

<b>3</b>	<b>The Hartree-Fock Approximation</b>	<b>3</b>
3.1	The Hartree-Fock Equations . . . . .	3
3.1.1	The Coulomb and Exchange Operators . . . . .	3
3.1.2	The Fock Operator . . . . .	3
	Exercise 3.1 . . . . .	3
3.2	Derivation of the Hartree-Fock Equations . . . . .	3
3.2.1	Functional Variation . . . . .	3
3.2.2	Minimization of the Energy of a Single Determinant . . . . .	3
	Exercise 3.2 . . . . .	3
	Exercise 3.3 . . . . .	4
3.2.3	The Canonical Hartree-Fock Equations . . . . .	5
3.3	Interpretation of Solutions to the Hartree-Fock Equations . . . . .	5
3.3.1	Orbital Energies and Koopmans' Theorem . . . . .	5
	Exercise 3.4 . . . . .	5
	Exercise 3.5 . . . . .	5
	Exercise 3.6 . . . . .	6
3.3.2	Brillouin's Theorem . . . . .	6
3.3.3	The Hartree-Fock Hamiltonian . . . . .	6
	Exercise 3.7 . . . . .	6
	Exercise 3.8 . . . . .	6
3.4	Restricted Closed-Shell Hartree-Fock: The Roothaan Equations . . . . .	7
3.4.1	Closed-Shell Hartree-Fock: Restricted Spin Orbitals . . . . .	7
	Exercise 3.9 . . . . .	7
3.4.2	Introduction of a Basis: The Roothaan Equations . . . . .	8
	Exercise 3.10 . . . . .	8
3.4.3	The Charge Density . . . . .	8
	Exercise 3.11 . . . . .	8
	Exercise 3.12 . . . . .	8
	Exercise 3.13 . . . . .	9
3.4.4	Expression for the Fock Matrix . . . . .	9
	Exercise 3.14 . . . . .	9
3.4.5	Orthogonalization of the Basis . . . . .	10
	Exercise 3.15 . . . . .	10
	Exercise 3.16 . . . . .	10
3.4.6	The SCF Procedure . . . . .	11
3.4.7	Expectation Values and Population Analysis . . . . .	11
	Exercise 3.17 . . . . .	11
	Exercise 3.18 . . . . .	11
3.5	Model Calculations on $H_2$ and $HeH^+$ . . . . .	11
3.5.1	The 1s Minimal STO-3G Basis set . . . . .	11
	Exercise 3.19 . . . . .	11
	Exercise 3.20 . . . . .	12
3.5.2	STO-3G $H_2$ . . . . .	13
	Exercise 3.21 . . . . .	13
	Exercise 3.22 . . . . .	13
	Exercise 3.23 . . . . .	13
	Exercise 3.24 . . . . .	14
	Exercise 3.25 . . . . .	14
	Exercise 3.26 . . . . .	15

	Exercise 3.27 . . . . .	16
3.5.3	An SCF Calculation on STO-3G HeH <sup>+</sup> . . . . .	16
	Exercise 3.28 . . . . .	16
	Exercise 3.29 . . . . .	17
3.6	Polyatomic Basis Sets . . . . .	17
3.6.1	Contracted Gaussian Functions . . . . .	17
3.6.2	Minimal Basis Sets: STO-3G . . . . .	17
3.6.3	Double Zeta Basis Sets: 4-31G . . . . .	17
	Exercise 3.30 . . . . .	17
3.6.4	Polarized Basis Sets: 6-31G* and 6-31G** . . . . .	18
	Exercise 3.31 . . . . .	18
3.7	Some Illustrative Closed-Shell Calculations . . . . .	19
3.7.1	Total Energies . . . . .	19
	Exercise 3.32 . . . . .	19
3.7.2	Ionization Potentials . . . . .	20
3.7.3	Equilibrium Geometries . . . . .	20
3.7.4	Population Analysis and Dipole Moments . . . . .	20
3.8	Unrestricted Open-Shell Hartree-Fock: The Pople-Nesbet	
	Equations . . . . .	20
3.8.1	Open-Shell Hartree Fock: Unrestricted Spin Orbitals . . . . .	20
	Exercise 3.33 . . . . .	20
	Exercise 3.34 . . . . .	22
	Exercise 3.35 . . . . .	22
3.8.2	Introduction of a Basis: The Pople-Nesbet Equations . . . . .	23
3.8.3	Unrestricted Density Matrices . . . . .	23
	Exercise 3.36 . . . . .	23
	Exercise 3.37 . . . . .	23
	Exercise 3.38 . . . . .	23
	Exercise 3.39 . . . . .	24
3.8.4	Expression for the Fock Matrices . . . . .	25
3.8.5	Solution of the Unrestricted SCF Equations . . . . .	25
	Exercise 3.40 . . . . .	25
3.8.6	Illustrative Unrestricted Calculations . . . . .	26
	Exercise 3.41 . . . . .	26
3.8.7	The Dissociation Problem and its Unrestricted Solution . . . . .	27
	Exercise 3.42 . . . . .	27
	Exercise 3.43 . . . . .	27
	Exercise 3.44 . . . . .	27

## 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

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

###### Solution 3.1

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

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

Thus, we get that

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

#### 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

$$\mathcal{L}^*[\{\chi_a\}] = E_0^*[\{\chi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba}^* ([a|b] - \delta_{ab})^* = E_0^*[\{\chi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ab}^* ([a|b] - \delta_{ab}). \quad (\text{a})$$

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

$$\mathcal{L}^*[\{\chi_a\}] = \mathcal{L}[\{\chi_a\}] = E_0^*[\{\chi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} ([a|b] - \delta_{ab}). \quad (\text{b})$$

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

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

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

$$\varepsilon_{ba} = \varepsilon_{ab}^*. \quad (3.2-1)$$

**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

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

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

### 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

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

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  $\chi_c$  and one from  $\chi_d$  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

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

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

**Exercise 3.6**

Use Eq.(3.87) to obtain an expression for  $^{N+1}E^r$  and then subtract it from  $^NE_0$  (Eq.(3.88)) to show that

$$^NE_0 - ^{N+1}E^r = -\langle r|h|r \rangle - \sum_b \langle rb||rb \rangle.$$

**Solution 3.6**

The proof is direct.

$$\begin{aligned}
^NE_0 - ^{N+1}E^r &= \left[ \sum_a \langle a|h|a \rangle + \frac{1}{2} \sum_a \sum_b \langle ab||ab \rangle \right] - \left[ \sum_{a+r} \langle a|h|a \rangle + \frac{1}{2} \sum_{a+r} \sum_{b+r} \langle ab||ab \rangle \right] \\
&= -\left[ \sum_{a+r} \langle a|h|a \rangle - \sum_a \langle a|h|a \rangle \right] - \frac{1}{2} \left[ \sum_{a+r} \sum_{b+r} \langle ab||ab \rangle - \sum_a \sum_b \langle ab||ab \rangle \right] \\
&= -\langle r|h|r \rangle - \frac{1}{2} \left[ \sum_{a+r} \sum_b \langle ab||ab \rangle + \sum_{a+r} \langle ar||ar \rangle - \sum_a \sum_b \langle ab||ab \rangle \right] \\
&= -\langle r|h|r \rangle - \frac{1}{2} \left[ \sum_a \sum_b \langle ab||ab \rangle + \sum_b \langle rb||rb \rangle + \sum_a \langle ar||ar \rangle + \langle rr||rr \rangle - \sum_a \sum_b \langle ab||ab \rangle \right] \\
&= -\langle r|h|r \rangle - \frac{1}{2} \left[ \sum_b \langle rb||rb \rangle + \sum_b \langle br||br \rangle \right] = -\langle r|h|r \rangle - \sum_b \langle rb||rb \rangle.
\end{aligned}$$

**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  $\mathcal{H}_0$  commutes with any operator that permutes the electron labels, to show that  $|\Psi_0\rangle$  is an eigenfunction of  $\mathcal{H}_0$  with eigenvalue  $\sum_a \varepsilon_a$ . Why does  $\mathcal{H}_0$  commute with the permutation operator?

**Solution 3.7**

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

**Exercise 3.8**

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

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

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

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

### Solution 3.9

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

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

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

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

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

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

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

### 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

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

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

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

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.,

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

#### 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

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

**Solution 3.13**

From (3.122), we obtain that

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

**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  $[(\mu\nu|\lambda\sigma) = (\nu\mu|\lambda\sigma) = (\lambda\sigma|\mu\nu), \text{ etc.}]$  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  $S_{\mu\nu} = \int d\mathbf{r} \phi_\mu^* \phi_\nu$  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  $c_\mu^{i*}$  and sum, where  $\mathbf{c}^i$  is the  $i$ th column of  $\mathbf{U}$ .

#### Solution 3.15

From (3.166),

$$\mathbf{S}\mathbf{U} = \mathbf{U}\mathbf{s} \Leftrightarrow (\mathbf{S}\mathbf{U})_{\mu i} = (\mathbf{U}\mathbf{s})_{\mu i} \Leftrightarrow \sum_\nu S_{\mu\nu} c_\nu^i = c_\mu^i s_i,$$

which can be multiplied by  $c_\mu^{i*}$  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

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

Thus, we get that

$$s_i = \frac{\sum_{\mu\nu} c_\mu^{i*} S_{\mu\nu} c_\nu^i}{\sum_\mu |c_\mu^i|^2} > 0, \quad \forall i = 1, 2, \dots, K. \quad (3.15-1)$$

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

$$\mathbf{C} = \mathbf{X}\mathbf{C}'. \quad (3.16-1)$$

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

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

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

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

#### 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

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

Hence, we get

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

## 3.5 Model Calculations on H<sub>2</sub> and HeH<sup>+</sup>

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

#### Exercise 3.19

Derive Eq.(3.207).

**Solution 3.19**

Note that

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

The coefficients of the exponential part are simplified as follows.

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

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

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

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:

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

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

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

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<sub>2</sub>

## 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

Since  $1.24^2 \times 0.270950 = 0.416613$ , we get that

$$\phi_{1s}^{\text{CGF}}(\zeta = 1.24, \text{STO} - 1\text{G}) = \phi_{1s}^{\text{GF}}(0.416613),$$

and thus using (A.1-5),

$$\begin{aligned} S_{12} &= \int d\mathbf{r} \phi_{1s}^{\text{GF}}(0.416613, \mathbf{r} - \mathbf{R}_A) \phi_{1s}^{\text{GF}}(0.416613, \mathbf{r} - \mathbf{R}_B) \\ &= \left( \frac{4 \times 0.416613 \times 0.416613}{(0.416613 + 0.416613)^2} \right)^{\frac{3}{4}} e^{-\frac{0.416613 \times 0.416613}{0.416613 + 0.416613} \times 1.4^2} = 0.6648. \end{aligned}$$

## Exercise 3.22

Derive the coefficients  $[2(1 + S_{12})]^{-1/2}$  and  $[2(1 - S_{12})]^{-1/2}$  in the basis function expansion of  $\psi_1$  and  $\psi_2$  by requiring  $\psi_1$  and  $\psi_2$  to be normalized.

## Solution 3.22

The solution to this exercise is not essentially different from that of Exercise 2.6.

## Exercise 3.23

The coefficients of minimal basis H<sub>2</sub><sup>+</sup> are also determined by symmetry and are identical to those of minimal basis H<sub>2</sub>. Use the above result for the coefficients to solve Eq.(3.234) for the orbital energies of minimal basis H<sub>2</sub><sup>+</sup> at  $R = 1.4$  a.u. and show they are

$$\begin{aligned} \varepsilon_1 &= \frac{H_{11}^{\text{core}} + H_{12}^{\text{core}}}{1 + S_{12}} = -1.2528 \text{ a.u.}, \\ \varepsilon_2 &= \frac{H_{11}^{\text{core}} - H_{12}^{\text{core}}}{1 - S_{12}} = -0.4756 \text{ a.u.} \end{aligned}$$

## Solution 3.23

From (3.234), we know that

$$\begin{pmatrix} H_{11}^{\text{core}} & H_{12}^{\text{core}} \\ H_{12}^{\text{core}} & H_{22}^{\text{core}} \end{pmatrix} \begin{pmatrix} c_1 & c_2 \\ c_1 & -c_2 \end{pmatrix} = \begin{pmatrix} 1 & S_{12} \\ S_{12} & 1 \end{pmatrix} \begin{pmatrix} c_1 & c_2 \\ c_1 & -c_2 \end{pmatrix} \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix}.$$

Thus,

$$\begin{aligned} H_{11}^{\text{core}} c_1 + H_{12}^{\text{core}} c_1 &= (H_{11}^{\text{core}} + H_{12}^{\text{core}}) c_1 = \varepsilon_1 c_1 + S_{12} \varepsilon_1 c_1 = (1 + S_{12}) \varepsilon_1 c_1, \\ H_{11}^{\text{core}} c_2 - H_{12}^{\text{core}} c_2 &= (H_{11}^{\text{core}} - H_{12}^{\text{core}}) c_2 = \varepsilon_2 c_2 - S_{12} \varepsilon_2 c_2 = (1 - S_{12}) \varepsilon_2 c_2, \end{aligned}$$

which equals

$$\begin{aligned} \varepsilon_1 &= \frac{H_{11}^{\text{core}} + H_{12}^{\text{core}}}{1 + S_{12}} = \frac{(-1.1204 \text{ a.u.}) + (-0.9584 \text{ a.u.})}{1 + 0.6593} = -1.2528 \text{ a.u.}, \\ \varepsilon_2 &= \frac{H_{11}^{\text{core}} - H_{12}^{\text{core}}}{1 - S_{12}} = \frac{(-1.1204 \text{ a.u.}) - (-0.9584 \text{ a.u.})}{1 - 0.6593} = -0.4755 \text{ a.u.} \end{aligned}$$

Here, using data from (3.229) and (3.233), the final result is a little different from the result delivered by this exercise.

**Exercise 3.24**

Use the general definition (3.145) of the density matrix to derive (3.239). What is the corresponding density matrix for  $H_2^+$ ?

**Solution 3.24**

Using (3.145), we calculate the matrix elements of the density matrix:

$$\begin{aligned} P_{11} &= 2C_{11}C_{11}^* = 2 \times \frac{1}{\sqrt{2(1+S_{12})}} \times \frac{1}{\sqrt{2(1+S_{12})}} = \frac{1}{1+S_{12}}, \\ P_{12} &= 2C_{11}C_{21}^* = 2 \times \frac{1}{\sqrt{2(1+S_{12})}} \times \frac{1}{\sqrt{2(1+S_{12})}} = \frac{1}{1+S_{12}}, \\ P_{21} &= 2C_{21}C_{11}^* = 2 \times \frac{1}{\sqrt{2(1+S_{12})}} \times \frac{1}{\sqrt{2(1+S_{12})}} = \frac{1}{1+S_{12}}, \\ P_{22} &= 2C_{21}C_{21}^* = 2 \times \frac{1}{\sqrt{2(1+S_{12})}} \times \frac{1}{\sqrt{2(1+S_{12})}} = \frac{1}{1+S_{12}}. \end{aligned}$$

Thus the final density matrix of  $H_2$  is

$$\mathbf{P} = \begin{pmatrix} P_{11} & P_{12} \\ P_{21} & P_{22} \end{pmatrix} = \begin{pmatrix} \frac{1}{1+S_{12}} & \frac{1}{1+S_{12}} \\ \frac{1}{1+S_{12}} & \frac{1}{1+S_{12}} \end{pmatrix} = \frac{1}{1+S_{12}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}.$$

Due to the same symmetry as  $H_2$  but only one electron in  $H_2^+$ , we get its final density matrix is

$$\mathbf{P} = \frac{1}{2} \begin{pmatrix} P_{11} & P_{12} \\ P_{21} & P_{22} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \frac{1}{1+S_{12}} & \frac{1}{1+S_{12}} \\ \frac{1}{1+S_{12}} & \frac{1}{1+S_{12}} \end{pmatrix} = \frac{1}{2(1+S_{12})} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}.$$

**Exercise 3.25**

Use the general definition (3.154) of the Fock matrix to show that the converged values of its elements for minimal basis  $H_2$  are

$$\begin{aligned} F_{11} = F_{22} &= H_{11}^{\text{core}} + \frac{\frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1) + (\phi_1\phi_1|\phi_2\phi_2) + (\phi_1\phi_1|\phi_1\phi_2) - \frac{1}{2}(\phi_1\phi_2|\phi_1\phi_2)}{1+S_{12}} = -0.3655 \text{ a.u.}, \\ F_{12} = F_{21} &= H_{12}^{\text{core}} + \frac{-\frac{1}{2}(\phi_1\phi_1|\phi_2\phi_2) + (\phi_1\phi_1|\phi_1\phi_2) + \frac{3}{2}(\phi_1\phi_2|\phi_1\phi_2)}{1+S_{12}} = -0.5939 \text{ a.u.} \end{aligned}$$

**Solution 3.25**

From (3.154) and (3.235), we get that

$$\begin{aligned} G_{11} &= \sum_{\lambda=1}^2 \sum_{\sigma=1}^2 P_{\lambda\sigma} \left[ (11|\sigma\lambda) - \frac{1}{2}(1\lambda|\sigma 1) \right] \\ &= P_{11} \left[ (11|11) - \frac{1}{2}(11|11) \right] + P_{12} \left[ (11|21) - \frac{1}{2}(11|21) \right] \\ &\quad + P_{21} \left[ (11|12) - \frac{1}{2}(12|11) \right] + P_{22} \left[ (11|22) - \frac{1}{2}(12|21) \right] \\ &= \frac{1}{1+S_{12}} \left[ \frac{1}{2}(11|11) + (11|12) + (11|22) - \frac{1}{2}(12|12) \right] = 0.7549 \text{ a.u.}, \\ F_{11} &= H_{11}^{\text{core}} + G_{11} = H_{11}^{\text{core}} + \frac{1}{1+S_{12}} \left[ \frac{1}{2}(11|11) + (11|12) + (11|22) - \frac{1}{2}(12|12) \right] \\ &= -1.1204 \text{ a.u.} + 0.7549 \text{ a.u.} = -0.3655 \text{ a.u.} \end{aligned}$$

Similarly, we get other matrix elements as follows. Note that  $P_{\lambda\sigma} = P_{\sigma\lambda}$ , and thus

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

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

Besides, note that  $H_{\lambda\sigma}^{\text{core}} = H_{\sigma\lambda}^{\text{core}}$ .

- The calculation of  $F_{12}$ :

$$\begin{aligned} G_{12} &= \sum_{\lambda=1}^2 \sum_{\sigma=1}^2 P_{\lambda\sigma} \left[ (12|\sigma\lambda) - \frac{1}{2}(1\lambda|\sigma 2) \right] \\ &= P_{11} \left[ (12|11) - \frac{1}{2}(11|12) \right] + P_{12} \left[ (12|21) - \frac{1}{2}(11|22) \right] \\ &\quad + P_{21} \left[ (12|12) - \frac{1}{2}(12|12) \right] + P_{22} \left[ (12|22) - \frac{1}{2}(12|22) \right] \\ &= \frac{1}{1+S_{12}} \left[ \frac{1}{2}(11|12) + \frac{3}{2}(12|12) - \frac{1}{2}(11|22) + \frac{1}{2}(12|22) \right] \\ &= \frac{1}{1+S_{12}} \left[ \frac{1}{2}(11|12) + \frac{3}{2}(12|12) - \frac{1}{2}(11|22) + \frac{1}{2}(11|12) \right] \\ &= \frac{1}{1+S_{12}} \left[ (11|12) + \frac{3}{2}(12|12) - \frac{1}{2}(11|22) \right] = 0.3645 \text{ a.u.}, \\ F_{12} &= H_{12}^{\text{core}} + G_{12} = H_{12}^{\text{core}} + \frac{1}{1+S_{12}} \left[ (11|12) + \frac{3}{2}(12|12) - \frac{1}{2}(11|22) \right] \\ &= -0.9584 \text{ a.u.} + 0.3645 \text{ a.u.} = -0.5939 \text{ a.u.} \end{aligned}$$

- The calculation of  $F_{21}$ :

$$\begin{aligned} F_{21} &= H_{21}^{\text{core}} + G_{21} = H_{12}^{\text{core}} + G_{12} \\ &= H_{12}^{\text{core}} + \frac{1}{1+S_{12}} \left[ (11|12) + \frac{3}{2}(12|12) - \frac{1}{2}(11|22) \right] = -0.5939 \text{ a.u.} \end{aligned}$$

- The calculation of  $F_{22}$ :

$$\begin{aligned} G_{22} &= \sum_{\lambda=1}^2 \sum_{\sigma=1}^2 P_{\lambda\sigma} \left[ (22|\sigma\lambda) - \frac{1}{2}(2\lambda|\sigma 2) \right] \\ &= P_{11} \left[ (22|11) - \frac{1}{2}(21|12) \right] + P_{12} \left[ (22|21) - \frac{1}{2}(21|22) \right] \\ &\quad + P_{21} \left[ (22|12) - \frac{1}{2}(22|12) \right] + P_{22} \left[ (22|22) - \frac{1}{2}(22|22) \right] \\ &= \frac{1}{1+S_{12}} \left[ \frac{1}{2}(22|22) + (11|22) + (12|22) - \frac{1}{2}(12|12) \right] \\ &= \frac{1}{1+S_{12}} \left[ \frac{1}{2}(11|11) + (11|22) + (11|12) - \frac{1}{2}(12|12) \right] = 0.7549 \text{ a.u.}, \\ F_{22} &= H_{22}^{\text{core}} + G_{22} = H_{11}^{\text{core}} + \frac{1}{1+S_{12}} \left[ \frac{1}{2}(11|11) + (11|22) + (11|12) - \frac{1}{2}(12|12) \right] = -0.3655 \text{ a.u.} \end{aligned}$$

### Exercise 3.26

Use the result of Exercise 3.23 to show that the orbital energies of minimal basis H<sub>2</sub>, that are a solution to the Roothaan equations  $\mathbf{FC} = \mathbf{SC}\epsilon$ , are

$$\begin{aligned} \epsilon_1 &= \frac{F_{11} + F_{12}}{1 + S_{12}} = -0.5782 \text{ a.u.}, \\ \epsilon_2 &= \frac{F_{11} - F_{12}}{1 - S_{12}} = +0.6703 \text{ a.u.}, \end{aligned}$$

**Solution 3.26**

Similar to Exercise 3.23, we obtain that

$$\begin{aligned}\varepsilon_1 &= \frac{F_{11} + F_{12}}{1 + S_{12}} = \frac{-0.3655 \text{ a.u.} + (-0.5939 \text{ a.u.})}{1 + 0.6593} = -0.5782 \text{ a.u.}, \\ \varepsilon_2 &= \frac{F_{11} - F_{12}}{1 - S_{12}} = \frac{-0.3655 \text{ a.u.} - (-0.5939 \text{ a.u.})}{1 - 0.6593} = 0.6704 \text{ a.u.}\end{aligned}$$

Here, using data from Exercise 3.25, the final result is a little different from the result delivered by this exercise.

**Exercise 3.27**

Use the general result (3.184) for the total electronic energy to show that the electronic energy of minimal basis  $\text{H}_2$  is

$$E_0 = \frac{F_{11} + H_{11}^{\text{core}} + F_{12} + H_{12}^{\text{core}}}{1 + S_{12}} = -1.8310 \text{ a.u.}$$

and that the total energy including nuclear repulsion is

$$E_{\text{tot}} = -1.1167 \text{ a.u.}$$

**Solution 3.27**

From (3.184) and Exercise 3.25, we find that

$$\begin{aligned}E_0 &= \frac{1}{2} \sum_{\mu=1}^2 \sum_{\nu=1}^2 P_{\nu\mu} (H_{\mu\nu}^{\text{core}} + F_{\mu\nu}) \\ &= \frac{1}{2} [P_{11}(H_{11}^{\text{core}} + F_{11}) + P_{21}(H_{12}^{\text{core}} + F_{12}) + P_{12}(H_{21}^{\text{core}} + F_{21}) + P_{22}(H_{22}^{\text{core}} + F_{22})] \\ &= \frac{1}{2} \frac{1}{1 + S_{12}} (H_{11}^{\text{core}} + F_{11} + H_{12}^{\text{core}} + F_{12} + H_{12}^{\text{core}} + F_{12} + H_{11}^{\text{core}} + F_{11}) \\ &= \frac{H_{11}^{\text{core}} + F_{11} + H_{12}^{\text{core}} + F_{12}}{1 + S_{12}} \\ &= \frac{-1.1204 \text{ a.u.} + (-0.3655 \text{ a.u.}) + (-0.9584 \text{ a.u.}) + (-0.5939 \text{ a.u.})}{1 + 0.6593} = -1.8311 \text{ a.u.}\end{aligned}$$

The nuclear repulsion energy is

$$E_{\text{nucl}} = \frac{1 \times 1}{1.4} \text{ a.u.} = 0.7143 \text{ a.u.},$$

and thus the total energy is

$$E_{\text{tot}} = E_0 + E_{\text{nucl}} = -1.8311 \text{ a.u.} + 0.7143 \text{ a.u.} = -1.1168 \text{ a.u.}$$

The final result is a little different from the result delivered by this exercise.

**3.5.3 An SCF Calculation on STO-3G  $\text{HeH}^+$** **Exercise 3.28**

Show that the above transformation produces orthonormal basis functions.

**Solution 3.28**

From (3.258), we know that

$$\begin{aligned}\phi'_1 &= \sum_{\nu=1} X_{\nu 1} \phi_{\nu} = X_{11} \phi_1 + X_{21} \phi_2 = \phi_1, \\ \phi'_2 &= \sum_{\nu=1} X_{\nu 2} \phi_{\nu} = X_{12} \phi_1 + X_{22} \phi_2 = \frac{-S_{12}}{\sqrt{1 - S_{12}^2}} \phi_1 + \frac{1}{\sqrt{1 - S_{12}^2}} \phi_2.\end{aligned}$$

To prove that the above transformation produces orthonormal basis functions, verifying the inner product



of new basis functions is enough.

$$\begin{aligned}
\langle \phi'_1 | \phi'_1 \rangle &= \langle \phi_1 | \phi_1 \rangle = 1, \\
\langle \phi'_1 | \phi'_2 \rangle &= \langle \phi_1 | \left( \frac{-S_{12}}{\sqrt{1-S_{12}^2}} |\phi_1\rangle + \frac{1}{\sqrt{1-S_{12}^2}} |\phi_2\rangle \right) = \frac{-S_{12}}{\sqrt{1-S_{12}^2}} \langle \phi_1 | \phi_1 \rangle + \frac{1}{\sqrt{1-S_{12}^2}} \langle \phi_1 | \phi_2 \rangle \\
&= \frac{-S_{12}}{\sqrt{1-S_{12}^2}} + \frac{S_{12}}{\sqrt{1-S_{12}^2}} = 0, \\
\langle \phi'_2 | \phi'_1 \rangle &= \left( \frac{-S_{12}}{\sqrt{1-S_{12}^2}} \langle \phi_1 | + \frac{1}{\sqrt{1-S_{12}^2}} \langle \phi_2 | \right) |\phi_1\rangle = \frac{-S_{12}}{\sqrt{1-S_{12}^2}} \langle \phi_1 | \phi_1 \rangle + \frac{1}{\sqrt{1-S_{12}^2}} \langle \phi_2 | \phi_1 \rangle \\
&= \frac{-S_{12}}{\sqrt{1-S_{12}^2}} + \frac{S_{12}}{\sqrt{1-S_{12}^2}} = 0, \\
\langle \phi'_2 | \phi'_2 \rangle &= \left( \frac{-S_{12}}{\sqrt{1-S_{12}^2}} \langle \phi_1 | + \frac{1}{\sqrt{1-S_{12}^2}} \langle \phi_2 | \right) \left( \frac{-S_{12}}{\sqrt{1-S_{12}^2}} |\phi_1\rangle + \frac{1}{\sqrt{1-S_{12}^2}} |\phi_2\rangle \right) \\
&= \frac{S_{12}^2}{1-S_{12}^2} \langle \phi_1 | \phi_1 \rangle + \frac{-S_{12}}{1-S_{12}^2} \langle \phi_1 | \phi_2 \rangle + \frac{-S_{12}}{1-S_{12}^2} \langle \phi_2 | \phi_1 \rangle + \frac{1}{1-S_{12}^2} \langle \phi_2 | \phi_2 \rangle \\
&= \frac{S_{12}^2}{1-S_{12}^2} - \frac{S_{12}^2}{1-S_{12}^2} - \frac{S_{12}^2}{1-S_{12}^2} + \frac{1}{1-S_{12}^2} = \frac{1-S_{12}^2}{1-S_{12}^2} = 1.
\end{aligned}$$

Thus, we conclude that the above transformation produces orthonormal basis functions.

#### Exercise 3.29

Use expression (3.184) for the electronic energy, expression (3.154) for the Fock matrix, and the asymptotic density matrix (3.281) to show that

$$E_0(R \rightarrow \infty) = 2T_{11} + 2V_{11}^1 + (\phi_1 \phi_1 | \phi_1 \phi_1).$$

This is just the proper energy of the He atom, for the minimal basis, as discussed previously in the text.

#### Solution 3.29

Note that only  $P_{11}$  in  $\mathbf{P}$  is nonzero. Thus we care about  $G_{11}$ , which is

$$G_{11} = \sum_{\lambda=1}^2 \sum_{\sigma=1}^2 P_{\lambda\sigma} \left[ (11|\sigma\lambda) - \frac{1}{2}(1\lambda|\sigma 1) \right] = P_{11} \left[ (11|11) - \frac{1}{2}(11|11) \right] = 2 \times \frac{1}{2}(11|11) = (11|11).$$

Thus,

$$E_0 = \frac{1}{2} \sum_{\mu=1}^2 \sum_{\nu=1}^2 P_{\nu\mu} (2H_{\mu\nu}^{\text{core}} + G_{\mu\nu}) = \frac{1}{2} P_{11} (2H_{11}^{\text{core}} + G_{11}) = 2T_{11} + 2V_{11}^1 + (11|11).$$

## 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

#### Exercise 3.30

A 4-31G basis for He has not been officially defined. Huzinaga,<sup>8</sup> however, in an SCF calculation on the He atom using four uncontracted 1s Gaussians, found the coefficients and optimum exponents of the normalized 1s orbital of He to be

$\alpha_\mu$	$C_{\mu i}$
0.298073	0.51380
1.242567	0.46954
5.782948	0.15457
38.47497	0.02373

Use the expression for overlaps given in Appendix A to derive the contraction parameters for a 4-31G He basis set.

### Solution 3.30

We choose the outer basis function as

$$\phi_{2s} = g_{1s}(0.298073, \mathbf{r}),$$

and the unnormalized inner basis function as

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

Note that

$$\begin{aligned}\langle g_{1s}(1.242567, \mathbf{r}) | g_{1s}(5.782948, \mathbf{r}) \rangle &= 0.666622, \\ \langle g_{1s}(1.242567, \mathbf{r}) | g_{1s}(38.47497, \mathbf{r}) \rangle &= 0.205445, \\ \langle g_{1s}(5.782948, \mathbf{r}) | g_{1s}(38.47497, \mathbf{r}) \rangle &= 0.553419.\end{aligned}$$

Therefore, we can get the norm of  $\phi'_{1s}(\mathbf{r})$ , namely,

$$\langle \phi'_{1s} | \phi'_{1s} \rangle = N^2 (0.46954, 0.15457, 0.02373) \begin{pmatrix} 1 & 0.666622 & 0.205445 \\ 0.666622 & 1 & 0.553419 \\ 0.205445 & 0.553419 & 1 \end{pmatrix} \begin{pmatrix} 0.46954 \\ 0.15457 \\ 0.02373 \end{pmatrix} = 0.35032N^2.$$

And we can obtain the normalization parameter  $N$ , viz.,

$$N = \sqrt{\frac{1}{0.35032}} = 1.6895,$$

and then

$$\begin{aligned}\phi'_{1s} &= 1.6895[0.46954g_{1s}(1.242567, \mathbf{r}) + 0.15457g_{1s}(5.782948, \mathbf{r}) + 0.02373g_{1s}(38.47497, \mathbf{r})] \\ &= 0.79328g_{1s}(1.242567, \mathbf{r}) + 0.26115g_{1s}(5.782948, \mathbf{r}) + 0.04009g_{1s}(38.47497, \mathbf{r}).\end{aligned}$$

The information of 4-31G basis set for He atoms can be seen in subdirectory `./basis_sets/He`. These information is generated by “Basis Set Exchange” whose url is <https://www.basissetexchange.org>.

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

#### Exercise 3.31

Determine the total number of basis functions for STO-3G, 4-31G, 6-31G\*, and 6-31G\*\* calculations on benzene.

#### Solution 3.31

The total number of uncontracted basis functions for STO-3G, 4-31G, 6-31G\*, and 6-31G\*\* calculations on benzene has been summarized in the table below.

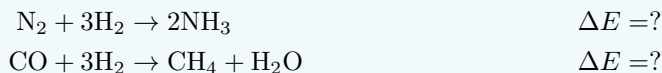
basis set	STO-3G	4-31G	6-31G*(Cartesian)	6-31G**(Cartesian)
Number of basis functions for C	$2 + 3 \times 1$	$3 + 3 \times 2$	$3 + 3 \times 2 + 6 \times 1$	$3 + 3 \times 2 + 6 \times 1$
Number of basis functions for H	1	2	2	$2 + 3 \times 1$
Total number of basis functions	36	66	102	120

## 3.7 Some Illustrative Closed-Shell Calculations

### 3.7.1 Total Energies

#### Exercise 3.32

Use the results of Tables 3.11 to 3.13 to calculate, for each basis set and at the Hartree-Fock limit, the energy difference for the following two reactions,



Are the results consistent for different basis sets? Does Hartree-Fock theory predict these reactions to be exoergic or endoergic? The experimental hydrogenation energies (heats of reaction  $\Delta H^\circ$ ) at zero degrees Kelvin are  $-18.604 \text{ kcal} \cdot \text{mol}^{-1}$  ( $\text{N}_2$ ) and  $-45.894 \text{ kcal} \cdot \text{mol}^{-1}$  ( $\text{CO}$ ), with 1 a.u. of energy equivalent to  $627.51 \text{ kcal} \cdot \text{mol}^{-1}$ .

Differences in the zero-point vibrational energies of reactants and products also contribute to reaction energies. From the experimental vibrational spectra, the  $3N - 6$  (or  $3N - 5$ ) zero-point energies ( $h\nu_0/2$ ) for the relevant molecules (with degeneracies in parenthesis) are:

Molecule	$h\nu_0/2$ ( $\text{kcal} \cdot \text{mol}^{-1}$ )
$\text{H}_2$	6.18
$\text{N}_2$	3.35
$\text{CO}$	3.08
$\text{H}_2\text{O}$	2.28
	5.13
	5.33
$\text{NH}_3$	1.35
	2.32(2)
	4.77
	4.85(2)
$\text{CH}_4$	1.86(3)
	2.17(2)
	4.14
	4.2(3)

Calculate the contribution of zero-point vibrations to the energy of the above two reactions. Is it a reasonable approximation to neglect the effect of zero-point vibrations?

#### Solution 3.32

All SCF total energy data used in this exercise can be listed in Table 3.1.

Table 3.1: SCF total energy (a.u.) for several molecules with the standard basis sets.

molecules	basis set				
	STO-3G	4-31G	6-31G*	6-31G**	HF-limit
$\text{H}_2$	-1.117	-1.127	-1.127	-1.131	-1.134
$\text{N}_2$	-107.496	-108.754	-108.942	-108.942	-108.997
$\text{CO}$	-111.225	-112.552	-112.737	-112.737	-112.791
$\text{NH}_3$	-55.454	-56.102	-56.184	-56.195	-56.225
$\text{CH}_4$	-39.727	-40.140	-40.195	-40.202	-40.225
$\text{H}_2\text{O}$	-74.963	-75.907	-76.011	-76.023	-76.065

The enthalpy change of reaction 1 is

$$\begin{aligned} \Delta H(\text{STO} - 3\text{G}) &= 2H(\text{NH}_3, \text{STO} - 3\text{G}) - 3H(\text{H}_2, \text{STO} - 3\text{G}) - H(\text{N}_2, \text{STO} - 3\text{G}) \\ &= 2 \times (-55.454 \text{ a.u.}) - 3 \times (-1.117 \text{ a.u.}) - (-107.496 \text{ a.u.}) \\ &= -0.061 \text{ a.u.} = -0.061 \text{ a.u.} \times 627.51 \text{ kcal} \cdot \text{mol}^{-1} / \text{a.u.} = -38.3 \text{ kcal} \cdot \text{mol}^{-1}. \end{aligned}$$

In the same way, we can calculate the enthalpy change of the reaction 1 under various basis sets. These results are listed in Table 3.2.

Table 3.2: The enthalpy change of the reaction 1 under various standard basis sets.

basis set	$\Delta H(\text{a.u.})$	$\Delta H(\text{kcal} \cdot \text{mol}^{-1})$	exergic or endoergic
STO-3G	-0.061	-38.3	exoergic
4-31G	-0.069	-43.3	exoergic
6-31G*	-0.045	-28.2	exoergic
6-31G**	-0.055	-34.5	exoergic
HF-limit	-0.051	-32.0	exoergic

Similarly, we summarize the results of the enthalpy change of the reaction 2 under various basis sets. These results are listed in Table 3.3.

Table 3.3: The enthalpy change of the reaction 2 under various standard basis sets.

basis set	$\Delta H(\text{a.u.})$	$\Delta H(\text{kcal} \cdot \text{mol}^{-1})$	exergic or endoergic
STO-3G	-0.114	-71.5	exoergic
4-31G	-0.114	-71.5	exoergic
6-31G*	-0.088	-55.2	exoergic
6-31G**	-0.095	-59.6	exoergic
HF-limit	-0.097	-60.9	exoergic

Now pay attention to the zero-point energy. For example, as for  $\text{CH}_4$ , it is a nonlinear molecule and there are 5 atoms, thus it has  $3 \times 5 - 6 = 9$  degrees of freedom, and its total zero-point energy is

$$(1.86 \times 3 + 2.17 \times 2 + 4.14 + 4.2 \times 3) \text{ kcal} \cdot \text{mol}^{-1} = 26.66 \text{ kcal} \cdot \text{mol}^{-1}.$$

And we can establish the table of the zero-point energy of these molecules, as shown in Table 3.4.

Table 3.4: The zero-point energy of several molecules .

molecules	$N$	linear or nonlinear	degrees of freedom	total zero-point energy ( $\text{kcal} \cdot \text{mol}^{-1}$ )
$\text{H}_2$	2	linear	1	6.18
$\text{N}_2$	2	linear	1	3.35
$\text{CO}$	2	linear	1	3.08
$\text{H}_2\text{O}$	3	nonlinear	3	12.74
$\text{NH}_3$	4	nonlinear	6	20.46
$\text{CH}_4$	5	nonlinear	9	26.66

For the reaction 1, its zero-point energy is

$$(2 \times 20.46 - 3 \times 6.18 - 1 \times 3.35) \text{ kcal} \cdot \text{mol}^{-1} = 19.03 \text{ kcal} \cdot \text{mol}^{-1}.$$

And for the reaction 2, its zero-point energy is

$$(1 \times 26.66 + 1 \times 12.74 - 3 \times 6.18 - 1 \times 3.08) \text{ kcal} \cdot \text{mol}^{-1} = 17.78 \text{ kcal} \cdot \text{mol}^{-1}.$$

It is evident that the effect of zero-point vibrations should not be ignored in the reaction 1 and 2.

### 3.7.2 Ionization Potentials

### 3.7.3 Equilibrium Geometries

### 3.7.4 Population Analysis and Dipole Moments

## 3.8 Unrestricted Open-Shell Hartree-Fock: The Pople-Nesbet Equations

### 3.8.1 Open-Shell Hartree Fock: Unrestricted Spin Orbitals

#### Exercise 3.33

Rather than use the simple technique of writing down  $f^\alpha(1)$  by inspection of the possible interactions, as we have done above, use expression (3.314) for  $f^\alpha(1)$  and explicitly integrate over spin and carry

through the algebra, as was done in Subsection 3.4.1 for the restricted closed-shell case, to derive

$$f^\alpha(1) = h(1) + \sum_a^{N^\alpha} [J_a^\alpha(1) - K_a^\alpha(1)] + \sum_a^{N^\beta} J_a^\beta(1).$$

### Solution 3.33

From (3.115), we find that for a general  $\psi_i^\alpha(\mathbf{r}_1)$ ,

$$\begin{aligned} f^\alpha(\mathbf{x}_1)\psi_i^\alpha(\mathbf{r}_1) &= \int d\omega_1 \alpha^*(\omega_1)h(\mathbf{r}_1)\alpha(\omega_1)\psi_i^\alpha(\mathbf{r}_1) \\ &\quad + \int d\omega_1 \alpha^*(\omega_1) \left[ \sum_c^N \int d\mathbf{x}_2 \chi_c^*(\mathbf{x}_2)r_{12}^{-1}(1 - \mathcal{P}_{12})\chi_c(\mathbf{x}_2) \right] \alpha(\omega_1)\psi_i^\alpha(\mathbf{r}_1) \\ &= h(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_1) + \sum_c^N \int d\omega_1 \alpha^*(\omega_1)\alpha(\omega_1) \int d\mathbf{x}_2 \chi_c^*(\mathbf{x}_2)r_{12}^{-1}\chi_c(\mathbf{x}_2)\psi_i^\alpha(\mathbf{r}_1) \\ &\quad - \int d\omega_1 \alpha^*(\omega_1)\alpha(\omega_2) \int d\mathbf{x}_2 \chi_c^*(\mathbf{x}_2)r_{12}^{-1}\chi_c(\mathbf{x}_1)\psi_i^\alpha(\mathbf{r}_2) \\ &= h(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_1) + \left( \sum_c^{N^\alpha} + \sum_c^{N^\beta} \right) \int d\omega_1 \alpha^*(\omega_1)\alpha(\omega_1) \int d\mathbf{x}_2 \chi_c^*(\mathbf{x}_2)r_{12}^{-1}\chi_c(\mathbf{x}_2)\psi_i^\alpha(\mathbf{r}_1) \\ &\quad - \left( \sum_c^{N^\alpha} + \sum_c^{N^\beta} \right) \int d\omega_1 \alpha^*(\omega_1)\alpha(\omega_2) \int d\mathbf{x}_2 \chi_c^*(\mathbf{x}_2)r_{12}^{-1}\chi_c(\mathbf{x}_1)\psi_i^\alpha(\mathbf{r}_2) \\ &= h(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_1) \\ &\quad + \sum_c^{N^\alpha} \int d\omega_1 \alpha^*(\omega_1)\alpha(\omega_1) \int d\omega_2 \alpha^*(\omega_2)\alpha(\omega_2) \int d\mathbf{r}_2 \psi_c^{\alpha*}(\mathbf{r}_2)r_{12}^{-1}\psi_c^\alpha(\mathbf{r}_2)\psi_i^\alpha(\mathbf{r}_1) \\ &\quad + \sum_c^{N^\beta} \int d\omega_1 \alpha^*(\omega_1)\alpha(\omega_1) \int d\omega_2 \beta^*(\omega_2)\beta(\omega_2) \int d\mathbf{r}_2 \psi_c^{\beta*}(\mathbf{r}_2)r_{12}^{-1}\psi_c^\beta(\mathbf{r}_2)\psi_i^\alpha(\mathbf{r}_1) \\ &\quad - \sum_c^{N^\alpha} \int d\omega_1 \alpha^*(\omega_1)\alpha(\omega_1) \int d\omega_2 \alpha^*(\omega_2)\alpha(\omega_2) \int d\mathbf{r}_2 \psi_c^{\alpha*}(\mathbf{r}_2)r_{12}^{-1}\psi_c^\alpha(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_2) \\ &\quad - \sum_c^{N^\beta} \int d\omega_1 \alpha^*(\omega_1)\beta(\omega_1) \int d\omega_2 \beta^*(\omega_2)\alpha(\omega_2) \int d\mathbf{r}_2 \psi_c^{\beta*}(\mathbf{r}_2)r_{12}^{-1}\psi_c^\beta(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_2) \\ &= h(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_1) + \sum_c^{N^\alpha} \int d\mathbf{r}_2 \psi_c^{\alpha*}(\mathbf{r}_2)r_{12}^{-1}\psi_c^\alpha(\mathbf{r}_2)\psi_i^\alpha(\mathbf{r}_1) \\ &\quad + \sum_c^{N^\beta} \int d\mathbf{r}_2 \psi_c^{\beta*}(\mathbf{r}_2)r_{12}^{-1}\psi_c^\beta(\mathbf{r}_2)\psi_i^\alpha(\mathbf{r}_1) - \sum_c^{N^\alpha} \int d\mathbf{r}_2 \psi_c^{\alpha*}(\mathbf{r}_2)r_{12}^{-1}\psi_c^\alpha(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_2). \end{aligned}$$

Using (3.319) and (3.320), we get that

$$\begin{aligned} f^\alpha(\mathbf{x}_1)\psi_i^\alpha(\mathbf{r}_1) &= h(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_1) + \sum_c^{N^\alpha} J_c^\alpha(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_1) + \sum_c^{N^\beta} J_c^\beta(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_1) - \sum_c^{N^\alpha} K_c^\alpha(\mathbf{r}_1)\psi_i^\alpha(\mathbf{r}_1) \\ &= \left[ h(\mathbf{r}_1) + \sum_c^{N^\alpha} J_c^\alpha(\mathbf{r}_1) - K_c^\alpha(\mathbf{r}_1) + \sum_c^{N^\beta} J_c^\beta(\mathbf{r}_1) \right] \psi_i^\alpha(\mathbf{r}_1). \end{aligned}$$

As  $\psi_i^\alpha(\mathbf{r}_1)$  is a general wave function, we obtain that

$$f^\alpha(\mathbf{x}_1) = h(\mathbf{r}_1) + \sum_c^{N^\alpha} J_c^\alpha(\mathbf{r}_1) - K_c^\alpha(\mathbf{r}_1) + \sum_c^{N^\beta} J_c^\beta(\mathbf{r}_1).$$

**Exercise 3.34**

The unrestricted doublet ground state of the Li atom is  $|\Psi_0\rangle = |\psi_1^\alpha(1)\bar{\psi}_1^\beta(2)\psi_2^\alpha(3)\rangle$ . Show that the energy of this state is

$$E_0 = h_{11}^\alpha + h_{11}^\beta + h_{22}^\alpha + J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha} + J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta}.$$

**Solution 3.34**

Using (3.327), we obtain that

$$\begin{aligned} E_0 &= \sum_{a=1}^2 h_{aa}^\alpha + \sum_{a=1}^1 h_{aa}^\beta + \frac{1}{2} \sum_{a=1}^2 \sum_{a=1}^2 (J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \frac{1}{2} \sum_{a=1}^1 \sum_{a=1}^1 (J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}) + \sum_{a=1}^2 \sum_{b=1}^1 J_{ab}^{\alpha\beta} \\ &= h_{11}^\alpha + h_{22}^\alpha + h_{11}^\beta + (J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha}) + (J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta}) \\ &= h_{11}^\alpha + h_{11}^\beta + h_{22}^\alpha + J_{12}^{\alpha\alpha} - K_{12}^{\alpha\alpha} + J_{11}^{\alpha\beta} + J_{21}^{\alpha\beta}. \end{aligned}$$

**Exercise 3.35**

The unrestricted orbital energies are  $\varepsilon_i^\alpha = (\psi_i^\alpha | f^\alpha | \psi_i^\alpha)$  and  $\varepsilon_i^\beta = (\psi_i^\beta | f^\beta | \psi_i^\beta)$ . Show that these are given by

$$\begin{aligned} \varepsilon_i^\alpha &= h_{ii}^\alpha + \sum_a^{N^\alpha} (J_{ia}^{\alpha\alpha} - K_{ia}^{\alpha\alpha}) + \sum_a^{N^\beta} J_{ia}^{\alpha\beta}, \\ \varepsilon_i^\beta &= h_{ii}^\beta + \sum_a^{N^\beta} (J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta}) + \sum_a^{N^\alpha} J_{ia}^{\beta\alpha}. \end{aligned}$$

Derive an expression for  $E_0$  in terms of the orbital energies and the coulomb and exchange energies.

**Solution 3.35**

From the conclusion of Exercise 3.33, we find that

$$\begin{aligned} \varepsilon_i^\alpha &= (\psi_i^\alpha | f^\alpha | \psi_i^\alpha) = \left( \psi_i^\alpha \left| h + \sum_c^{N^\alpha} J_c^\alpha - K_c^\alpha + \sum_c^{N^\beta} J_c^\beta \right| \psi_i^\alpha \right) \\ &= (\psi_i^\alpha | h | \psi_i^\alpha) + \sum_c^{N^\alpha} (\psi_i^\alpha | J_c^\alpha | \psi_i^\alpha) - \sum_c^{N^\alpha} (\psi_i^\alpha | K_c^\alpha | \psi_i^\alpha) + \sum_c^{N^\beta} (\psi_i^\alpha | J_c^\beta | \psi_i^\alpha) \\ &= h_{ii}^\alpha + \sum_c^{N^\alpha} J_{ic}^{\alpha\alpha} - \sum_c^{N^\alpha} K_{ic}^{\alpha\alpha} + \sum_c^{N^\beta} J_{ic}^{\alpha\beta}. \end{aligned}$$

In the same way, we can prove that

$$\varepsilon_i^\beta = h_{ii}^\beta + \sum_a^{N^\beta} (J_{ia}^{\beta\beta} - K_{ia}^{\beta\beta}) + \sum_a^{N^\alpha} J_{ia}^{\beta\alpha}.$$

Thus, we can find that

$$\begin{aligned} \sum_a^{N^\alpha} \varepsilon_a^\alpha + \sum_a^{N^\beta} \varepsilon_a^\beta &= \sum_a^{N^\alpha} \left( h_{aa}^\alpha + \sum_b^{N^\alpha} J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha} + \sum_b^{N^\beta} J_{ab}^{\alpha\beta} \right) + \sum_a^{N^\beta} \left( h_{aa}^\beta + \sum_b^{N^\beta} J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta} + \sum_a^{N^\alpha} J_{ab}^{\beta\alpha} \right) \\ &= \sum_a^{N^\alpha} h_{aa}^\alpha + \sum_a^{N^\beta} h_{aa}^\beta + \sum_a^{N^\alpha} \sum_b^{N^\alpha} J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha} + \sum_a^{N^\beta} \sum_b^{N^\beta} J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta} + 2 \sum_a^{N^\alpha} \sum_b^{N^\beta} J_{ab}^{\alpha\beta} \\ &= \left[ \sum_a^{N^\alpha} h_{aa}^\alpha + \sum_a^{N^\beta} h_{aa}^\beta + \frac{1}{2} \sum_a^{N^\alpha} \sum_b^{N^\alpha} J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha} + \frac{1}{2} \sum_a^{N^\beta} \sum_b^{N^\beta} J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta} + \sum_a^{N^\alpha} \sum_b^{N^\beta} J_{ab}^{\alpha\beta} \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} \sum_a^{N^\alpha} \sum_b^{N^\alpha} J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha} + \frac{1}{2} \sum_a^{N^\beta} \sum_b^{N^\beta} J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta} + \sum_a^{N^\alpha} \sum_b^{N^\beta} J_{ab}^{\alpha\beta} \\
& = E_0 + \frac{1}{2} \sum_a^{N^\alpha} \sum_b^{N^\alpha} J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha} + \frac{1}{2} \sum_a^{N^\beta} \sum_b^{N^\beta} J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta} + \sum_a^{N^\alpha} \sum_b^{N^\beta} J_{ab}^{\alpha\beta},
\end{aligned}$$

which means that

$$E_0 = \sum_a^{N^\alpha} \varepsilon_a^\alpha + \sum_a^{N^\beta} \varepsilon_a^\beta - \frac{1}{2} \sum_a^{N^\alpha} \sum_b^{N^\alpha} J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha} - \frac{1}{2} \sum_a^{N^\beta} \sum_b^{N^\beta} J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta} - \sum_a^{N^\alpha} \sum_b^{N^\beta} J_{ab}^{\alpha\beta}. \quad (3.35-1)$$

### 3.8.2 Introduction of a Basis: The Pople-Nesbet Equations

### 3.8.3 Unrestricted Density Matrices

#### Exercise 3.36

Use definitions (3.335) and (3.336) and Eq.(2.254) to show that the integral over all space of the spin density is  $2\langle \mathcal{S}_z \rangle$ .

#### Solution 3.36

The proof is direct.

$$\int d\mathbf{r} \rho^{\mathbf{S}}(\mathbf{r}) = \int d\mathbf{r} \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) = N^\alpha - N^\beta = 2\langle \mathcal{S}_z \rangle, \quad (3.36-1)$$

where (2.254) and (3.339) has been used.

#### Exercise 3.37

Carry through the missing steps that led to Eqs.(3.340) to (3.343).

#### Solution 3.37

From (3.340), we can find that

$$\begin{aligned}
\rho^\alpha(\mathbf{r}) &= \sum_a^{N^\alpha} |\psi_a^\alpha(\mathbf{r})|^2 = \sum_a^{N^\alpha} \psi_a^\alpha(\mathbf{r}) \psi_a^{\alpha*}(\mathbf{r}) = \sum_a^{N^\alpha} \left( \sum_\mu C_{\mu a}^\alpha \phi_\mu^\alpha(\mathbf{r}) \right) \left( \sum_\nu C_{\nu a}^\alpha \phi_\nu^\alpha(\mathbf{r}) \right)^* \\
&= \sum_\mu \sum_\nu \left( \sum_a^{N^\alpha} C_{\mu a}^\alpha C_{\nu a}^{\alpha*} \right) \phi_\mu^\alpha(\mathbf{r}) \phi_\nu^\alpha(\mathbf{r}).
\end{aligned}$$

If we define  $P_{\mu\nu}^\alpha$  as (3.342), we will obtain that the right side of (3.340). In the same way, if we define  $P_{\mu\nu}^\beta$  as (3.343), we will derive (3.341).

#### Exercise 3.38

Show that expectation values of spin-independent sums of one-electron operators  $\sum_{i=1}^N h(i)$  are given by

$$\langle \mathcal{O}_1 \rangle = \sum_\mu \sum_\nu P_{\mu\nu}^T(\nu|h|\mu)$$

for any unrestricted single determinant.

**Solution 3.38**

Using (3.342) to (3.344), we find that

$$\begin{aligned}
 \langle \mathcal{O}_1 \rangle &= \sum_{a=1}^N \langle a|h|a \rangle = \sum_{a=1}^{N^\alpha} \langle a|h|a \rangle + \sum_{\bar{a}=1}^{N^\beta} \langle \bar{a}|h|\bar{a} \rangle = \sum_{a=1}^{N^\alpha} (a|h|a) + \sum_{\bar{a}=1}^{N^\beta} (\bar{a}|h|\bar{a}) \\
 &= \sum_{a=1}^{N^\alpha} \left( \sum_{\nu} C_{\nu a}^\alpha \phi_\nu \left| h \right| \sum_{\mu} C_{\mu a}^\alpha \phi_\mu \right) + \sum_{\bar{a}=1}^{N^\beta} \left( \sum_{\nu} C_{\nu \bar{a}}^\beta \phi_\nu \left| h \right| \sum_{\mu} C_{\mu \bar{a}}^\beta \phi_\mu \right) \\
 &= \sum_{\mu} \sum_{\nu} (\phi_\nu |h| \phi_\mu) \sum_{a=1}^{N^\alpha} C_{\nu a}^{\alpha*} C_{\mu a}^\alpha + \sum_{\mu} \sum_{\nu} (\phi_\nu |h| \phi_\mu) \sum_{\bar{a}=1}^{N^\beta} C_{\nu \bar{a}}^{\beta*} C_{\mu \bar{a}}^\beta \\
 &= \sum_{\mu} \sum_{\nu} (\phi_\nu |h| \phi_\mu) (P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta) = \sum_{\mu} \sum_{\nu} (\phi_\nu |h| \phi_\mu) P_{\mu\nu}^T.
 \end{aligned}$$

**Exercise 3.39**

Consider the following spin-dependent operator which is a sum of one-electron operators,

$$\hat{\rho}^S = 2 \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{R}) s_z(i).$$

Use the rules for evaluating matrix elements, given in Chapter 2, to show that the expectation value of  $\hat{\rho}^S$  for any unrestricted single determinant is

$$\langle \hat{\rho}^S \rangle = \rho^S(\mathbf{R}) = \text{tr}(\mathbf{P}^S \mathbf{A})$$

where

$$A_{\mu\nu} = \phi_\mu^*(\mathbf{R}) \phi_\nu(\mathbf{R}).$$

This matrix element is important in the theory of the Fermi contact contribution to ESR and NMR coupling constants.

**Solution 3.39**

The proof is direct.

$$\begin{aligned}
 \langle \hat{\rho}^S \rangle &= \left\langle \Psi \left| 2 \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{R}) s_z(i) \right| \Psi \right\rangle = 2 \left\langle \Psi \left| \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{R}) s_z(i) \right| \Psi \right\rangle \\
 &= 2 \sum_{a=1}^N |a(\mathbf{R})|^2 \langle a | s_z(i) | a \rangle \\
 &= 2 \left( \sum_{a=1}^{N^\alpha} |a(\mathbf{R})|^2 \langle a | s_z(i) | a \rangle + \sum_{\bar{a}=1}^{N^\beta} |\bar{a}(\mathbf{R})|^2 \langle \bar{a} | s_z(i) | \bar{a} \rangle \right) \\
 &= 2 \left( \sum_{a=1}^{N^\alpha} \frac{1}{2} |a(\mathbf{R})|^2 + \sum_{\bar{a}=1}^{N^\beta} -\frac{1}{2} |\bar{a}(\mathbf{R})|^2 \right) \\
 &= \sum_{a=1}^{N^\alpha} |a(\mathbf{R})|^2 - \sum_{\bar{a}=1}^{N^\beta} |\bar{a}(\mathbf{R})|^2 = \rho^\alpha(\mathbf{R}) - \rho^\beta(\mathbf{R}) = \rho^S(\mathbf{R}).
 \end{aligned}$$

Moreover, we can find that

$$\begin{aligned}
 \langle \hat{\rho}^S \rangle &= \sum_{a=1}^{N^\alpha} |a(\mathbf{R})|^2 - \sum_{\bar{a}=1}^{N^\beta} |\bar{a}(\mathbf{R})|^2 \\
 &= \sum_{a=1}^{N^\alpha} \left( \sum_{\mu} C_{\mu a}^{\alpha*} \phi_\mu^*(\mathbf{R}) \right) \left( \sum_{\nu} C_{\nu a}^\alpha \phi_\nu(\mathbf{R}) \right) - \sum_{\bar{a}=1}^{N^\beta} \left( \sum_{\mu} C_{\mu \bar{a}}^{\beta*} \phi_\mu^*(\mathbf{R}) \right) \left( \sum_{\nu} C_{\nu \bar{a}}^\beta \phi_\nu(\mathbf{R}) \right)
 \end{aligned}$$



$$\begin{aligned}
&= \sum_{\mu} \sum_{\nu} \phi_{\mu}^*(\mathbf{R}) \phi_{\nu}(\mathbf{R}) \left( \sum_{a=1}^{N^{\alpha}} C_{\mu a}^{\alpha*} C_{\nu a}^{\alpha} - \sum_{a=1}^{N^{\beta}} C_{\mu a}^{\beta*} C_{\nu a}^{\beta} \right) = \sum_{\mu} \sum_{\nu} A_{\mu\nu} (P_{\nu\mu}^{\alpha} - P_{\nu\mu}^{\beta}) \\
&= \sum_{\mu} \sum_{\nu} A_{\mu\nu} P_{\nu\mu}^S = \text{tr}(\mathbf{A}\mathbf{P}^S) = \text{tr}(\mathbf{P}^S\mathbf{A}).
\end{aligned}$$

### 3.8.4 Expression for the Fock Matrices

### 3.8.5 Solution of the Unrestricted SCF Equations

#### Exercise 3.40

Substitute the basis set expansion of the unrestricted molecular orbitals into Eq.(3.327) for the electronic energy  $E_0$  to show that

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

#### Solution 3.40

The proof is direct but a little lengthy. Note that what we have to expand is only  $\psi_b$ .  $\psi_a$  is no need to be expand in this derivation.

$$\begin{aligned}
E_0 &= \sum_{a=1}^{N^{\alpha}} h_{aa}^{\alpha} + \sum_{a=1}^{N^{\beta}} h_{aa}^{\beta} + \frac{1}{2} \sum_{a=1}^{N^{\alpha}} \sum_{b=1}^{N^{\alpha}} (J_{ab}^{\alpha\alpha} - K_{ab}^{\alpha\alpha}) + \frac{1}{2} \sum_{a=1}^{N^{\beta}} \sum_{b=1}^{N^{\beta}} (J_{ab}^{\beta\beta} - K_{ab}^{\beta\beta}) + \sum_{a=1}^{N^{\alpha}} \sum_{b=1}^{N^{\beta}} J_{ab}^{\alpha\beta} \\
&= \sum_{a=1}^{N^{\alpha}} (\psi_a^{\alpha} | h | \psi_a^{\alpha}) + \sum_{a=1}^{N^{\beta}} (\psi_a^{\beta} | h | \psi_a^{\beta}) + \frac{1}{2} \sum_{a=1}^{N^{\alpha}} \sum_{b=1}^{N^{\alpha}} (\psi_a^{\alpha} \psi_a^{\alpha} | \psi_b^{\alpha} \psi_b^{\alpha}) - (\psi_a^{\alpha} \psi_b^{\alpha} | \psi_a^{\alpha} \psi_b^{\alpha}) \\
&\quad + \frac{1}{2} \sum_{a=1}^{N^{\beta}} \sum_{b=1}^{N^{\beta}} (\psi_a^{\beta} \psi_a^{\beta} | \psi_b^{\beta} \psi_b^{\beta}) - (\psi_a^{\beta} \psi_b^{\beta} | \psi_a^{\beta} \psi_b^{\beta}) + \sum_{a=1}^{N^{\alpha}} \sum_{b=1}^{N^{\beta}} (\psi_a^{\alpha} \psi_a^{\alpha} | \psi_b^{\beta} \psi_b^{\beta}) \\
&= \sum_{a=1}^{N^{\alpha}} \left( \sum_{\mu} \phi_{\mu} C_{\mu a}^{\alpha} \left| h \right| \sum_{\nu} \phi_{\nu} C_{\nu a}^{\alpha} \right) + \sum_{a=1}^{N^{\beta}} \left( \sum_{\mu} \phi_{\mu} C_{\mu a}^{\beta} \left| h \right| \sum_{\nu} \phi_{\nu} C_{\nu a}^{\beta} \right) \\
&\quad + \frac{1}{2} \sum_{a=1}^{N^{\alpha}} \sum_{b=1}^{N^{\alpha}} \left( \psi_a^{\alpha} \psi_a^{\alpha} \left| \sum_{\mu} \phi_{\mu} C_{\mu b}^{\alpha} \sum_{\nu} \phi_{\nu} C_{\nu b}^{\alpha} \right| \right) - \left( \psi_a^{\alpha} \sum_{\nu} \phi_{\nu} C_{\nu b}^{\alpha} \left| \sum_{\mu} \phi_{\mu} C_{\mu b}^{\alpha} \psi_a^{\alpha} \right| \right) \\
&\quad + \frac{1}{2} \sum_{a=1}^{N^{\beta}} \sum_{b=1}^{N^{\beta}} \left( \psi_a^{\beta} \psi_a^{\beta} \left| \sum_{\mu} \phi_{\mu} C_{\mu b}^{\beta} \sum_{\nu} \phi_{\nu} C_{\nu b}^{\beta} \right| \right) - \left( \psi_a^{\beta} \sum_{\nu} \phi_{\nu} C_{\nu b}^{\beta} \left| \sum_{\mu} \phi_{\mu} C_{\mu b}^{\beta} \psi_a^{\beta} \right| \right) \\
&\quad + \sum_{a=1}^{N^{\alpha}} \sum_{b=1}^{N^{\beta}} \left( \psi_a^{\alpha} \psi_a^{\alpha} \left| \sum_{\mu} \phi_{\mu} C_{\mu b}^{\beta} \sum_{\nu} \phi_{\nu} C_{\nu b}^{\beta} \right| \right) \\
&= \sum_{\mu} \sum_{\nu} (\phi_{\mu} | h | \phi_{\nu}) \sum_{a=1}^{N^{\alpha}} C_{\mu a}^{\alpha*} C_{\nu a}^{\alpha} + \sum_{\mu} \sum_{\nu} (\phi_{\mu} | h | \phi_{\nu}) \sum_{a=1}^{N^{\beta}} C_{\mu a}^{\beta*} C_{\nu a}^{\beta} \\
&\quad + \frac{1}{2} \sum_{a=1}^{N^{\alpha}} \sum_{\mu} \sum_{\nu} (\psi_a^{\alpha} \psi_a^{\alpha} | \phi_{\mu} \phi_{\nu}) \sum_{b=1}^{N^{\alpha}} C_{\mu b}^{\alpha*} C_{\nu b}^{\alpha} - (\psi_a^{\alpha} \phi_{\nu} | \phi_{\mu} \psi_a^{\alpha}) \sum_{b=1}^{N^{\alpha}} C_{\mu b}^{\alpha*} C_{\nu b}^{\alpha} \\
&\quad + \frac{1}{2} \sum_{a=1}^{N^{\beta}} \sum_{\mu} \sum_{\nu} (\psi_a^{\beta} \psi_a^{\beta} | \phi_{\mu} \phi_{\nu}) \sum_{b=1}^{N^{\beta}} C_{\mu b}^{\beta*} C_{\nu b}^{\beta} - (\psi_a^{\beta} \phi_{\nu} | \phi_{\mu} \psi_a^{\beta}) \sum_{b=1}^{N^{\beta}} C_{\mu b}^{\beta*} C_{\nu b}^{\beta} \\
&\quad + \sum_{a=1}^{N^{\alpha}} \sum_{\mu} \sum_{\nu} (\psi_a^{\alpha} \psi_a^{\alpha} | \phi_{\mu} \phi_{\nu}) \sum_{b=1}^{N^{\beta}} C_{\mu b}^{\beta*} C_{\nu b}^{\beta}
\end{aligned}$$

$$\begin{aligned}
&= \sum_{\mu} \sum_{\nu} H_{\mu\nu}^{\text{core}} P_{\nu\mu}^{\alpha} + \sum_{\mu} \sum_{\nu} H_{\mu\nu}^{\text{core}} P_{\nu\mu}^{\beta} + \frac{1}{2} \sum_{a=1}^{N^{\alpha}} \sum_{\mu} \sum_{\nu} (\psi_a^{\alpha} \psi_a^{\alpha} | \phi_{\mu} \phi_{\nu}) P_{\nu\mu}^{\alpha} - (\psi_a^{\alpha} \phi_{\nu} | \phi_{\mu} \psi_a^{\alpha}) P_{\nu\mu}^{\alpha} \\
&\quad + \frac{1}{2} \sum_{a=1}^{N^{\beta}} \sum_{\mu} \sum_{\nu} (\psi_a^{\beta} \psi_a^{\beta} | \phi_{\mu} \phi_{\nu}) P_{\nu\mu}^{\beta} - (\psi_a^{\beta} \phi_{\nu} | \phi_{\mu} \psi_a^{\beta}) P_{\nu\mu}^{\beta} + \sum_{a=1}^{N^{\alpha}} \sum_{\mu} \sum_{\nu} (\psi_a^{\alpha} \psi_a^{\alpha} | \phi_{\mu} \phi_{\nu}) P_{\nu\mu}^{\beta} \\
&= \frac{1}{2} \sum_{\mu} \sum_{\nu} H_{\mu\nu}^{\text{core}} P_{\nu\mu}^{\alpha} + \frac{1}{2} \sum_{\mu} \sum_{\nu} \left[ H_{\mu\nu}^{\text{core}} + \sum_a^{N^{\alpha}} (\psi_a^{\alpha} \psi_a^{\alpha} | \phi_{\mu} \phi_{\nu}) - (\psi_a^{\alpha} \phi_{\nu} | \phi_{\mu} \psi_a^{\alpha}) \right] P_{\nu\mu}^{\alpha} \\
&\quad + \frac{1}{2} \sum_{\mu} \sum_{\nu} H_{\mu\nu}^{\text{core}} P_{\nu\mu}^{\beta} + \frac{1}{2} \sum_{\mu} \sum_{\nu} \left[ H_{\mu\nu}^{\text{core}} + \sum_a^{N^{\beta}} (\psi_a^{\beta} \psi_a^{\beta} | \phi_{\mu} \phi_{\nu}) - (\psi_a^{\beta} \phi_{\nu} | \phi_{\mu} \psi_a^{\beta}) \right] P_{\nu\mu}^{\beta} \\
&\quad + \frac{1}{2} \sum_{a=1}^{N^{\alpha}} \sum_{\mu} \sum_{\nu} (\psi_a^{\alpha} \psi_a^{\alpha} | \phi_{\mu} \phi_{\nu}) P_{\nu\mu}^{\beta} + \frac{1}{2} \sum_{a=1}^{N^{\beta}} \sum_{\mu} \sum_{\nu} (\psi_a^{\alpha} \psi_a^{\alpha} | \phi_{\mu} \phi_{\nu}) P_{\nu\mu}^{\alpha} \\
&= \frac{1}{2} \sum_{\mu} \sum_{\nu} H_{\mu\nu}^{\text{core}} P_{\nu\mu}^{\alpha} + \frac{1}{2} \sum_{\mu} \sum_{\nu} H_{\mu\nu}^{\text{core}} P_{\nu\mu}^{\beta} \\
&\quad + \frac{1}{2} \sum_{\mu} \sum_{\nu} \left[ H_{\mu\nu}^{\text{core}} + \sum_a^{N^{\alpha}} (\psi_a^{\alpha} \psi_a^{\alpha} | \phi_{\mu} \phi_{\nu}) - (\psi_a^{\alpha} \phi_{\nu} | \phi_{\mu} \psi_a^{\alpha}) + (\psi_a^{\alpha} \psi_a^{\alpha} | \phi_{\mu} \phi_{\nu}) \right] P_{\nu\mu}^{\alpha} \\
&\quad + \frac{1}{2} \sum_{\mu} \sum_{\nu} \left[ H_{\mu\nu}^{\text{core}} + \sum_a^{N^{\beta}} (\psi_a^{\beta} \psi_a^{\beta} | \phi_{\mu} \phi_{\nu}) - (\psi_a^{\beta} \phi_{\nu} | \phi_{\mu} \psi_a^{\beta}) + (\psi_a^{\alpha} \psi_a^{\alpha} | \phi_{\mu} \phi_{\nu}) \right] P_{\nu\mu}^{\beta} \\
&= \frac{1}{2} \sum_{\mu} \sum_{\nu} H_{\mu\nu}^{\text{core}} P_{\nu\mu}^T + \frac{1}{2} \sum_{\mu} \sum_{\nu} F_{\mu\nu}^{\alpha} P_{\nu\mu}^{\alpha} + \frac{1}{2} \sum_{\mu} \sum_{\nu} F_{\mu\nu}^{\beta} P_{\nu\mu}^{\beta} \\
&= \frac{1}{2} \sum_{\mu} \sum_{\nu} [H_{\mu\nu}^{\text{core}} P_{\nu\mu}^T + F_{\mu\nu}^{\alpha} P_{\nu\mu}^{\alpha} + F_{\mu\nu}^{\beta} P_{\nu\mu}^{\beta}].
\end{aligned}$$

### 3.8.6 Illustrative Unrestricted Calculations

#### Exercise 3.41

Assume the unrestricted Hartree-Fock (UHF) calculations of Table 3.26 contain only the leading quartet contaminant. That is,

$$\Psi_{\text{UHF}} = c_1 {}^2\Psi + c_2 {}^4\Psi.$$

If the percent contamination is defined as  $\frac{100c_2^2}{c_1^2 + c_2^2}$ , calculate the percent contamination of each of the four calculations from the quoted value of  $\langle \mathcal{S}^2 \rangle$ .

#### Solution 3.41

For the sake of simplicity, we request that  $\Psi_{\text{UHF}}$  is normalized. Thus,

$$|c_1|^2 + |c_2|^2 = 1,$$

and then the expectation of  $\mathcal{S}^2$  is

$$\begin{aligned}
\langle \Psi_{\text{UHF}} | \mathcal{S}^2 | \Psi_{\text{UHF}} \rangle &= (c_1^* \langle {}^2\Psi | + c_2^* \langle {}^4\Psi |) \mathcal{S}^2 (c_1 | {}^2\Psi \rangle + c_2 | {}^4\Psi \rangle) \\
&= |c_1|^2 \langle {}^2\Psi | \mathcal{S}^2 | {}^2\Psi \rangle + c_1^* c_2 \langle {}^2\Psi | \mathcal{S}^2 | {}^4\Psi \rangle + c_2^* c_1 \langle {}^4\Psi | \mathcal{S}^2 | {}^2\Psi \rangle + |c_2|^2 \langle {}^4\Psi | \mathcal{S}^2 | {}^4\Psi \rangle \\
&= |c_1|^2 \frac{1}{2} \left( \frac{1}{2} + 1 \right) + |c_2|^2 \frac{3}{2} \left( \frac{3}{2} + 1 \right) = \frac{3}{4} |c_1|^2 + \frac{15}{4} |c_2|^2 = \frac{3}{4} + 3 |c_2|^2,
\end{aligned}$$

which means

$$|c_2| = \sqrt{\frac{1}{3} \left( \langle \mathcal{S}^2 \rangle - \frac{3}{4} \right)}.$$

According to this equation, we can calculate the percent contamination of each of the four calculations and these results are listed in Table 3.5.

Table 3.5: The percent contamination of each of the four calculations.

basis set	$\langle \mathcal{S}^2 \rangle$	$ c_2 $	percent contamination (%)
STO-3G	0.7652	0.07118	0.5067
4-31G	0.7622	0.06377	0.4067
6-31G*	0.7618	0.06272	0.3934
6-31G**	0.7614	0.06164	0.3800

### 3.8.7 The Dissociation Problem and its Unrestricted Solution

#### Exercise 3.42

Show that the set of  $\alpha$  orbitals  $\{\psi_1^\alpha, \psi_2^\alpha\}$  and the set of  $\beta$  orbitals  $\{\psi_1^\beta, \psi_2^\beta\}$  form separate orthonormal sets.

#### Solution 3.42

This conclusion can be proved in the same way as Exercise 2.6.

#### Exercise 3.43

Use the molecular integrals given in Appendix D to show that no unrestricted solution exists for minimal basis STO-3G  $\text{H}_2$  at  $R = 1.4$  a.u. Repeat the calculation for  $R = 4.0$  a.u. and show that an unrestricted solution exists with  $\theta = 39.5^\circ$ . Remember that  $\varepsilon_1 = h_{11} + J_{11}$  and  $\varepsilon_2 = h_{22} + 2J_{12} - K_{12}$ .

#### Solution 3.43

When  $R = 1.4$  a.u., we know that

$$\begin{aligned} \varepsilon_1 &= -0.5782 \text{ a.u.}, & \varepsilon_2 &= 0.6703 \text{ a.u.}, & J_{11} &= 0.6746 \text{ a.u.}, \\ J_{12} &= 0.6636 \text{ a.u.}, & J_{22} &= 0.6975 \text{ a.u.}, & K_{12} &= 0.1813 \text{ a.u.}, \end{aligned}$$

and thus

$$h_{11} = \varepsilon_1 - J_{11} = -1.2528 \text{ a.u.}, \quad h_{22} = \varepsilon_2 - 2J_{12} + K_{12} = -0.4756 \text{ a.u.}$$

Using (3.375) and (3.376), we find that

$$\cos^2 \theta = \eta = \frac{h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} = \frac{1.1627}{0.7701} = 1.5098 > 1.$$

Thus we conclude that no unrestricted solution exists for minimal basis STO-3G  $\text{H}_2$  at  $R = 1.4$  a.u. Similarly, we list all integrals at  $R = 4.0$  a.u..

$$\begin{aligned} \varepsilon_1 &= -0.2542 \text{ a.u.}, & \varepsilon_2 &= 0.0916 \text{ a.u.}, & J_{11} &= 0.5026 \text{ a.u.}, \\ J_{12} &= 0.5121 \text{ a.u.}, & J_{22} &= 0.5259 \text{ a.u.}, & K_{12} &= 0.2651 \text{ a.u.}, \end{aligned}$$

and thus

$$h_{11} = \varepsilon_1 - J_{11} = -0.7568 \text{ a.u.}, \quad h_{22} = \varepsilon_2 - 2J_{12} + K_{12} = -0.6675 \text{ a.u.}$$

Using (3.375) and (3.376), we find that

$$\cos^2 \theta' = \eta' = \frac{h_{22} - h_{11} + J_{22} - J_{12} + 2K_{12}}{J_{11} + J_{22} - 2J_{12} + 4K_{12}} = \frac{0.6333}{1.0647} = 0.5948 \leq 1,$$

which leads to  $\theta' = \frac{1}{2} \arccos 2\eta' - 1 = 0.6900 = 39.54^\circ$ . Thus we conclude that an unrestricted solution exists for minimal basis STO-3G  $\text{H}_2$  at  $R = 4.0$  a.u.

#### Exercise 3.44

Derive Eq.(3.379) from Eq.(3.382).

**Solution 3.44**

From (3.382), we find that

$$1 + 1$$