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

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 $\mathscr{H}_0$ 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

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Solution 3.9

3-9 so

3.4.2 Introduction of a Basis: The Roothaan Equations

Exercise 3.10

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Solution 3.10

3-10 so

3.4.3 The Charge Density

Exercise 3.11

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Solution 3.11

3-11 so

Exercise 3.12

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Solution 3.12

3-12 so

Exercise 3.13

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Solution 3.13

3-13 so

3.4.4 Expression for the Fock Matrix

Exercise 3.14

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Solution 3.14

3-14 so

3.4.5 Orthogonalization of the Basis

Exercise 3.15

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Solution 3.15

3-15 so

Exercise 3.16

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Solution 3.16

3-16 so

3.4.6 The SCF Procedure

3.4.7 Expectation Values and Population Analysis

Exercise 3.17

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Solution 3.17

3-17 so

Exercise 3.18

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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

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Solution 3.19

3-19 so

Exercise 3.20

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Solution 3.20

3-20 so

3.5.2 STO-3G H_2

Exercise 3.21

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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

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Solution 3.23

3-23 so

Exercise 3.24

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Solution 3.24

3-24 so

Exercise 3.25

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Solution 3.25

3-25 so

Exercise 3.26

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Solution 3.26

3-26 so

Exercise 3.27

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Solution 3.27

3-27 so

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

Exercise 3.28

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Solution 3.28

3-28 so

Exercise 3.29

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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

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Solution 3.30

3-30 so

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

Exercise 3.31

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Solution 3.31

3-31 so

3.7 Some Illustrative Closed-Shell Calculations

Exercise 3.32

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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

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Solution 3.33

3-33 so

Exercise 3.34

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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

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Solution 3.36

3-36 so

Exercise 3.37

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Solution 3.37

3-37 so

Exercise 3.38

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Solution 3.38

3-38 so

Exercise 3.39

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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

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Solution 3.40

3-40 so

3.8.6 Illustrative Unrestricted Calculations

Exercise 3.41

111

Solution 3.41

3-41 so

3.8.7 The Dissociation Problem and its Unrestricted Solution

Exercise 3.42

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Solution 3.42

3-42 so

Exercise 3.43

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Solution 3.43

3-43 so

Exercise 3.44

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

Solution 3.44

3-44 so