

# 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

3-2 so

### 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

3-2 so

fff

fff

##### 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

3-2 so

### 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

3-4 so

#### 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

3-5 so

#### 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

3-6 so

### 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

3-7 so

#### 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

3-8 so

## 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

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

#### Solution 3.9

3-9 so

### 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

3-10 so

### 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

3-11 so

#### 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

3-12 so

#### 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

3-13 so

### 3.4.4 Expression for the Fock Matrix

#### Exercise 3.14

Assume that the basis functions are real and use the symmetry of 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

3-14 so

### 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  $S$  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

3-15 so

#### Exercise 3.16

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

#### Solution 3.16

3-16 so

### 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

3-17 so

#### 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

3-18 so

## 3.5 Model Calculations on $\text{H}_2$ and $\text{HeH}^+$

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

#### Exercise 3.19

Derive Eq.(3.207).

#### Solution 3.19

3-19 so

**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  $\frac{1}{\sqrt{\pi}}$  for a Slater function ( $\zeta = 1.0$ ).

**Solution 3.20**

3-20 so

**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**

3-21 so

**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**

3-22 so

**Exercise 3.23**

The coefficients of minimal basis  $H_2^+$  are also determined by symmetry and are identical to those of minimal basis  $H_2$ . Use the above result for the coefficients to solve Eq.(3.234) for the orbital energies of minimal basis  $H_2^+$  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**

3-23 so

**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**

3-24 so

**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**

3-25 so

**Exercise 3.26**

Use the result of Exercise 3.23 to show that the orbital energies of minimal basis  $H_2$ , that are a solution to the Roothaan equations  $\mathbf{FC} = \mathbf{SC}\varepsilon$ , are

$$\varepsilon_1 = \frac{F_{11} + F_{12}}{1 + S_{12}} = -0.5782 \text{ a.u.},$$

$$\varepsilon_2 = \frac{F_{11} - F_{12}}{1 - S_{12}} = +0.6703 \text{ a.u.},$$

**Solution 3.26**

3-26 so

**Exercise 3.27**

Use the general result (3.184) for the total electronic energy to show that the electronic energy of minimal basis  $H_2$  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**

3-27 so

**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**

3-28 so

**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**

3-29 so

## 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

3-30 so

### 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.

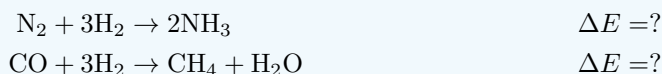
#### Solution 3.31

3-31 so

## 3.7 Some Illustrative Closed-Shell Calculations

#### 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	$h\nu_0/2$ (kcal · mol <sup>-1</sup> )
H <sub>2</sub>	6.18
N <sub>2</sub>	3.35
CO	3.08
H <sub>2</sub> O	2.28
	5.13
	5.33
NH <sub>3</sub>	1.35
	2.32(2)
	4.77
	4.85(2)
CH <sub>4</sub>	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

3-32 so

### 3.7.1 Total Energies

### 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

3-33 so

#### 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

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

#### Solution 3.34

3-34 so



**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

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

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

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

**Solution 3.35**

3-35 so

**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**

3-36 so

**Exercise 3.37**

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

**Solution 3.37**

3-37 so

**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**

3-38 so

**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

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

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

3-39 so

### 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 restricted 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

3-40 so

### 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

3-41 so

### 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

3-42 so

#### 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

3-43 so

**Exercise 3.44**

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

**Solution 3.44**

3-44 so