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 NE_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 \mathcal{V} , expression (3.18) for the Hartree-Fock potential $v^{\mathrm{HF}}(i)$, and the rules for evaluating matrix elements to explicitly show that $\langle \Psi_0 | \mathcal{V} | \Psi_0 \rangle = -\frac{1}{2} \sum_a \sum_b \langle ab \| ab \rangle$ 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
111

Solution 3.9
3-9 so

3.4.2 Introduction of a Basis: The Roothaan Equations

Exercise 3.10
111

Solution 3.10
3-10 so

3.4.3 The Charge Density

Exercise 3.11
111

Solution 3.11
3-11 so

Exercise 3.12
111

Solution 3.12
3-12 so

Exercise 3.13
111

Solution 3.13
3-13 so

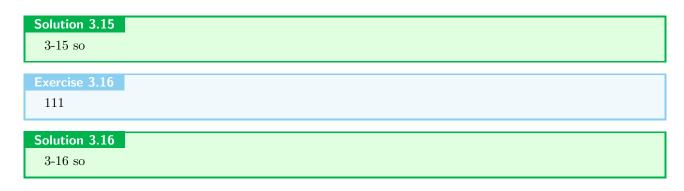
3.4.4 Expression for the Fock Matrix

Exercise 3.14
111

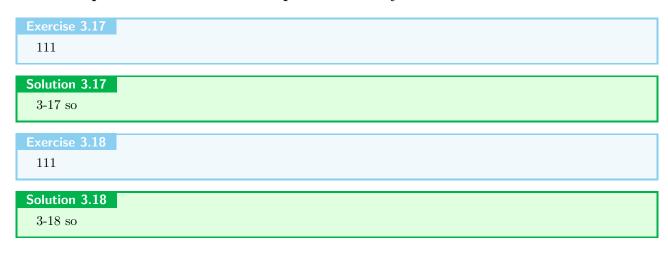
Solution 3.14
3-14 so

3.4.5 Orthogonalization of the Basis

Exercise 3.15
111



- 3.4.6 The SCF Procedure
- 3.4.7 Expectation Values and Population Analysis



- 3.5 Model Calculations on H_2 and HeH^+
- 3.5.1 The 1s Minimal STO-3G Basis set

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Exercise 3.19
111

Solution 3.19
3-19 so

Exercise 3.20
111

Solution 3.20
3-20 so
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3.5.2 STO-3G H_2

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Exercise 3.21
111

Solution 3.21
3-21 so
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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

111

Solution 3.23

3-23 so

Exercise 3.24

111

Solution 3.24

3-24 so

Exercise 3.25

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Solution 3.25

3-25 so

Exercise 3.26

111

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

111

Solution 3.28

3-28 so

Exercise 3.29

111

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

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Exercise 3.30
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Solution 3.30
3-30 so
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3.6.4 Polarized Basis Sets: 6-31G* and 6-31G**

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Exercise 3.31
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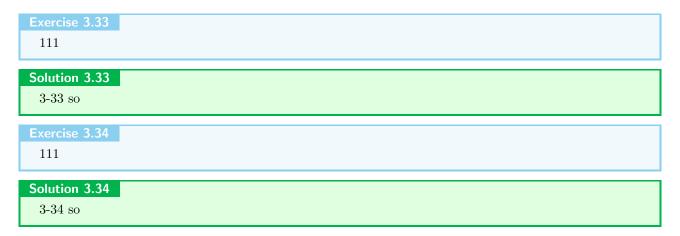
Solution 3.31
3-31 so
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3.7 Some Illustrative Closed-Shell Calculations

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Exercise 3.32
111

Solution 3.32
3-32 so
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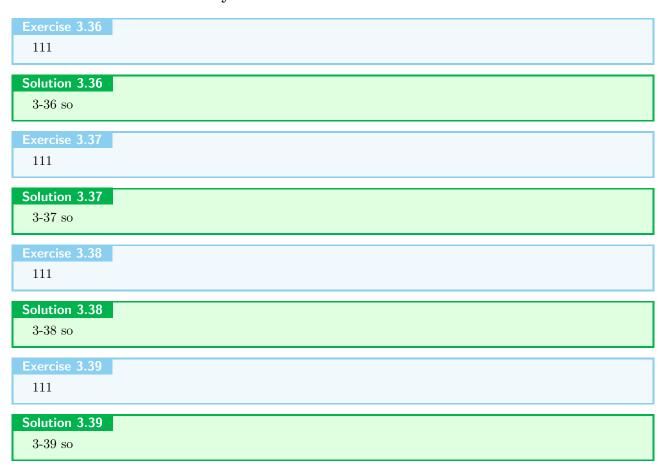
- 3.7.1 Total Energies
- 3.7.2 Ionization Potentials
- 3.7.3 Equilibrium Geometries
- 3.7.4 Population Analysis and Dipole Moments
- 3.8 Unrestricted Open-Shell Hartree-Fock: The Pople-Nesbet Equations
- 3.8.1 Open-Shell Hartree Fock: Unrestricted Spin Orbitals



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Exercise 3.35
111

Solution 3.35
3-35 so
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- 3.8.2 Introduction of a Basis: The Pople-Nesbet Equations
- 3.8.3 Unrestricted Density Matrices



- 3.8.4 Expression for the Fock Matrices
- 3.8.5 Solution of the Unrestricted SCF Equations

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Exercise 3.40
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Solution 3.40
3-40 so
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3.8.6 Illustrative Unrestricted Calculations

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Exercise 3.41
111

Solution 3.41
3-41 so
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3.8.7 The Dissociation Problem and its Unrestricted Solution

Exercise 3.42			
Solution 3.42 3-42 so			
Exercise 3.43			
Solution 3.43 3-43 so			
Exercise 3.44 Derive Eq.(3.3	79) from Eq.(3.382).		
Solution 3.44 3-44 so			