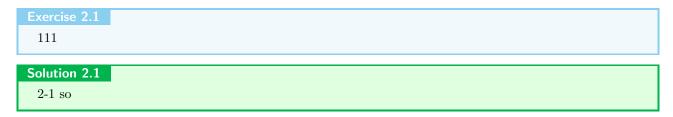
# CHAPTER 2

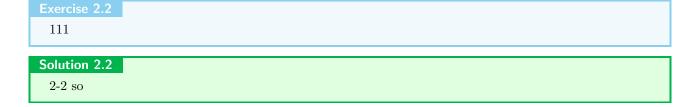
## Many Electron Wave Functions and Operators

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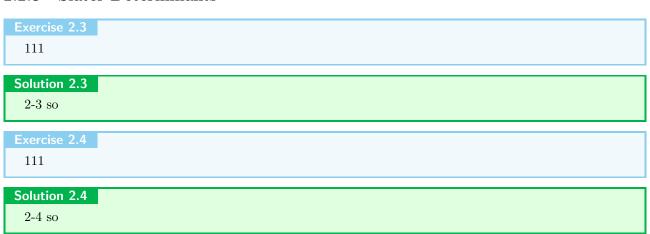
- 2.1.1 Atomic Units
- 2.1.2 The Born-Oppenheimer Approximation
- 2.1.3 The Antisymmetry or Pauli Exclusion Principle
- 2.2 Orbitals, Slater Determinants, and Basis Functions
- 2.2.1 Spin Orbitals and Spatial Orbitals

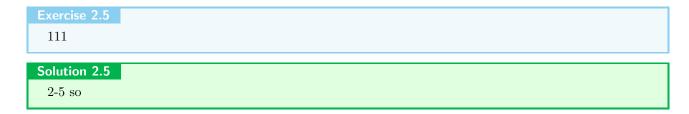


### 2.2.2 Hartree Products



### 2.2.3 Slater Determinants





- 2.2.4 The Hartree-Fock Approximation
- 2.2.5 The Minimal Basis H<sub>2</sub> Model

```
Exercise 2.6 Show that \psi_1 and \psi_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
111

Solution 2.7
2-7 so
```

- 2.3 Operators and Matrix Elements
- 2.3.1 Minimal Basis H<sub>2</sub> Matrix Elements

```
Exercise 2.8
111

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
111

Solution 2.10
2-10 so
```

Exercise 2.11 111	
<b>Solution 2.11</b> 2-11 so	
Exercise 2.12 111	
<b>Solution 2.12</b> 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

```
Exercise 2.15
111

Solution 2.15
2-15 so

Exercise 2.16
111

Solution 2.16
2-16 so
```

## 2.3.5 Transition from Spin Orbitals to Spatial Orbitals

```
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

111

**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			
Solution 2.26 2-26 so			
Exercise 2.27			
Solution 2.27 2-27 so			
Exercise 2.28			
<b>Solution 2.28</b> 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
E : 0.25
Exercise 2.35
111
Solution 2.35
2-35 so
Exercise 2.36
111
Solution 2.36
2-36 so
Exercise 2.37
111
Solution 2.37
2-37 so
2 01 30
2.5.2 Restricted Determinants and Spin-Adapted Configurations
Exercise 2.38
111
Solution 2.38
2-38 so
F 2.20
Exercise 2.39
111
Solution 2.39
2-39 so
2-07-50
Exercise 2.40
111
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