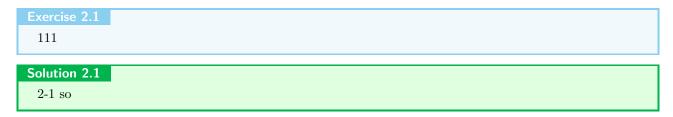
CHAPTER 2

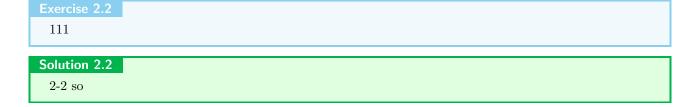
Many Electron Wave Functions and Operators

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2.1	The	Electron	1 Prob	IAM
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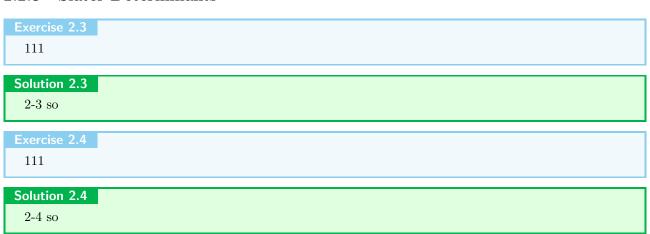
- 2.1.1 Atomic Units
- 2.1.2 The Born-Oppenheimer Approximation
- 2.1.3 The Antisymmetry or Pauli Exclusion Principle
- 2.2 Orbitals, Slater Determinants, and Basis Functions
- 2.2.1 Spin Orbitals and Spatial Orbitals

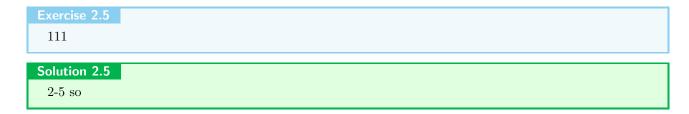


2.2.2 Hartree Products



2.2.3 Slater Determinants





- 2.2.4 The Hartree-Fock Approximation
- 2.2.5 The Minimal Basis H₂ Model

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Exercise 2.6 Show that \psi_1 and \psi_2 form an orthonormal set.

Solution 2.6 2-6 so
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- 2.2.6 Excited Determinants
- 2.2.7 Form of the Exact Wave Function and Configuration Interaction

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Exercise 2.7
111

Solution 2.7
2-7 so
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- 2.3 Operators and Matrix Elements
- 2.3.1 Minimal Basis H₂ Matrix Elements

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Exercise 2.8
111

Solution 2.8
2-8 so

Exercise 2.9
111

Solution 2.9
2-9 so
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- 2.3.2 Notations for One- and Two-Electron Integrals
- 2.3.3 General Rules for Matrix Elements

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Exercise 2.10
111

Solution 2.10
2-10 so
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Exercise 2.11 111	
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	
2-14 so	

2.3.4 Derivation of the Rules for Matrix Elements

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Exercise 2.15
111

Solution 2.15
2-15 so

Exercise 2.16
111

Solution 2.16
2-16 so
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2.3.5 Transition from Spin Orbitals to Spatial Orbitals

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Exercise 2.17
111

Solution 2.17
2-17 so

Exercise 2.18
111

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

$$J_{ii} = K_{ii}, \quad J_{ij}^* = J_{ij}, \quad K_{ij}^* = K_{ij}, J_{ij} = J_{ji}, \quad K_{ij} = K_{ji}.$$

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

111

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

111

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

111

Solution 2.32 2-32 so111 Solution 2.33 2-33 so111 Solution 2.34 2-34 soExercise 2.35 111 Solution 2.35 2-35 soGiven two nondegenerate eigenfunctions of a hermitian operator $\mathscr A$ that commutes with $\mathscr H$, i.e., $\mathscr{A}|\Psi_1\rangle = a_1|\Psi_1\rangle, \ \mathscr{A}|\Psi_2\rangle = a_2|\Psi_2\rangle, \ a_1 \neq a_2, \text{ show that } \langle \Psi_1|\mathscr{H}|\Psi_2\rangle = 0.$ Thus the matrix element of the Hamiltonian between, say, singlet and triplet spin-adapted configurations is zero. Solution 2.36 2-36 so 111 Solution 2.37 2-37 so 2.5.2Restricted Determinants and Spin-Adapted Configurations 111 Solution 2.38 2-38 so 111 Solution 2.39 2-39 so

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