} \rangle - \langle i\bar{c} \,|\, \bar{c}i \rangle) \tag{3.4.1}
$$

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

$$\varepsilon_i = (i|h|i) + \sum_c^{N/2} [(ic|ic)\langle\alpha\,|\,\alpha\rangle\langle\alpha\,|\,\alpha\rangle - (ic|ci)\langle\alpha\,|\,\alpha\rangle\langle\alpha\,|\,\alpha\rangle] + \sum_c^{N/2} [(ic|ic)\langle\alpha\,|\,\alpha\rangle\langle\beta\,|\,\beta\rangle - (ic|ci)\langle\alpha\,|\,\beta\rangle\langle\beta\,|\,\alpha\rangle]$$

$$= (i|h|i) + \sum_c^{N/2} [2(ic|ic) - (ic|ci)]$$

$$= (i|h|i) + \sum_n^{N/2} (2J_{ib} - K_{ib}) \tag{3.4.2}$$

3.4.2 Introduction of a Basis: The Roothaan Equations

Ex 3.10

$$(\mathbf{C}^\dagger \mathbf{S} \mathbf{C})_{\mu\nu} = \sum_i \sum_j C_{\mu i}^\dagger S_{ij} C_{j\nu}$$

$$= \sum_i \sum_j C_{i\mu}^* \langle\phi_i\,|\,\phi_j\rangle C_{j\nu}$$

$$= \langle\phi_\mu\,|\,\phi_\nu\rangle$$

$$= \delta_{\mu\nu} \tag{3.4.3}$$

thus

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

3.4.3 The Charge Density

Ex 3.11

$$\rho(\mathbf{r}) = \langle\Psi_0\,|\,\hat\rho(\mathbf{r})\,|\,\Psi_0\rangle$$

$$= \sum_i^N \frac{1}{N!} \sum_I^{N!} \sum_J^{N!} (-1)^{p_I}(-1)^{p_J} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \hat{\mathscr{P}}_I\{\chi_1(1)\cdots\chi_N(N)\}^* \delta(\mathbf{r}_i - \mathbf{r})\hat{\mathscr{P}}_J\{\chi_1(1)\cdots\chi_N(N)\} \tag{3.4.5}$$

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

$$\rho(\mathbf{r}) = \sum_i^N \frac{1}{N!} \sum_I^{N!} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \hat{\mathscr{P}}_I\{\chi_1(1)\cdots\chi_N(N)\}^* \delta(\mathbf{r}_i - \mathbf{r})\hat{\mathscr{P}}_I\{\chi_1(1)\cdots\chi_N(N)\}$$

$$= \sum_i^N \frac{1}{N!}(N-1)! \sum_s^N \int d\mathbf{x}_i \chi_s^*(\mathbf{x}_i)\delta(\mathbf{r}_i - \mathbf{r})\chi_s(\mathbf{x}_i)$$

$$= \sum_i^N \frac{1}{N} \cdot 2 \sum_s^{N/2} \int d\mathbf{r}_i \phi_s(\mathbf{r}_i)\delta(\mathbf{r}_i - \mathbf{r})\phi_s(\mathbf{r}_i)$$

$$= \sum_i^N \frac{2}{N} \sum_s^{N/2} \phi_s(\mathbf{r})\phi_s(\mathbf{r})$$

$$= N\frac{2}{N} \sum_s^{N/2} \phi_s(\mathbf{r})\phi_s(\mathbf{r})$$

$$= 2 \sum_s^{N/2} \phi_s(\mathbf{r})\phi_s(\mathbf{r}) \tag{3.4.6}$$

Ex 3.12 From Ex 3.10, we have

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

i.e.

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

thus

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

thus

$$\mathbf{PSP} = 2\mathbf{P} \tag{3.4.10}$$

Ex 3.13   Eq. 3.122 shows

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

thus

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

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 $\because$

$$\mathbf{U}^\dagger \mathbf{S}\mathbf{U} = \mathbf{s} \tag{3.4.13}$$

$\therefore$

$$\mathbf{S}\mathbf{U} = \mathbf{U}\mathbf{s} \tag{3.4.14}$$

i.e.

$$\sum_\nu S_{\mu\nu} U_{\nu i} = U_{\mu i} s_i \tag{3.4.15}$$

thus

$$\sum_\mu U_{\mu i}^* \sum_\nu S_{\mu\nu} U_{\nu i} = \sum_\mu U_{\mu i}^* U_{\mu i} s_i \tag{3.4.16}$$

$$\sum_\mu \sum_\nu U_{\mu i}^* \langle \phi_\mu \,|\, \phi_\nu \rangle U_{\nu i} = s_i \sum_\mu |U_{\mu i}|^2 \tag{3.4.17}$$

Suppose

$$\phi_i' = \sum_\nu U_{\nu i} \phi_\nu \tag{3.4.18}$$

thus

$$\langle \phi_i' \,|\, \phi_i' \rangle = s_i \sum_\mu |U_{\mu i}|^2 \tag{3.4.19}$$

$\because$

$$\langle \phi_i' \,|\, \phi_i' \rangle > 0 \qquad |U_{\mu i}|^2 > 0 \tag{3.4.20}$$

$\therefore$

$$s_i > 0 \tag{3.4.21}$$

Ex 3.16

- (3.174)

Since (ϕ, ϕ', ψ are row vectors)

$$\boldsymbol{\psi} = \boldsymbol{\phi}\mathbf{C} \tag{3.4.22}$$

$$\boldsymbol{\psi} = \boldsymbol{\phi}'\mathbf{C}' = \boldsymbol{\phi}\mathbf{X}\mathbf{C}' \tag{3.4.23}$$

we have

$$\mathbf{C} = \mathbf{X}\mathbf{C}' \tag{3.4.24}$$

i.e.

$$\mathbf{C}' = \mathbf{X}^{-1}\mathbf{C} \tag{3.4.25}$$

- (3.177)

$$
\begin{aligned}
F_{\mu\nu}' &= \langle \phi_\mu' \,|\, f \,|\, \phi_\nu' \rangle \\
&= \left\langle \sum_i \phi_i X_{i\mu} \,\middle|\, f \,\middle|\, \sum_j \phi_j X_{j\nu} \right\rangle \\
&= \sum_i \sum_j X_{i\mu}^* X_{j\nu} \langle \phi_i \,|\, f \,|\, \phi_j \rangle \\
&= \sum_i \sum_j X_{i\mu}^* F_{ij} X_{j\nu}
\end{aligned} \tag{3.4.26}
$$

i.e.

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F}\mathbf{X} \tag{3.4.27}$$

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

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

thus

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

$$\tag{3.4.29}$$

Ex 3.18 For symmetrically orthogonalized basis,

$$\mathbf{C}' = \mathbf{S}^{1/2}\mathbf{C} \tag{3.4.30}$$

thus

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

i.e.

$$\mathbf{P}' = \mathbf{S}^{1/2}\mathbf{P}\mathbf{S}^{1/2} \tag{3.4.32}$$

thus

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

3.5 Model Calculations on H_2 and HeH^+

3.5.1 The $1s$ Minimal STO-3G Basis Set

Ex 3.19

$$\phi_{1s}^{\mathrm{GF}}(\alpha, \mathbf{r} - \mathbf{R}_A)\phi_{1s}^{\mathrm{GF}}(\alpha, \mathbf{r} - \mathbf{R}_B) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \mathrm{e}^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2} \left(\frac{2\beta}{\pi}\right)^{3/4} \mathrm{e}^{-\beta|\mathbf{r}-\mathbf{R}_B|^2}$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \mathrm{e}^{-\alpha|\mathbf{r}-\mathbf{R}_A|^2-\beta|\mathbf{r}-\mathbf{R}_B|^2}$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \exp\left(-\left[(\alpha+\beta)|\mathbf{r}|^2 - 2\mathbf{r}\cdot(\alpha\mathbf{R}_A + \beta\mathbf{R}_B) + \alpha|\mathbf{R}_A|^2 + \beta|\mathbf{R}_B|^2\right]\right)$$

$$(3.5.1)$$

Let

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

we have

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

$$= \left(\frac{2\alpha}{\pi}\frac{2\beta}{\pi}\right)^{3/4} \exp\left(-\left[p|\mathbf{r}-\mathbf{R}_P|^2 - p|\mathbf{R}_P|^2 + \alpha|\mathbf{R}_A|^2 + \beta|\mathbf{R}_B|^2\right]\right)$$

$$= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4}\left(\frac{2p}{\pi}\right)^{3/4} \mathrm{e}^{-p|\mathbf{r}-\mathbf{R}_P|^2} \exp\left(p|\mathbf{R}_P|^2 - \alpha|\mathbf{R}_A|^2 - \beta|\mathbf{R}_B|^2\right)$$

$$(3.5.3)$$

Let

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

thus

$$K_{AB} = \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\left(p|\mathbf{R}_P|^2 - \alpha|\mathbf{R}_A|^2 - \beta|\mathbf{R}_B|^2\right)$$

$$= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\left(\frac{1}{p}(\alpha^2|\mathbf{R}_A|^2 + \beta^2|\mathbf{R}_B|^2 + 2\alpha\beta\mathbf{R}_A\cdot\mathbf{R}_B) - \alpha|\mathbf{R}_A|^2 - \beta|\mathbf{R}_B|^2\right)$$

$$= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\left(\frac{1}{p}\left(\alpha^2|\mathbf{R}_A|^2 + \beta^2|\mathbf{R}_B|^2 + 2\alpha\beta\mathbf{R}_A\cdot\mathbf{R}_B - p\alpha|\mathbf{R}_A|^2 - p\beta|\mathbf{R}_B|^2\right)\right)$$

$$= \left(\frac{2\alpha\beta/p}{\pi}\right)^{3/4} \exp\left(\frac{1}{p}\left(-\alpha\beta|\mathbf{R}_A|^2 - \alpha\beta|\mathbf{R}_B|^2 + 2\alpha\beta\mathbf{R}_A\cdot\mathbf{R}_B\right)\right)$$

$$= \left(\frac{2\alpha\beta}{p\pi}\right)^{3/4} \exp\left(-\frac{\alpha\beta}{p}|\mathbf{R}_A - \mathbf{R}_B|^2\right) \tag{3.5.5}$$

Ex 3.20 At $r = 0$,

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

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

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

while

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

3.5.2 STO-3G H$_2$

Ex 3.21

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

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

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

thus

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

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

$$S_{12} = 0.6648 \tag{3.5.13}$$

Ex 3.22 Let

$$\psi_1 = c_1(\phi_1 + \phi_2) \qquad \psi_2 = c_2(\phi_1 - \phi_2) \tag{3.5.14}$$

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

$\therefore$

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

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

$\therefore$

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

Ex 3.23 Suppose

$$\psi_1 = c_1(\phi_1 + \phi_2) \qquad \psi_2 = c_2(\phi_1 - \phi_2) \tag{3.5.19}$$

thus

$$\mathbf{H}^{\text{core}}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\varepsilon} \tag{3.5.20}$$

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

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

$\therefore$

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

$$\varepsilon_1 = (-1.1204 - 0.9584)/(1 + 0.6593) = -1.2528 \tag{3.5.24}$$

$$\varepsilon_2 = (-1.1204 + 0.9584)/(1 - 0.6593) = -0.4755 \tag{3.5.25}$$

Ex 3.24

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

$\therefore$

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

For $H_2{}^+$,

$$\mathbf{P}_{H_2^+} = \frac{1}{2}(1+S_{12})^{-1}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \tag{3.5.28}$$

Ex 3.25

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

$\therefore$

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

$$
\begin{aligned}
F_{11} = F_{22} &= -1.1204 + (1+0.6593)^{-1}\left(\frac{1}{2}\times 0.7746 + 0.4441 + 0.5697 - \frac{1}{2}\times 0.2970\right) \\
&= -0.3655
\end{aligned}
\tag{3.5.31}
$$

$$
\begin{aligned}
F_{12} &= H_{12}^{\text{core}} + (1+S_{12})^{-1}\left[(12|11) - \frac{1}{2}(11|12) + (12|21) - \frac{1}{2}(11|22) + (12|12) - \frac{1}{2}(12|12) + (12|22) - \frac{1}{2}(12|22)\right] \\
&= H_{12}^{\text{core}} + (1+S_{12})^{-1}\left[(11|12) - \frac{1}{2}(11|22) + \frac{3}{2}(12|12)\right]
\end{aligned}
\tag{3.5.32}
$$

$$
\begin{aligned}
F_{12} = F_{21} &= -0.9584 + (1+0.6593)^{-1}\left(0.4441 - \frac{1}{2}\times 0.5697 + \frac{3}{2}\times 0.2970\right) \\
&= -0.5939
\end{aligned}
\tag{3.5.33}
$$

Ex 3.26 Similar to the procedure in Ex 3.23, we get

$$\varepsilon_1 = \frac{F_{11}+F_{12}}{1+S_{12}} = \frac{-0.3655-0.5939}{1+0.6593} = -0.5782 \tag{3.5.34}$$

$$\varepsilon_2 = \frac{F_{11}-F_{12}}{1-S_{12}} = \frac{-0.3655+0.5939}{1-0.6593} = 0.6703 \tag{3.5.35}$$

Ex 3.27

$$E_0 = \sum_{\mu\nu} \frac{1}{2} P_{\nu\mu}(H_{\mu\nu}^{\text{core}} + F_{\mu\nu})$$

$$= \frac{1}{2}\frac{1}{1+S_{12}}(H_{11}^{\text{core}} + F_{11} + H_{12}^{\text{core}} + F_{12} + H_{21}^{\text{core}} + F_{21} + H_{22}^{\text{core}} + F_{22})$$

$$= \frac{H_{11}^{\text{core}} + F_{11} + H_{12}^{\text{core}} + F_{12}}{1+S_{12}}$$

$$= \frac{-1.1204 - 0.3655 - 0.9584 - 0.5939}{1+0.6593}$$

$$= -1.8310 \tag{3.5.36}$$

$$E_{tot} = E_0 + \frac{1}{R} = -1.1167 \tag{3.5.37}$$

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

Ex 3.28

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

$$= \begin{pmatrix} 1 & S_{12} \\ 0 & \sqrt{1-S_{12}^2} \end{pmatrix}\begin{pmatrix} 1 & -S_{12}/\sqrt{1-S_{12}^2} \\ 0 & 1/\sqrt{1-S_{12}^2} \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{3.5.38}$$

thus the Schmidt transformation produces orthonormal basis.

Ex 3.29

$$E_0(R\to\infty) = \frac{1}{2}\sum_\mu\sum_\nu P_{\nu\mu}(R\to\infty)[2H_{\mu\nu}^{\text{core}} + G_{\mu\nu}] \tag{3.5.39}$$

where

$$P_{\nu\mu}(R\to\infty) = \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix} \tag{3.5.40}$$

$$G_{\mu\nu} = \sum_\lambda\sum_\sigma P_{\lambda\sigma}(R\to\infty)\left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right]$$

$$= 2\left[(\mu\nu|\phi_1\phi_1) - \frac{1}{2}(\mu\phi_1|\phi_1\nu)\right] \tag{3.5.41}$$

thus

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

$$= \frac{1}{2}\times 2[2H_{11}^{\text{core}} + G_{11}]$$

$$= 2(T_{11} + V_{11}^1) + 2\left[(\phi_1\phi_1|\phi_1\phi_1) - \frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)\right]$$

$$= 2T_{11} + 2V_{11}^1 + (\phi_1\phi_1|\phi_1\phi_1) \tag{3.5.42}$$

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

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

Renormalize it, we get

$$N = 1.689 \qquad (3.6.3)$$

thus

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

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

Reaction II

basis	$\Delta E/$ a.u.	$\Delta E/$(kcal/mol)	
STO-3G	0.186	116.72	endoergic
4-31G	-0.114	-71.54	
6-31G*	-0.088	-55.22	exoergic
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 $-0.37\,\text{kcal/mol}$, to the energy change of reaction II would be $17.78\,\text{kcal/mol}$. Thus the effect of zero-point vibrations should not be ignored.

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

3.8.1 Open-shell HF: Unrestricted Spin Orbitals

Ex 3.33

$$
f^\alpha(1) = \int d\omega_1 \alpha^*(\omega_1) \left[h(1) + \sum_a \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} (1 - \hat{\mathscr{P}}_{12}) \chi_a(2) \right] \alpha(\omega_1)
$$

$$
= h(1) + \sum_a^{N_\alpha} \left[\int d\omega_1 \alpha^*(\omega_1) \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} \chi_a(2) \alpha(\omega_1) - \int d\omega_1 \alpha^*(\omega_1) \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} \chi_a(1) \alpha(\omega_2) \right]
$$

$$
+ \sum_a^{N_\beta} \left[\int d\omega_1 \alpha^*(\omega_1) \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} \chi_a(2) \alpha(\omega_1) - \int d\omega_1 \alpha^*(\omega_1) \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} \chi_a(1) \alpha(\omega_2) \right]
$$

$$
= h(1) + \sum_a^{N_\alpha} \left[\int d\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\alpha(\mathbf{r}_2) - \int d\mathbf{r}_2 \int d\omega_2 \int d\omega_1 \alpha^*(\omega_1) \alpha^*(\omega_2) \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\alpha(\mathbf{r}_1) \alpha(\omega_1) \alpha(\omega_2) \right]
$$

$$
+ \sum_a^{N_\beta} \left[\int d\mathbf{r}_2 \psi_a^{\beta*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\beta(\mathbf{r}_2) - \int d\mathbf{r}_2 \int d\omega_2 \int d\omega_1 \alpha^*(\omega_1) \beta^*(\omega_2) \psi_a^{\beta*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\beta(\mathbf{r}_1) \beta(\omega_1) \alpha(\omega_2) \right]
$$

$$
= h(1) + \sum_a^{N_\alpha} \left[\int d\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\alpha(\mathbf{r}_2) - \int d\mathbf{r}_2 \psi_a^{\alpha*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\alpha(\mathbf{r}_1) \right] + \sum_a^{N_\beta} \left[\int d\mathbf{r}_2 \psi_a^{\beta*}(\mathbf{r}_2) r_{12}^{-1} \psi_a^\beta(\mathbf{r}_2) - 0 \right]
$$

$$
= h(1) + \sum_a^{N_\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N_\beta} J_a^\beta(1) \tag{3.8.1}
$$

Ex 3.34

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

$$
= h_{11}^\alpha + h_{22}^\alpha + h_{11}^\alpha + J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha} + J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta} \tag{3.8.2}
$$

Ex 3.35

$$
\varepsilon_i^\alpha = (\psi_i^\alpha(1) | h(1) + \sum_a^{N_\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N_\beta} J_a^\beta(1) | \psi_i^\alpha(1))
$$

$$
= h_{ii}^\alpha + \sum_a^{N_\alpha} [J_{ia}^{\alpha\alpha} - K_{ia}^{\alpha\alpha}] + \sum_a^{N_\beta} J_{ia}^{\alpha\beta} \tag{3.8.3}
$$

$$
\varepsilon_i^\beta = (\psi_i^\beta(1) | h(1) + \sum_a^{N_\alpha} [J_a^\beta(1) - K_a^\beta(1)] + \sum_a^{N_\beta} J_a^\alpha(1) | \psi_i^\beta(1))
$$

$$
= h_{ii}^\beta + \sum_a^{N_\alpha} \left[J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta} \right] + \sum_a^{N_\beta} J_{ia}^{\beta\alpha} \tag{3.8.4}
$$

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

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

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

Since

$$\left\langle \hat{\mathscr{S}}_z \right\rangle = \frac{1}{2}(N_\alpha - N_\beta) \tag{3.8.9}$$

we get

$$\int \mathrm{d}\mathbf{r} \rho^S(\mathbf{r}) = 2 \left\langle \hat{\mathscr{S}}_z \right\rangle \tag{3.8.10}$$

Ex 3.37

$$\rho^\alpha(\mathbf{r}) = \sum_a^{N_\alpha} \psi_a^{\alpha*}(\mathbf{r}) \psi_a^\alpha(\mathbf{r})$$

$$= \sum_a^{N_\alpha} \sum_\nu C_{\nu a}^{\alpha*} \phi_\nu^*(\mathbf{r}) \sum_\mu C_{\mu a}^\alpha \phi_\mu(\mathbf{r})$$

$$= \sum_\nu \sum_\mu \left[\sum_a^{N_\alpha} C_{\nu a}^{\alpha*} C_{\mu a}^\alpha \right] \phi_\nu^*(\mathbf{r}) \phi_\mu(\mathbf{r})$$

$$\tag{3.8.11}$$

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

$$\langle \mathscr{O}_1 \rangle = \sum_i^N \langle \chi_i | h | \chi_i \rangle$$

$$= \sum_i^{N_\alpha} (\psi_i^\alpha | h | \psi_i^\alpha) + \sum_i^{N_\beta} (\psi_i^\beta | h | \psi_i^\beta)$$

$$= \sum_i^{N_\alpha} \sum_\nu \sum_\mu C_{\nu a}^{\alpha*} (\phi_\nu | h | \phi_\mu) C_{\mu a}^\alpha + \sum_i^{N_\beta} \sum_\nu \sum_\mu C_{\nu a}^{\beta*} (\phi_\nu | h | \phi_\mu) C_{\mu a}^\beta$$

$$= \sum_\nu \sum_\mu P_{\mu\nu}^\alpha (\phi_\nu | h | \phi_\mu) + \sum_\nu \sum_\mu P_{\mu\nu}^\beta (\phi_\nu | h | \phi_\mu)$$

$$= \sum_\nu \sum_\mu P_{\mu\nu}^T (\phi_\nu | h | \phi_\mu) \tag{3.8.14}$$

Ex 3.39

$$\langle \hat{\rho}^S \rangle = \langle \Psi_0 \, | \, \hat{\rho}^S \, | \, \Psi_0 \rangle$$

$$= \frac{1}{N!} \sum_{i,j}^{N!} (-1)^{p_i} (-1)^{p_j} \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \hat{\mathscr{P}}_i \{\chi_1(1) \cdots \chi_N(N)\} \sum_m^N 2\delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \hat{\mathscr{P}}_j \{\chi_1(1) \cdots \chi_N(N)\}$$

$$= \frac{2}{N!} \sum_i^{N!} \sum_m^N \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \hat{\mathscr{P}}_i \{\chi_1(1) \cdots \chi_N(N)\} \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \hat{\mathscr{P}}_i \{\chi_1(1) \cdots \chi_N(N)\}$$

$$= \frac{2}{N} \sum_s^N \sum_m^N \int d\mathbf{x}_m \chi_s^*(m) \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \chi_s(m)$$

$$= \frac{2}{N} \sum_m^N \left[\sum_s^{N_\alpha} \int d\mathbf{r}_m \psi_s^{\alpha*}(m) \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \psi_s^\alpha(m) + \sum_s^{N_\beta} \int d\mathbf{r}_m \psi_s^{\beta*}(m) \delta(\mathbf{r}_m - \mathbf{R}) s_z(m) \psi_s^\beta(m) \right]$$

$$= \frac{2}{N} \sum_m^N \left[\frac{1}{2} \sum_s^{N_\alpha} \int d\mathbf{r}_m \psi_s^{\alpha*}(m) \delta(\mathbf{r}_m - \mathbf{R}) \psi_s^\alpha(m) - \frac{1}{2} \sum_s^{N_\beta} \int d\mathbf{r}_m \psi_s^{\beta*}(m) \delta(\mathbf{r}_m - \mathbf{R}) \psi_s^\beta(m) \right]$$

$$= \frac{2}{N} N \left[\frac{1}{2} \sum_s^{N_\alpha} \psi_s^{\alpha*}(\mathbf{R}) \psi_s^\alpha(\mathbf{R}) - \frac{1}{2} \sum_s^{N_\beta} \psi_s^{\beta*}(\mathbf{R}) \psi_s^\beta(\mathbf{R}) \right]$$

$$= 2 \left[\frac{1}{2} \rho^\alpha(\mathbf{R}) - \frac{1}{2} \rho^\beta(\mathbf{R}) \right]$$

$$= \rho^S(\mathbf{R}) \tag{3.8.15}$$

where

$$\rho^S(\mathbf{R}) = \sum_\nu \sum_\mu P_{\nu\mu}^S \phi_\mu^*(\mathbf{R}) \phi_\nu(\mathbf{R})$$

$$= \sum_\nu (\mathbf{P}^S \mathbf{A})_{\nu\nu}$$

$$= \text{tr}(\mathbf{P}^S \mathbf{A}) \tag{3.8.16}$$

3.8.4 Expression for the Fock Matrices

3.8.5 Solution of the Unrestricted SCF Equations

Ex 3.40

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

$$= \sum_\mu \sum_\nu P_{\nu\mu}^\alpha H_{\mu\nu}^{\text{core}} + \sum_\mu \sum_\nu P_{\nu\mu}^\beta H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma P_{\nu\mu}^\alpha P_{\sigma\lambda}^\alpha [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)]$$

$$+ \frac{1}{2} \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma P_{\nu\mu}^\beta P_{\sigma\lambda}^\beta [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] + \sum_\mu \sum_\nu \sum_\lambda \sum_\sigma P_{\nu\mu}^\alpha P_{\sigma\lambda}^\beta (\mu\nu|\lambda\sigma)$$

$$= \sum_\mu \sum_\nu P_{\nu\mu}^\alpha \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_\lambda \sum_\sigma P_{\sigma\lambda}^\alpha [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] + \frac{1}{2} \sum_\lambda \sum_\sigma P_{\sigma\lambda}^\beta (\mu\nu|\lambda\sigma) \right\}$$

$$+ \sum_\mu \sum_\nu P_{\nu\mu}^\beta \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_\lambda \sum_\sigma P_{\sigma\lambda}^\beta [(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)] + \frac{1}{2} \sum_\lambda \sum_\sigma P_{\sigma\lambda}^\alpha (\mu\nu|\lambda\sigma) \right\}$$

$$= \sum_\mu \sum_\nu P_{\nu\mu}^\alpha \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_\lambda \sum_\sigma [P_{\sigma\lambda}^T (\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^\alpha (\mu\sigma|\lambda\nu)] \right\}$$

$$+ \sum_\mu \sum_\nu P_{\nu\mu}^\beta \left\{ H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_\lambda \sum_\sigma [P_{\sigma\lambda}^T (\mu\nu|\lambda\sigma) - P_{\sigma\lambda}^\beta (\mu\sigma|\lambda\nu)] \right\}$$

$$\tag{3.8.17}$$

while

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

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

thus

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

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

3.8.6 Illustrative Unrestricted Calculations

Ex 3.41

$$\left\langle \hat{\mathscr{S}}^2 \right\rangle = \left\langle c_1{}^2\Psi + c_2{}^4\Psi \,\middle|\, \hat{\mathscr{S}}^2 \,\middle|\, c_1{}^2\Psi + c_2{}^4\Psi \right\rangle$$

$$= \frac{3}{4} c_1^2 + \frac{15}{4} c_2^2$$

$$= \frac{3}{4} (1 - c_2^2) + \frac{15}{4} c_2^2$$

$$= \frac{3}{4} + 3c_2^2 \tag{3.8.21}$$

thus

basis	$\left\langle \hat{\mathscr{S}}^2 \right\rangle$	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

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

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

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

thus $\{\psi_1^\alpha, \psi_2^\alpha\}$ is orthonormal.
Similarly conclusion can be derived for β orbitals.

Ex 3.43 For $R = 1.4$,

$$\eta = \frac{h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}}$$

$$= \frac{(\varepsilon_2 - 2J_{12} + K_{12}) - (\varepsilon_1 - J_{11}) + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}}$$

$$= \frac{\varepsilon_2 - \varepsilon_1 + J_{11} + J_{22} - 3J_{12} + 3K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}}$$

$$= \frac{0.6703 + 0.5782 + 0.6746 + 0.6975 - 3 \times 0.6636 + 3 \times 0.1813}{0.6746 + 0.6975 - 2 \times 0.6636 + 4 \times 0.1813} notag \tag{3.8.25}$$

$$= 1.524 > 1 \tag{3.8.26}$$

thus unrestricted solution does not exist for this case.
For $R = 4.0$,

$$\eta = \frac{\varepsilon_2 - \varepsilon_1 + J_{11} + J_{22} - 3J_{12} + 3K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}}$$

$$= \frac{0.0916 + 0.2542 + 0.5026 + 0.5259 - 3 \times 0.5121 + 3 \times 0.2651}{0.5026 + 0.5259 - 2 \times 0.5121 + 4 \times 0.2651} notag \tag{3.8.27}$$

$$= 0.5948 \tag{3.8.28}$$

$$\theta = \arccos(\sqrt{\eta}) = 0.6900 = 39.53° \tag{3.8.29}$$

Ex 3.44

$$\lim_{R \to \infty} |\Psi_0\rangle = \frac{1}{2}\Big[|\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle - \sqrt{2}\,|^3\Psi_1^2\rangle\Big]$$

$$= \frac{1}{2}\Big[|\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle - \big(|\psi_1\bar{\psi}_2\rangle - |\psi_2\bar{\psi}_1\rangle\big)\Big]$$

$$= \frac{1}{2}\Big[\frac{1}{2}|(\phi_1 + \phi_2)(\bar{\phi}_1 + \bar{\phi}_2)\rangle - \frac{1}{2}|(\phi_1 - \phi_2)(\bar{\phi}_1 - \bar{\phi}_2)\rangle - \Big(\frac{1}{2}|(\phi_1 + \phi_2)(\bar{\phi}_1 - \bar{\phi}_2)\rangle - \frac{1}{2}|(\phi_1 - \phi_2)(\bar{\phi}_1 + \bar{\phi}_2)\rangle\Big)\Big]$$

$$= \frac{1}{4}\big(|\phi_1\bar{\phi}_1\rangle + |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle\big) - \frac{1}{4}\big(|\phi_1\bar{\phi}_1\rangle - |\phi_1\bar{\phi}_2\rangle - |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle\big)$$

$$\quad - \frac{1}{4}\Big[\big(|\phi_1\bar{\phi}_1\rangle - |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle - |\phi_2\bar{\phi}_2\rangle\big) - \big(|\phi_1\bar{\phi}_1\rangle + |\phi_1\bar{\phi}_2\rangle - |\phi_2\bar{\phi}_1\rangle - |\phi_2\bar{\phi}_2\rangle\big)\Big]$$

$$= \frac{1}{2}\big(|\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle\big) - \frac{1}{4}\big(-2|\phi_1\bar{\phi}_2\rangle + 2|\phi_2\bar{\phi}_1\rangle\big)$$

$$= |\phi_1\bar{\phi}_2\rangle \tag{3.8.30}$$