CHAPTER 2

Many Electron Wave Functions and Operators

2.1 The Electron Problem

2.1.1 Atomic Units

2.1.2 The Born-Oppenheimer Approximation

2.1.3 The Antisymmetry or Pauli Exclusion Principle

2.2 Orbitals, Slater Determinants, and Basis Functions

2.2.1 Spin Orbitals and Spatial Orbitals

Exercise 2.1

111

Solution 2.1

2-1 so

2.2.2 Hartree Products

Exercise 2.2

111

Solution 2.2

2-2 so

2.2.3 Slater Determinants

Exercise 2.3

111

Solution 2.3

2-3 so

Exercise 2.4

111

Solution 2.4

2-4 so

Exercise 2.5

111

Solution 2.5

2-5 so

2.2.4 The Hartree-Fock Approximation

2.2.5 The Minimal Basis H_2 Model

Exercise 2.6

Show that ψ_1 and ψ_2 form an orthonormal set.

Solution 2.6

2-6 so

2.2.6 Excited Determinants

2.2.7 Form of the Exact Wave Function and Configuration Interaction

Exercise 2.7

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Solution 2.7

2-7 so

2.3 Operators and Matrix Elements

2.3.1 Minimal Basis H_2 Matrix Elements

Exercise 2.8

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Solution 2.8

2-8 so

Exercise 2.9

111

Solution 2.9

2-9 so

2.3.2 Notations for One- and Two-Electron Integrals

2.3.3 General Rules for Matrix Elements

Exercise 2.10

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Solution 2.10

2-10 so

Exercise 2.11

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Solution 2.11

2-11 so

Exercise 2.12

111

Solution 2.12

2-12 so

Exercise 2.13

111

Solution 2.13

2-13 so

Exercise 2.14

111

Solution 2.14

2-14 so

2.3.4 Derivation of the Rules for Matrix Elements

Exercise 2.15

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Solution 2.15

2-15 so

Exercise 2.16

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Solution 2.16

2-16 so

2.3.5 Transition from Spin Orbitals to Spatial Orbitals

Exercise 2.17

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Solution 2.17

2-17 so

Exercise 2.18

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Solution 2.18

2-18 so

2.3.6 Coulomb and Exchange Integrals

Exercise 2.19

Prove the following properties of coulomb and exchange integrals

$$\begin{aligned} &J_{ii} = K_{ii}, \quad J_{ij}^* = J_{ij}, \quad K_{ij}^* = K_{ij}, \\ &J_{ij} = J_{ji}, \quad K_{ij} = K_{ji}. \end{aligned}$$

Solution 2.19

2-19 so

Exercise 2.20

Show that for *real* spatial orbitals

$$K_{ij} = (ij|ij) = (ji|ji) = \langle ii|jj\rangle = \langle jj|ii\rangle.$$

Solution 2.20

2-20 so

Exercise 2.21

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Solution 2.21

2-21 so

Exercise 2.22

111

Solution 2.22

2-22 so

2.3.7 Pseudo-Classical Interpretation of Determinantal Energies

Exercise 2.23

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Solution 2.23

2-23 so

2.4 Second Quantization

2.4.1 Creation and Annihilation Operators and Their Anticommutation Relations

Exercise 2.24

111

Solution 2.24

2-24 so

Exercise 2.25

111

Solution 2.25

2-25 so

Exercise 2.26

Show using second quantization that $\langle \chi_i | \chi_j \rangle = \delta_{ij}$.

Solution 2.26

2-26 so

Exercise 2.27

Given a state

$$|K\rangle = |\chi_1 \chi_2 \cdots \chi_N\rangle = a_1^\dagger a_2^\dagger \cdots a_N^\dagger |\rangle,$$

show that $\langle K | a_i^\dagger a_j | K \rangle = 1$ if $i = j$ and $i \in \{1, 2, \cdots, N\}$, but is zero otherwise.

Solution 2.27

2-27 so

Exercise 2.28

111

Solution 2.28

2-28 so

2.4.2 Second-Quantized Operators and Their Matrix Elements

Exercise 2.29

111

Solution 2.29

2-29 so

Exercise 2.30

111

Solution 2.30

2-30 so

Exercise 2.31

111

Solution 2.31

2-31 so

2.5 Spin-Adapted Configurations

2.5.1 Spin Operators

Exercise 2.32

111

Solution 2.32

2-32 so

Exercise 2.33

111

Solution 2.33

2-33 so

Exercise 2.34

111

Solution 2.34

2-34 so

Exercise 2.35

111

Solution 2.35

2-35 so

Exercise 2.36

Given two nondegenerate eigenfunctions of a hermitian operator $\mathscr{A}$ that commutes with $\mathscr{H}$, i.e., $\mathscr{A}|\Psi_1\rangle = a_1|\Psi_1\rangle$, $\mathscr{A}|\Psi_2\rangle = a_2|\Psi_2\rangle$, $a_1 \neq a_2$, show that $\langle\Psi_1|\mathscr{H}|\Psi_2\rangle = 0$. Thus the matrix element of the Hamiltonian between, say, singlet and triplet spin-adapted configurations is zero.

Solution 2.36

2-36 so

Exercise 2.37

111

Solution 2.37

2-37 so

2.5.2 Restricted Determinants and Spin-Adapted Configurations

Exercise 2.38

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Solution 2.38

2-38 so

Exercise 2.39

111

Solution 2.39

2-39 so

Exercise 2.40

111

Solution 2.40

2-40 so

2.5.3 Unrestricted Determinants

Exercise 2.41

Consider the determinant $|K\rangle = |\psi_1^\alpha \bar{\psi}_1^\beta\rangle$ formed from *nonorthogonal* spatial orbitals, $\langle\psi_1^\alpha|\psi_1^\beta\rangle = S_{11}^{\alpha\beta}$.

a. Show that $|K\rangle$ is an eigenfunction of $\mathscr{S}^2$ only if $\psi_1^\alpha = \psi_1^\beta$.

b. Show that $\langle K|\mathscr{S}^2|K\rangle = 1$ - $|S_{11}^{\alpha\beta}|^2$ in agreement with Eq.(2.271).

Solution 2.41

2-41 so