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 $^NE_0$ (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

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

Solution 3.7

3-7 so

Exercise 3.8

Use expression (3.108) for $\mathscr{V}$, expression (3.18) for the Hartree-Fock potential $v^{\mathrm{HF}}(i)$, and the rules for evaluating matrix elements to explicitly show that $\langle \Psi_0 | \mathscr{V} | \Psi_0 \rangle = -\frac{1}{2} \sum_a \sum_b \langle ab\|ab \rangle$ and hence that $E_0^{[1]}$ cancels the double counting of electron-electron repulsions in $E_0^{(0)} = \sum_a \varepsilon_a$ to give the correct Hartree-Fock energy E_0.

Solution 3.8

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 $\mathbf{C}^\dagger \mathbf{SC} = \mathbf{1}$. *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 $\hat{\rho}(\mathrm{r}) = \sum_{i=1}^N \delta(\mathrm{r}_i - \mathrm{r})$, 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
>
> $$f(\mathbf{r}_1) = h(\mathbf{r}_1) + v^{\mathrm{HF}}(\mathbf{r}_1) = h(\mathbf{r}_1) + \frac{1}{2}\sum_{\lambda\sigma} P_{\lambda\sigma} \left[\int \mathrm{d}r_2 \, \phi_\sigma^*(\mathbf{r}_2)(2 - \mathscr{P}_{12}) r_{12}^{-1} \phi_\lambda(\mathbf{r}_2) \right].$$

> **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 ith 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 H_2

Exercise 3.21

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

Solution 3.21

3-21 so

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 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

$$\varepsilon_1 = \frac{H_{11}^{\text{core}} + H_{12}^{\text{core}}}{1 + S_{12}} = -1.2528 \, \text{a.u.},$$

$$\varepsilon_1 = \frac{H_{11}^{\text{core}} - H_{12}^{\text{core}}}{1 - S_{12}} = -0.4756 \, \text{a.u.}$$

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

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

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

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

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

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

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

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

3.5.3   An SCF Calculation on STO-3G HeH^+

Exercise 3.28

Show 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

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

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

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 $2\langle \mathscr{S}_z \rangle$.

> **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
>
> $$\langle \mathscr{O}_1 \rangle = \sum_{\mu} \sum_{\nu} P_{\mu\nu}^{T} (\nu|h|\mu)$$
>
> for any unrestricted single determinant.

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.

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

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

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 $\dfrac{100c_2^2}{c_1^2 + c_2^2}$, calculate the percent contamination of each of the four calculations from the quoted value of $\langle \mathscr{S}^2 \rangle$.

3.8.7 The Dissociation Problem and its Unrestricted Solution