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 $\because$

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

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

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

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

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

$\therefore$

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

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

while

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

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

thus

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

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

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

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

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

$$= f_{ij} \qquad (3.3.2)$$

thus the Fock operator is Hermitian.

Ex 3.5

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

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

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

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

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

$$= -\varepsilon_c - \varepsilon_d + \langle cd | cd \rangle - \langle cd | dc \rangle \qquad (3.3.3)$$

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)

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

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

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

thus

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

$$\tag{3.4.29}$$

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

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

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

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

$$(3.5.1)$$

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

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

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

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

$$(3.5.3)$$

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

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

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

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

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

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

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

Ex 3.25

Ex 3.26

Ex 3.27

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

Ex 3.28

$$
\begin{aligned}
\mathbf{X}_{\text{Schmidt}}^{\dagger}\mathbf{S}\mathbf{X}_{\text{Schmidt}} &= \begin{pmatrix} 1 & 0 \\ -S_{12}/\sqrt{1-S_{12}^2} & 1/\sqrt{1-S_{12}^2} \end{pmatrix}\begin{pmatrix} 1 & S_{12} \\ S_{12} & 1 \end{pmatrix}\begin{pmatrix} 1 & -S_{12}/\sqrt{1-S_{12}^2} \\ 0 & 1/\sqrt{1-S_{12}^2} \end{pmatrix} \\
&= \begin{pmatrix} 1 & S_{12} \\ 0 & \sqrt{1-S_{12}^2} \end{pmatrix}\begin{pmatrix} 1 & -S_{12}/\sqrt{1-S_{12}^2} \\ 0 & 1/\sqrt{1-S_{12}^2} \end{pmatrix} \\
&= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\end{aligned}
\tag{3.5.26}
$$

thus the Schmidt transformation produces orthonormal basis.

Ex 3.29

$$
E_0(R\rightarrow\infty) = \frac{1}{2}\sum_{\mu}\sum_{\nu}P_{\nu\mu}(R\rightarrow\infty)[2H_{\mu\nu}^{\text{core}} + G_{\mu\nu}]
\tag{3.5.27}
$$

where

$$
P_{\nu\mu}(R\rightarrow\infty) = \begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix}
\tag{3.5.28}
$$

$$
\begin{aligned}
G_{\mu\nu} &= \sum_{\lambda}\sum_{\sigma}P_{\lambda\sigma}(R\rightarrow\infty)\left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right] \\
&= 2\left[(\mu\nu|\phi_1\phi_1) - \frac{1}{2}(\mu\phi_1|\phi_1\nu)\right]
\end{aligned}
\tag{3.5.29}
$$

thus

$$
\begin{aligned}
E_0(R\rightarrow\infty) &= \frac{1}{2}\sum_{\mu}\sum_{\nu}P_{\nu\mu}(R\rightarrow\infty)[2H_{\mu\nu}^{\text{core}} + G_{\mu\nu}] \\
&= \frac{1}{2}\times 2[2H_{11}^{\text{core}} + G_{11}] \\
&= 2(T_{11} + V_{11}^1) + 2\left[(\phi_1\phi_1|\phi_1\phi_1) - \frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)\right] \\
&= 2T_{11} + 2V_{11}^1 + (\phi_1\phi_1|\phi_1\phi_1)
\end{aligned}
\tag{3.5.30}
$$

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	ΔE/ a.u.	ΔE/(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	ΔE/ a.u.	ΔE/(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 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

$$f^\alpha(\mathbf{r}_1, \omega_1) = \int d\omega_1 \alpha^*(\omega_1) \left[h(1) + \sum_a \int d\mathbf{x}_2 \chi_a^*(2) r_{12}^{-1} (1 - \hat{\mathscr{P}}_{12}) \chi_a(2) \right] \alpha(\omega_1)$$

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

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

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

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

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

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

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