Contents

CHAPTER 3

The Hartree-Fock Approximation

3.1 The Hartree-Fock Equations

3.1.1 The Coulomb and Exchange Operators

3.1.2 The Fock Operator

Exercise 3.1

Show that the general matrix element of the Fock operator has the form

$$\langle\chi_i|f|\chi_j\rangle = \langle i|h|j\rangle + \sum_b [ij|bb] - [ib|bj] = \langle i|h|j\rangle + \sum_b \langle ib||jb\rangle.$$

Solution 3.1

From (3.10) and (3.11), we find that

$$\begin{aligned}
\langle i|\mathscr{J}_b|j\rangle &= \int \mathrm{d}\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\left[\int \mathrm{d}\mathbf{x}_2\, \chi_b^*(\mathbf{x}_2) r_{12}^{-1}\chi_b(\mathbf{x}_2)\right]\chi_j(\mathbf{x}_1)\\
&= \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_b^*(\mathbf{x}_2) r_{12}^{-1}\chi_j(\mathbf{x}_1)\chi_b(\mathbf{x}_2) = \langle ib|jb\rangle,\\
\langle i|\mathscr{K}_b|j\rangle &= \int \mathrm{d}\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\left[\int \mathrm{d}\mathbf{x}_2\, \chi_b^*(\mathbf{x}_2) r_{12}^{-1}\chi_j(\mathbf{x}_2)\right]\chi_b(\mathbf{x}_1)\\
&= \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_b^*(\mathbf{x}_2) r_{12}^{-1}\chi_b(\mathbf{x}_1)\chi_j(\mathbf{x}_2) = \langle ib|bj\rangle.
\end{aligned}$$

Thus, we get that

$$\begin{aligned}
\langle\chi_i|f|\chi_j\rangle &= \langle i|h|j\rangle + \sum_b \langle i|\mathscr{J}_b|j\rangle - \langle i|\mathscr{K}_b|j\rangle = \langle i|h|j\rangle + \sum_b \langle ib|jb\rangle - \langle ib|bj\rangle\\
&= \langle i|h|j\rangle + \sum_b [ij|bb] - [ib|bj] = \langle i|h|j\rangle + \sum_b \langle ib||jb\rangle.
\end{aligned}$$

3.2 Derivation of the Hartree-Fock Equations

3.2.1 Functional Variation

3.2.2 Minimization of the Energy of a Single Determinant

Exercise 3.2

Prove Eq.(3.40).

Solution 3.2

From (3.38), we find that

$$\mathscr{L}^*[\{\chi_a\}] = E_0^*[\{\chi_a\}] - \sum_{a=1}^{N}\sum_{b=1}^{N} \varepsilon_{ba}^* \left([a|b] - \delta_{ab}\right)^* = E_0^*[\{\chi_a\}] - \sum_{a=1}^{N}\sum_{b=1}^{N} \varepsilon_{ab}^* \left([a|b] - \delta_{ab}\right). \tag{a}$$

As $\mathscr{L}$ and $E_0[\{\chi_a\}]$ are real, we obtain that

$$\mathscr{L}^*[\{\chi_a\}] = \mathscr{L}[\{\chi_a\}] = E_0^*[\{\chi_a\}] - \sum_{a=1}^{N}\sum_{b=1}^{N} \varepsilon_{ba} \left([a|b] - \delta_{ab}\right). \tag{b}$$

The equation (b) can be substracted by the equation (a), we obtain that

$$\sum_{a=1}^{N}\sum_{b=1}^{N} (\varepsilon_{ab}^* - \varepsilon_{ba}) \left([a|b] - \delta_{ab}\right) = 0.$$

Due to the linear independence of $[a|b] - \delta_{ab}$, we obtain that

$$\varepsilon_{ba} = \varepsilon_{ab}^*. \tag{3.2-1}$$

Exercise 3.3

Manipulate Eq.(3.44) to show that

$$\delta E_0 = \sum_{a=1}^{N} [\delta\chi_a|h|\chi_a] + \sum_{a=1}^{N}\sum_{b=1}^{N} [\delta\chi_a\chi_a|\chi_b\chi_b] - [\delta\chi_a\chi_b|\chi_b\chi_a] + \text{complex conjugate}.$$

Solution 3.3

Note that

$$\begin{aligned}
\sum_{a=1}^{N}\sum_{b=1}^{N} [\chi_a\chi_a|\delta\chi_b\chi_b] &= \sum_{a=1}^{N}\sum_{b=1}^{n} [\chi_b\chi_b|\delta\chi_a\chi_a] = \sum_{a=1}^{N}\sum_{b=1}^{n} [\delta\chi_a\chi_a|\chi_b\chi_b], \\
\sum_{a=1}^{N}\sum_{b=1}^{N} [\chi_a\chi_a|\chi_b\delta\chi_b] &= \sum_{a=1}^{N}\sum_{b=1}^{n} [\chi_b\chi_b|\chi_a\delta\chi_a] = \sum_{a=1}^{N}\sum_{b=1}^{n} [\chi_a\delta\chi_a|\chi_b\chi_b], \\
\sum_{a=1}^{N}\sum_{b=1}^{N} [\chi_a\chi_b|\delta\chi_b\chi_a] &= \sum_{a=1}^{N}\sum_{b=1}^{n} [\chi_b\chi_a|\delta\chi_a\chi_b] = \sum_{a=1}^{N}\sum_{b=1}^{n} [\delta\chi_a\chi_b|\chi_b\chi_a], \\
\sum_{a=1}^{N}\sum_{b=1}^{N} [\chi_a\chi_b|\chi_b\delta\chi_a] &= \sum_{a=1}^{N}\sum_{b=1}^{n} [\chi_b\chi_a|\chi_a\delta\chi_b] = \sum_{a=1}^{N}\sum_{b=1}^{n} [\chi_a\delta\chi_b|\chi_b\chi_a].
\end{aligned}$$

Hence, from (3.44), we obtain that

$$\begin{aligned}
\delta E_0 = \sum_{a=1}^{N} &[\delta\chi_a|h|\chi_a] + [\chi_a|h|\delta\chi_a] \\
&+ \frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N} [\delta\chi_a\chi_a|\chi_b\chi_b] + [\chi_a\delta\chi_a|\chi_b\chi_b] + [\chi_a\chi_a|\delta\chi_b\chi_b] + [\chi_a\chi_a|\chi_b\delta\chi_b] \\
&- \frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N} [\delta\chi_a\chi_b|\chi_b\chi_a] + [\chi_a\delta\chi_b|\chi_b\chi_a] + [\chi_a\chi_b|\delta\chi_b\chi_a] + [\chi_a\chi_b|\chi_b\delta\chi_a] \\
= \sum_{a=1}^{N} &[\delta\chi_a|h|\chi_a] + [\chi_a|h|\delta\chi_a] \\
&+ \sum_{a=1}^{N}\sum_{b=1}^{N} [\delta\chi_a\chi_a|\chi_b\chi_b] + [\chi_a\delta\chi_a|\chi_b\chi_b] - \sum_{a=1}^{N}\sum_{b=1}^{N} [\delta\chi_a\chi_b|\chi_b\chi_a] + [\chi_a\delta\chi_b|\chi_b\chi_a]
\end{aligned}$$

$$= \sum_{a=1}^{N} [\delta\chi_a|h|\chi_a] + \sum_{a=1}^{N}\sum_{b=1}^{N} [\delta\chi_a\chi_a|\chi_b\chi_b] - [\delta\chi_a\chi_b|\chi_b\chi_a] + \text{complex conjugate.}$$

3.2.3 The Canonical Hartree-Fock Equations

3.3 Interpretation of Solutions to the Hartree-Fock Equations

3.3.1 Orbital Energies and Koopmans' Theorem

Exercise 3.4

Use the result of Exercise 3.1 to show that the Fock operator is a Hermitian operator, by showing that $f_{ij} = \langle\chi_i|f|\chi_j\rangle$ is an element of a Hermitian matrix.

Solution 3.4

The verification is direct. We find that

$$\begin{aligned}
(\langle i|f|j\rangle)^* &= (\langle i|h|j\rangle)^* + \sum_b (\langle ib|jb\rangle)^* - (\langle ib|bj\rangle)^* = \langle j|h|i\rangle + \sum_b \langle jb|ib\rangle - \langle bj|ib\rangle \\
&= \langle j|h|i\rangle + \sum_b \langle jb|ib\rangle - \langle jb|bi\rangle = \langle j|h|i\rangle + \sum_b \langle jb||ib\rangle = \langle j|f|i\rangle.
\end{aligned}$$

Thus, $(f_{ij})^* = f_{ji}$, which means that the Fock operator is a Hermitian operator.

Exercise 3.5

Show that the energy required to remove an electron from χ_c and one from χ_d to produce the $(N-2)$-electron single determinant $|{}^{N-2}\Psi_{cd}\rangle$ is $-\varepsilon_c - \varepsilon_d + \langle cd|cd\rangle - \langle cd|dc\rangle$.

Solution 3.5

With (3.78) and (3.79), the ionization potential is

$$\begin{aligned}
{}^{N-2}E_{c,d} - {}^{N}E_0 &= \left[\sum_{a\neq c,d} \langle a|h|a\rangle + \frac{1}{2}\sum_{a\neq c,d}\sum_{b\neq c,d} \langle ab||ab\rangle\right] - \left[\sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_a\sum_b \langle ab||ab\rangle\right] \\
&= -\left[\sum_a \langle a|h|a\rangle - \sum_{a\neq c,d}\langle a|h|a\rangle\right] - \frac{1}{2}\left[\sum_a\sum_b \langle ab||ab\rangle - \sum_{a\neq c,d}\sum_{b\neq c,d}\langle ab||ab\rangle\right] \\
&= -\left(\langle c|h|c\rangle + \langle d|h|d\rangle\right) \\
&\qquad - \frac{1}{2}\left[\sum_a\sum_{b\neq c,d}\langle ab||ab\rangle + \sum_a \langle ac||ac\rangle + \sum_a \langle ad||ad\rangle - \sum_{a\neq c,d}\sum_{b\neq c,d}\langle ab||ab\rangle\right] \\
&= -\langle c|h|c\rangle - \langle d|h|d\rangle - \frac{1}{2}\sum_a \langle ac||ac\rangle - \frac{1}{2}\sum_a \langle ad||ad\rangle \\
&\qquad - \frac{1}{2}\left[\sum_{a\neq c,d}\sum_{b\neq c,d}\langle ab||ab\rangle + \sum_{b\neq c,d}\langle cb||cb\rangle + \sum_{b\neq c,d}\langle db||db\rangle - \sum_{a\neq c,d}\sum_{b\neq c,d}\langle ab||ab\rangle\right] \\
&= -\langle c|h|c\rangle - \langle d|h|d\rangle - \frac{1}{2}\sum_a \langle ac||ac\rangle - \frac{1}{2}\sum_a \langle ad||ad\rangle \\
&\qquad - \frac{1}{2}\left[\sum_b \langle cb||cb\rangle - \langle cc||cc\rangle - \langle cd||cd\rangle + \sum_b \langle db||db\rangle - \langle dc||dc\rangle - \langle dd||dd\rangle\right] \\
&= -\langle c|h|c\rangle - \langle d|h|d\rangle - \frac{1}{2}\sum_a \langle ac||ac\rangle - \frac{1}{2}\sum_a \langle ad||ad\rangle
\end{aligned}$$

$$
\begin{aligned}
& -\frac{1}{2}\sum_a\langle ca||ca\rangle-\frac{1}{2}\sum_a\langle da||da\rangle+\frac{1}{2}\langle cd||cd\rangle+\frac{1}{2}\langle dc||dc\rangle \\
&= -\langle c|h|c\rangle-\langle d|h|d\rangle-\sum_a\langle ac||ac\rangle-\sum_a\langle ad||ad\rangle+\langle cd||cd\rangle \\
&= -\left[\langle c|h|c\rangle+\sum_b\langle bc||bc\rangle\right]-\left[\langle d|h|d\rangle+\sum_b\langle bd||bd\rangle\right]+\langle cd||cd\rangle \\
&= -\varepsilon_c-\varepsilon_d+\langle cd|cd\rangle-\langle cd|dc\rangle .
\end{aligned}
$$

Exercise 3.6

Use Eq.(3.87) to obtain an expression for ${}^{N+1}E^r$ and then subtract it from ${}^{N}E_0$ (Eq.(3.88)) to show that

$$ {}^{N}E_0-{}^{N+1}E^r=-\langle r|h|r\rangle-\sum_b\langle rb||rb\rangle . $$

Solution 3.6

The proof is direct.

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

3.3.2 Brillouin's Theorem

3.3.3 The Hartree-Fock Hamiltonian

Exercise 3.7

Use definition (2.115) of a Slater determinant and the fact that $\mathscr{H}_0$ commutes with any operator that permutes the electron labels, to show that $|\Psi_0\rangle$ is an eigenfunction of $\mathscr{H}_0$ with eigenvalue $\sum_a \varepsilon_a$. Why does $\mathscr{H}_0$ commute with the permutation operator?

Solution 3.7

The proof is not fundamentally different from that of Exercise 2.15; it only requires replacing $\mathscr{H}=\sum_{i=1}^N h(i)$ with $\mathscr{H}_0=\sum_{i=1}^N f(i)$. The reason why $\mathscr{H}_0$ commutes with the permutation operator is that it is invariant to permutations of the electron labels.

Exercise 3.8

Use expression (3.108) for $\mathscr{V}$, expression (3.18) for the Hartree-Fock potential $v^{\mathrm{HF}}(i)$, and the rules for evaluating matrix elements to explicitly show that $\langle\Psi_0|\mathscr{V}|\Psi_0\rangle=-\frac{1}{2}\sum_a\sum_b\langle ab||ab\rangle$ and hence that

$E_0^{[1]}$ cancels the double counting of electron-electron repulsions in $E_0^{(0)} = \sum_a \varepsilon_a$ to give the correct Hartree-Fock energy E_0.

Solution 3.8

From (2.107), (3.18), (3.73) and (3.74), we find that

$$\begin{aligned}
E_0^{[1]} &= \langle\Psi_0|\mathscr{V}|\Psi_0\rangle = \langle\Psi_0|\mathscr{O}_2|\Psi_0\rangle - \langle\Psi_0|\sum_a v^{\mathrm{HF}}(a)|\Psi_0\rangle = \langle\Psi_0|\mathscr{O}_2|\Psi_0\rangle - \sum_{a=1}^{N}\langle\chi_a|\sum_b \mathscr{J}_b - \mathscr{K}_b|\chi_a\rangle \\
&= \frac{1}{2}\sum_{ab}\langle ab||ab\rangle - \sum_{ab}\langle\chi_b|\mathscr{J}_a|\chi_b\rangle - \langle\chi_b|\mathscr{K}_a|\chi_b\rangle = \frac{1}{2}\sum_{ab}\langle ab||ab\rangle - \sum_{ab}\langle ba|ba\rangle - \langle ba|ab\rangle \\
&= \frac{1}{2}\sum_{ab}\langle ab||ab\rangle - \sum_{ab}\langle ba||ba\rangle = \frac{1}{2}\sum_{ab}\langle ab||ab\rangle - \sum_{ab}\langle ab||ab\rangle = -\frac{1}{2}\sum_{ab}\langle ab||ab\rangle.
\end{aligned}$$

Hence, $E_0^{[1]}$ cancels the double counting of electron-electron repulsions in $E_0^{(0)} = \sum_a \varepsilon_a$ to give the correct Hartree-Fock energy E_0.

3.4 Restricted Closed-Shell Hartree-Fock: The Roothaan Equations

3.4.1 Closed-Shell Hartree-Fock: Restricted Spin Orbitals

Exercise 3.9

Convert the spin orbital expression for orbital energies

$$\varepsilon_i = \langle\chi_i|h|\chi_i\rangle + \sum_b^N \langle\chi_i\chi_b||\chi_i\chi_b\rangle$$

to the closed-shell expression

$$\varepsilon_i = (\psi_i|h|\psi_i) + \sum_b^{N/2} 2(ii|bb) - (ib|bi) = h_{ii} + \sum_b^{N/2} 2J_{ib} - K_{ib}. \tag{3.128}$$

Solution 3.9

When χ_i is a spatial orbital ψ_i multiplied by α, namely, $\chi_i = \psi_i$, we obtain that

$$\begin{aligned}
\varepsilon_i &= \langle i|h|i\rangle + \sum_b^N \langle ib||ib\rangle = \langle i|h|i\rangle + \sum_b^N \langle ib|ib\rangle - \langle ib|bi\rangle = \langle i|h|i\rangle + \sum_b^N [ii|bb] - [ib|bi] \\
&= (i|h|i) + \sum_b^{N/2} [ii|bb] - [ib|bi] + \sum_{\bar{b}}^{N/2} [ii|\bar{b}\bar{b}] - [i\bar{b}|\bar{b}i] = (i|h|i) + \sum_b^{N/2} (ii|bb) - (ib|bi) + \sum_b^{N/2} (ii|bb) \\
&= (i|h|i) + \sum_b^{N/2} 2(ii|bb) - (ib|bi) = h_{ii} + \sum_b^{N/2} 2J_{ib} - K_{ib}.
\end{aligned}$$

When χ_i is a spatial orbital ψ_i multiplied by β, namely, $\chi_i = \bar{\psi}_i$, we obtain that

$$\begin{aligned}
\varepsilon_{\bar{i}} &= \langle\bar{i}|h|\bar{i}\rangle + \sum_b^N \langle\bar{i}b||\bar{i}b\rangle = \langle\bar{i}|h|\bar{i}\rangle + \sum_b^N \langle\bar{i}b|\bar{i}b\rangle - \langle\bar{i}b|b\bar{i}\rangle = \langle\bar{i}|h|\bar{i}\rangle + \sum_b^N [\bar{i}\bar{i}|bb] - [\bar{i}b|b\bar{i}] \\
&= (i|h|i) + \sum_b^{N/2} [\bar{i}\bar{i}|bb] - [\bar{i}b|b\bar{i}] + \sum_{\bar{b}}^{N/2} [\bar{i}\bar{i}|\bar{b}\bar{b}] - [\bar{i}\bar{b}|\bar{b}\bar{i}] = (i|h|i) + \sum_b^{N/2} (ii|bb) + \sum_b^{N/2} (ii|bb) - (ib|bi)
\end{aligned}$$

$$= (i|h|i) + \sum_{b}^{N/2} 2(ii|bb) - (ib|bi) = h_{ii} + \sum_{b}^{N/2} 2J_{ib} - K_{ib}.$$

In conclusion, we conclude that in the closed-shell structure,

$$\varepsilon_i = (\psi_i|h|\psi_i) + \sum_{b}^{N/2} 2(ii|bb) - (ib|bi) = h_{ii} + \sum_{b}^{N/2} 2J_{ib} - K_{ib}. \tag{3.9-1}$$

3.4.2 Introduction of a Basis: The Roothaan Equations

Exercise 3.10

Show that $\mathbf{C}^\dagger\mathbf{S}\mathbf{C} = \mathbf{1}$. *Hint*: Use the fact that the molecular orbitals $\{\psi_i\}$ are orthonormal.

Solution 3.10

As the molecular orbitals $\{\psi_i\}$ are orthonormal, we can find that

$$\delta_{ij} = \langle\psi_i|\psi_j\rangle = \left(\sum_{\mu=1}^{K} C_{\mu i}^* \langle\phi_\mu|\right)\left(\sum_{\nu=1}^{K} C_{\nu j}|\phi_\nu\rangle\right) = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} C_{\mu i}^* C_{\nu j}\langle\phi_\mu|\phi_\nu\rangle$$
$$= \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} \mathbf{C}_{i\mu}^\dagger \mathbf{C}_{\nu j} S_{\mu\nu} = (\mathbf{C}^\dagger\mathbf{S}\mathbf{C})_{ij}.$$

Thus, we conclude that $\mathbf{C}^\dagger\mathbf{S}\mathbf{C} = \mathbf{1}$.

3.4.3 The Charge Density

Exercise 3.11

Use the density operator $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r}_i - \mathbf{r})$, the rules for evaluating matrix elements in Chapter 2, and the rules for converting from spin orbitals to spatial orbitals, to derive (3.142) from $\rho(\mathbf{r}) = \langle\Psi_0|\hat{\rho}(\mathbf{r})|\Psi_0\rangle$.

Solution 3.11

Using the rules for evaluating matrix elements in Chapter 2, we can obtain that

$$\langle\Psi_0|\hat{\rho}(\mathbf{r})|\Psi_0\rangle = \sum_a \langle a|\delta(\mathbf{r}_i - \mathbf{r})|a\rangle = \sum_a \int \mathrm{d}\mathbf{x}_1 \int \mathrm{d}\mathbf{x}_2\, \langle a|\mathbf{x}_1\rangle\langle\mathbf{x}_1|\delta(\mathbf{r}_2 - \mathbf{r})|\mathbf{x}_2\rangle\langle\mathbf{x}_2|a\rangle$$
$$= \sum_a \int \mathrm{d}\mathbf{r}_1\, \psi_a^*(\mathbf{r}_1)\psi_a(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}) \int \mathrm{d}\omega \langle a|\omega\rangle\langle\omega|a\rangle = \sum_a |\psi_a(\mathbf{r})|^2.$$

We find that $\langle\Psi_0|\hat{\rho}(\mathbf{r})|\Psi_0\rangle$ is independent of the spin of these spin orbitals. Thus, in a closed-shell molecule, the sum of the spin functions is converted into twice the sum of their spatial functions, viz.,

$$\rho(\mathbf{r}) = \langle\Psi_0|\hat{\rho}(\mathbf{r})|\Psi_0\rangle = \sum_a |\psi_a(\mathbf{r})|^2 = 2\sum_a^{N/2} |\psi_a(\mathbf{r})|^2. \tag{3.11-1}$$

Exercise 3.12

A matrix $\mathbf{A}$ is said to be idempotent if $\mathbf{A}^2 = \mathbf{A}$. Use the result of Exercise 3.10 to show that $\mathbf{PSP} = 2\mathbf{P}$, i.e., show that $\frac{1}{2}\mathbf{P}$ would be idempotent in an orthonormal basis.

Solution 3.12

Using the conclusion of Exercise 3.10, we know that with an orthonormal basis, we get that

$$\delta_{ij} = (\mathbf{C}^\dagger \mathbf{S}\mathbf{C})_{ij} = \sum_{\lambda\sigma} C^*_{\lambda i} S_{\lambda\sigma} C_{\sigma j}$$

With an orthonormal basis, namely, $\langle\psi_a|\psi_b\rangle = \delta_{ab}$, we find that

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

Exercise 3.13

Use the expression (3.122) for the closed-shell Fock operator to show that

$$f(\mathbf{r}_1) = h(\mathbf{r}_1) + v^{\mathrm{HF}}(\mathbf{r}_1) = h(\mathbf{r}_1) + \frac{1}{2}\sum_{\lambda\sigma} P_{\lambda\sigma}\left[\int \mathrm{d}\mathbf{r}_2\, \phi^*_\sigma(\mathbf{r}_2)(2-\mathscr{P}_{12})r_{12}^{-1}\phi_\lambda(\mathbf{r}_2)\right].$$

Solution 3.13

From (3.122), we obtain that

$$\begin{aligned}
f(\mathbf{r}_1) &= h(\mathbf{r}_1) + \sum_a^{N/2} \int \mathrm{d}\mathbf{r}_2\, \psi^*_a(\mathbf{r}_2)(2-\mathscr{P}_{12})r_{12}^{-1}\psi_a(\mathbf{r}_2) \\
&= h(\mathbf{r}_1) + \sum_a^{N/2} \int \mathrm{d}\mathbf{r}_2 \left(\sum_\sigma \phi^*_\sigma(\mathbf{r}_2)C^*_{\sigma a}\right)(2-\mathscr{P}_{12})r_{12}^{-1}\left(\sum_\lambda \phi_\lambda(\mathbf{r}_2)C_{\lambda a}\right) \\
&= h(\mathbf{r}_1) + \sum_a^{N/2} C^*_{\sigma a}C_{\lambda a}\sum_\sigma\sum_\lambda \int \mathrm{d}\mathbf{r}_2\, \phi^*_\sigma(\mathbf{r}_2)(2-\mathscr{P}_{12})r_{12}^{-1}\phi_\lambda(\mathbf{r}_2) \\
&= h(\mathbf{r}_1) + \frac{1}{2}\left(2\sum_a^{N/2} C^*_{\sigma a}C_{\lambda a}\right)\sum_{\lambda\sigma}\int \mathrm{d}\mathbf{r}_2\, \phi^*_\sigma(\mathbf{r}_2)(2-\mathscr{P}_{12})r_{12}^{-1}\phi_\lambda(\mathbf{r}_2) \\
&= h(\mathbf{r}_1) + \frac{1}{2}\sum_{\lambda\sigma} P_{\lambda\sigma}\left[\int \mathrm{d}\mathbf{r}_2\, \phi^*_\sigma(\mathbf{r}_2)(2-\mathscr{P}_{12})r_{12}^{-1}\phi_\lambda(\mathbf{r}_2)\right].
\end{aligned}$$

3.4.4 Expression for the Fock Matrix

Exercise 3.14

Assume that the basis functions are real and use the symmetry of the two-electron integrals [$(\mu\nu|\lambda\sigma) = (\nu\mu|\lambda\sigma) = (\lambda\sigma|\mu\nu)$, etc.] to show that for a basis set of size $K = 100$ there are 12,753,775 $= O(K^4/8)$ unique two-electron integrals.

Solution 3.14

Due to 8-fold symmetry of real two-electron integrals, what we have to consider is just the number of unique "electron pairs" $(\mu\nu)$. If the number of electrons is denoted as K, the number of unique electron pairs will be $\frac{K(K+1)}{2}$. For example, if there are 3 electrons, there will be 6 unique electron pairs, (11), (12), (13), (22), (23) and (33). For two-electron integrals, in the same way, their number is

$$\frac{1}{2}\left[\frac{K(K+1)}{2}\left(\frac{K(K+1)}{2}+1\right)\right] = \frac{1}{8}K(K+1)(K^2+K+2) = \frac{K(K+1)(K^2+K+2)}{8}.$$

Substituting the above formula into $K = 100$, we get 12753775.

3.4.5 Orthogonalization of the Basis

Exercise 3.15

Use the definition of $S_{\mu\nu} = \int \mathrm{d}\mathbf{r}\, \phi_\mu^* \phi_\nu$ to show that the eigenvalues of $\mathbf{S}$ are all positive. *Hint*: consider $\sum_\nu S_{\mu\nu} c_\nu^i = s_i c_\mu^i$, multiply by c_μ^{i*} and sum, where $\mathbf{c}^i$ is the ith column of $\mathbf{U}$.

Solution 3.15

From (3.166),

$$\mathbf{SU} = \mathbf{Us} \Leftrightarrow (\mathbf{SU})_{\mu i} = (\mathbf{Us})_{\mu i} \Leftrightarrow \sum_\nu S_{\mu\nu} c_\nu^i = c_\mu^i s_i,$$

which can be multiplied by c_μ^{i*} and sum, leading to

$$\sum_{\mu\nu} c_\mu^{i*} S_{\mu\nu} c_\nu^i = \sum_\mu s_i c_\mu^{i*} c_\mu^i = s_i \sum_\mu c_\mu^{i*} c_\mu^i = s_i \sum_\mu |c_\mu^i|^2.$$

For any nontrivial wave function, its inner product is always positive. We can find that

$$\sum_{\mu\nu} c_\mu^{i*} S_{\mu\nu} c_\nu^i = \sum_{\mu\nu} c_\mu^{i*} c_\nu^i \int \mathrm{d}\mathbf{r} \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r}) = \int \mathrm{d}\mathbf{r} \left(\sum_\mu c_\mu^{i*} \phi_\mu^*(\mathbf{r}) \right) \left(\sum_\nu c_\nu^i \phi_\nu(\mathbf{r}) \right) > 0.$$

Thus, we get that

$$s_i = \frac{\sum_{\mu\nu} c_\mu^{i*} S_{\mu\nu} c_\nu^i}{\sum_\mu |c_\mu^i|^2} > 0, \ \forall i = 1, 2, \ldots, K. \tag{3.1}$$

In other words, the eigenvalues of $\mathbf{S}$ are all positive.

Exercise 3.16

Use (3.179), (3.180), and (3.162) to derive (3.174) and (3.177).

Solution 3.16

From (3.133), (3.162) and (3.179), we find that

$$\psi_i = \sum_{\mu=1}^K C'_{\mu i} \phi'_\mu = \sum_{\mu=1}^K C'_{\mu i} \sum_{\nu=1}^K X_{\nu\mu} \phi_\nu = \sum_{\nu=1}^K \left(\sum_{\mu=1}^K X_{\nu\mu} C'_{\mu i} \right) \phi_\nu = \sum_{\nu=1}^K C_{\nu i} \phi_\nu.$$

Due to the linear independence of $\{\phi_\nu\}$, we get that

$$C_{\nu i} = \sum_{\mu=1}^K X_{\nu\mu} C'_{\mu i},$$

which equals

$$\mathbf{C} = \mathbf{X}\mathbf{C}'. \tag{3.16-1}$$

If $\mathbf{X}$ is reversible, we can obtain

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

Thus (3.174) has been verified.
From (3.162) and (3.180), we can find that

$$\begin{aligned} F'_{\mu\nu} &= \int \mathrm{d}\mathbf{r}_1 \phi'^*_\mu(1) f(1) \phi'_\nu(1) = \int \mathrm{d}\mathbf{r}_1 \left(\sum_\lambda \phi_\lambda^*(1) X_{\lambda\mu}^* \right) f(1) \left(\sum_\sigma X_{\sigma\nu} \phi_\sigma(1) \right) \\ &= \sum_{\lambda\sigma} X_{\lambda\mu}^* \int \mathrm{d}\mathbf{r}_1 \phi_\lambda^*(1) f(1) \phi_\sigma(1) X_{\sigma\nu} = \sum_{\lambda\sigma} X_{\lambda\mu}^* f_{\lambda\sigma} X_{\sigma\nu} = \sum_{\lambda\sigma} X_{\mu\lambda}^\dagger F_{\lambda\sigma} X_{\sigma\nu}. \end{aligned}$$

In other words,

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}.$$

Thus (3.177) has been verified.

3.4.6 The SCF Procedure

3.4.7 Expectation Values and Population Analysis

Exercise 3.17

Derive Equation (3.184) from (3.183).

Solution 3.17

With (3.145) and (3.149), we find that

$$\begin{aligned}
E_0 &= \sum_a^{N/2} h_{aa} + f_{aa} = \sum_a^{N/2} \left[\int \mathrm{d}\mathbf{r}_1 \psi_a^*(1) h(1) \psi_a(1) + \int \mathrm{d}\mathbf{r}_1 \psi_a^*(1) f(1) \psi_a(1) \right] \\
&= \sum_a^{N/2} \left[\int \mathrm{d}\mathbf{r}_1 \left(\sum_\mu C_{\mu a}^* \phi_\mu^*(1) \right) h(1) \left(\sum_\nu C_{\nu a} \phi_\nu(1) \right) \right. \\
&\qquad \left. + \int \mathrm{d}\mathbf{r}_1 \left(\sum_\mu C_{\mu a}^* \phi_\mu^*(1) \right) f(1) \left(\sum_\nu C_{\nu a} \phi_\nu(1) \right) \right] \\
&= \frac{1}{2} \sum_{\mu\nu} \left(\int \mathrm{d}\mathbf{r}_1 \phi_\mu^*(1) h(1) \phi_\nu(1) + \int \mathrm{d}\mathbf{r}_1 \phi_\mu^*(1) f(1) \phi_\nu(1) \right) \sum_a^{N/2} 2 C_{\mu a}^* C_{\nu a} \\
&= \frac{1}{2} \sum_{\mu\nu} P_{\nu\mu} \left(H_{\mu\nu}^{\mathrm{core}} + F_{\mu\nu} \right).
\end{aligned}$$

Exercise 3.18

Derive the right-hand side of Eq.(3.198), i.e., show that $\alpha = 1/2$ is equivalent to a population analysis based on the diagonal elements of $\mathbf{P}'$.

Solution 3.18

From (3.144) and (3.200), we find that

$$\begin{aligned}
\rho(\mathbf{r}) &= \sum_{\lambda\sigma} P_{\lambda\sigma} \phi_\lambda(\mathbf{r}) \phi_\sigma^*(\mathbf{r}) = \sum_{\lambda\sigma} (\mathbf{S}^{-\frac{1}{2}} \mathbf{S}^{\frac{1}{2}} \mathbf{P} \mathbf{S}^{\frac{1}{2}} \mathbf{S}^{-\frac{1}{2}})_{\lambda\sigma} \phi_\lambda(\mathbf{r}) \phi_\sigma^*(\mathbf{r}) \\
&= \sum_{\lambda\sigma} \phi_\lambda(\mathbf{r}) \phi_\sigma^*(\mathbf{r}) \sum_{\mu\nu} S_{\lambda\mu}^{-\frac{1}{2}} (\mathbf{S}^{\frac{1}{2}} \mathbf{P} \mathbf{S}^{\frac{1}{2}})_{\mu\nu} S_{\nu\sigma}^{-\frac{1}{2}} = \sum_{\mu\nu} (\mathbf{S}^{\frac{1}{2}} \mathbf{P} \mathbf{S}^{\frac{1}{2}})_{\mu\nu} \sum_{\lambda\sigma} \phi_\lambda(\mathbf{r}) \phi_\sigma^*(\mathbf{r}) S_{\lambda\mu}^{-\frac{1}{2}} S_{\nu\sigma}^{-\frac{1}{2}} \\
&= \sum_{\mu\nu} (\mathbf{S}^{\frac{1}{2}} \mathbf{P} \mathbf{S}^{\frac{1}{2}})_{\mu\nu} \left(\sum_\lambda S_{\lambda\mu}^{-\frac{1}{2}} \phi_\lambda(\mathbf{r}) \right) \left(\sum_\sigma S_{\nu\sigma}^{-\frac{1}{2}} \phi_\sigma^*(\mathbf{r}) \right) = \sum_{\mu\nu} (\mathbf{S}^{\frac{1}{2}} \mathbf{P} \mathbf{S}^{\frac{1}{2}})_{\mu\nu} \phi_\mu'(\mathbf{r}) \phi_\nu'(\mathbf{r}).
\end{aligned}$$

Compared to (3.199), due to the linear independence of $\{\phi_\mu'(\mathbf{r}) \phi_\nu'(\mathbf{r})\}$, we get that

$$\mathbf{P}_{\mu\nu}' = (\mathbf{S}^{\frac{1}{2}} \mathbf{P} \mathbf{S}^{\frac{1}{2}})_{\mu\nu}. \tag{3.18-1}$$

Hence, we get

$$\sum_\mu \mathbf{P}_{\mu\mu}' = \sum_\mu (\mathbf{S}^{\frac{1}{2}} \mathbf{P} \mathbf{S}^{\frac{1}{2}})_{\mu\mu}. \tag{3.18-2}$$

3.5 Model Calculations on H_2 and HeH^+

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

Exercise 3.19

Derive Eq.(3.207).

Solution 3.19

Note that

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

The coefficients of the exponential part are simplified as follows.

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

With (3.208), (3.209), and (3.210), we obtain that

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

In a nutshell, we have verified (3.207).

Exercise 3.20

Calculate the values of $\phi(\mathbf{r})$ at the origin for the three STO-LG contracted functions and compare with the value of $(\pi)^{-1/2}$ for a Slater function ($\zeta = 1.0$).

Solution 3.20

The value of $\phi(\mathbf{r})$ at the origin for the three STO-LG contracted functions are:

$$\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \mathrm{STO-1G}, (0,0,0)) = \left(\frac{2\times 0.270950}{\pi}\right)^{\frac{3}{4}} = 0.267656,$$
$$\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \mathrm{STO-2G}, (0,0,0))$$
$$= 0.678914 \times \left(\frac{2\times 0.151623}{\pi}\right)^{\frac{3}{4}} + 0.430129 \times \left(\frac{2\times 0.851819}{\pi}\right)^{\frac{3}{4}} = 0.389383,$$
$$\phi_{1s}^{\mathrm{CGF}}(\zeta = 1.0, \mathrm{STO-3G}, (0,0,0))$$
$$= 0.444635 \times \left(\frac{2\times 0.109818}{\pi}\right)^{\frac{3}{4}} + 0.535328 \times \left(\frac{2\times 0.405771}{\pi}\right)^{\frac{3}{4}} + 0.154329 \times \left(\frac{2\times 2.22766}{\pi}\right)^{\frac{3}{4}}$$
$$= 0.454986,$$

while the value of $\phi(\mathbf{r})$ at the origin for a Slater function ($\zeta = 1.0$) is

$$\phi_{1s}^{\mathrm{SF}}(\zeta = 1.0, (0,0,0)) = \left(\frac{1.0^3}{\pi}\right)^{\frac{1}{2}} = \pi^{-\frac{1}{2}} = 0.564189.$$

At the origin, the difference between the STO-LG contracted functions ($L = 1,2,3$) and the Slater function is very large.

3.5.2 STO-3G H_2

Exercise 3.21

Use definition (3.219) for the STO-1G function and the scaling relation (3.224) to show that the STO-1G overlap for an orbital exponent $\zeta = 1.24$ at $R = 1.4$ a.u., corresponding to result (3.229), is $S_{12} = 0.6648$. Use the formula in Appendix A for overlap integrals. Do not forget normalization.

Solution 3.21

3-21 so