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

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

Since

$$[ij|jj] - [ij|jj] = 0 \qquad (3.1.2)$$

we have

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

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

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

we have

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

i.e.

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

thus

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

$\therefore$

$$\varepsilon_{ba} = \varepsilon_{ab}^* \qquad (3.2.5)$$

Ex 3.3 $\because$

$$
\begin{aligned}
[\delta\chi_a|h|\chi_a] &= [\chi_a|h|\delta\chi_a]^* &(3.2.6)\\
[\chi_a\delta\chi_a|\chi_b\chi_b] &= [\delta\chi_a\chi_a|\chi_b\chi_b]^* &(3.2.7)\\
[\chi_a\chi_a|\chi_b\delta\chi_b] &= [\chi_a\chi_a|\delta\chi_b\chi_b]^* &(3.2.8)\\
[\chi_a\chi_b|\chi_b\delta\chi_a] &= [\chi_b\delta\chi_a|\chi_a\chi_b] = [\delta\chi_a\chi_b|\chi_b\chi_a]^* &(3.2.9)\\
[\chi_a\chi_b|\delta\chi_b\chi_a] &= [\delta\chi_b\chi_a|\chi_a\chi_b] = [\chi_a\delta\chi_b|\chi_b\chi_a]^* &(3.2.10)
\end{aligned}
$$

$\therefore$

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

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

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

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

thus the Fock operator is Hermitian.

Ex 3.5

$$\begin{aligned} \text{IP} &= {}^{N-2}E - E_0 \\ &= \sum_{a\neq c,d} \langle a \,|\, h \,|\, a \rangle + \frac{1}{2}\sum_{a\neq c,d}\sum_{b\neq c,d} \langle ab \,\|\, ab \rangle - \left[\sum_a \langle a \,|\, h \,|\, a \rangle + \frac{1}{2}\sum_a\sum_b \langle ab \,\|\, ab \rangle\right] \\ &= -\langle c \,|\, h \,|\, c \rangle - \langle d \,|\, h \,|\, d \rangle - \frac{1}{2}\sum_{a\neq c,d} \langle ac \,\|\, ac \rangle - \frac{1}{2}\sum_{a\neq c,d} \langle ad \,\|\, ad \rangle - \frac{1}{2}\sum_{b\neq c,d} \langle cb \,\|\, cb \rangle - \frac{1}{2}\sum_{b\neq c,d} \langle db \,\|\, db \rangle - \langle cd \,\|\, cd \rangle \\ &= -\langle c \,|\, h \,|\, c \rangle - \langle d \,|\, h \,|\, d \rangle - \sum_{a\neq c,d} \langle ac \,\|\, ac \rangle - \sum_{a\neq c,d} \langle ad \,\|\, ad \rangle - \langle cd \,\|\, cd \rangle \\ &= -\langle c \,|\, h \,|\, c \rangle - \langle d \,|\, h \,|\, d \rangle - \left(\sum_{a\neq c} \langle ac \,\|\, ac \rangle - \langle dc \,\|\, dc \rangle\right) - \left(\sum_{a\neq d} \langle ad \,\|\, ad \rangle - \langle cd \,\|\, cd \rangle\right) - \langle cd \,\|\, cd \rangle \\ &= -\varepsilon_c - \varepsilon_d + \langle cd \,|\, cd \rangle - \langle cd \,|\, dc \rangle \end{aligned} \tag{3.3.3}$$

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

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

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

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

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

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

3.4.2 Introduction of a Basis: The Roothaan Equations

Ex 3.10

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

thus

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

3.4.3 The Charge Density

Ex 3.11

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

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

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

Ex 3.12 From Ex 3.10, we have

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

i.e.

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

thus

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

thus

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

Ex 3.13 Eq. 3.122 shows

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

thus

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

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 $\because$

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

$\therefore$

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

i.e.

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

thus

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

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

Suppose

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

thus

$$\left\langle\phi'_i\,|\,\phi'_i\right\rangle = s_i\sum_\mu\left|U_{\mu i}\right|^2 \tag{3.4.19}$$

$\because$

$$\left\langle\phi'_i\,|\,\phi'_i\right\rangle > 0 \qquad \left|U_{\mu i}\right|^2 > 0 \tag{3.4.20}$$

$\therefore$

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

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)

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

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

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

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

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

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

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

Ex 3.20 At $r = 0$,

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

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

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

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

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

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

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

thus

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

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

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

Ex 3.22 Let

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

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

$\therefore$

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

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

$\therefore$

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

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

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

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

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

$\therefore$

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

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

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

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

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

thus the Schmidt transformation produces orthonormal basis.

Ex 3.29

$$E_0(R\to\infty) = \frac{1}{2}\sum_\mu\sum_\nu P_{\nu\mu}(R\to\infty)[2H^{\text{core}}_{\mu\nu} + G_{\mu\nu}] \qquad (3.5.27)$$

where

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

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

thus

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

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

$$\phi''_{1s}(\mathbf{r}) = g_{1s}(0.298073, \mathbf{r}) \qquad (3.6.1)$$

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