

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

Solution 3.5

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_μ^{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 H_2 and 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 H₂**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 ψ_1 and ψ_2 by requiring ψ_1 and ψ_2 to be normalized.

Solution 3.22

3-22 so

Exercise 3.23

The coefficients of minimal basis H₂⁺ are also determined by symmetry and are identical to those of minimal basis H₂. Use the above result for the coefficients to solve Eq.(3.234) for the orbital energies of minimal basis H₂⁺ 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 H₂⁺?

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 H₂ 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 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,⁸ 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

α_μ	$C_{\mu i}$
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

111

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

111

Solution 3.33

3-33 so

Exercise 3.34

111

Solution 3.34

3-34 so

Exercise 3.35

111

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 α orbitals $\{\psi_1^\alpha, \psi_2^\alpha\}$ and the set of β 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 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