

## Contents

### Preface *xi*

<b>1</b>	<b>Introduction</b>	<i>1</i>
1.1	Different Is Usually Controversial	<i>1</i>
1.2	The Plan: Addressing Dirac's Challenge	<i>2</i>
	Reference	<i>4</i>
<b>2</b>	<b>The Hydrogen Atom</b>	<i>5</i>
2.1	The Bohr Model	<i>5</i>
2.2	The Schrödinger Equation	<i>8</i>
2.3	The Electronic Structure of Atoms and the Periodic Table	<i>15</i>
	References	<i>18</i>
<b>3</b>	<b>Many-electron Atoms</b>	<i>19</i>
3.1	The Variational Principle	<i>19</i>
3.1.1	Estimating the Energy of a Helium Atom	<i>21</i>
3.2	The Hartree Approximation	<i>22</i>
3.3	The Hartree–Fock Approximation	<i>25</i>
	References	<i>27</i>
<b>4</b>	<b>The Free Electron Gas</b>	<i>29</i>
4.1	Free Electrons	<i>29</i>
4.2	Hartree–Fock Exchange in a Free Electron Gas	<i>35</i>
	References	<i>36</i>
<b>5</b>	<b>Density Functional Theory</b>	<i>37</i>
5.1	Thomas–Fermi Theory	<i>37</i>
5.2	The Kohn–Sham Equation	<i>40</i>
	References	<i>43</i>
<b>6</b>	<b>Pseudopotential Theory</b>	<i>45</i>
6.1	The Pseudopotential Approximation	<i>45</i>
6.1.1	Phillips–Kleinman Cancellation Theorem	<i>47</i>

6.2	Pseudopotentials Within Density Functional Theory	50
	References	57
<b>7</b>	<b>Methods for Atoms</b>	59
7.1	The Variational Approach	59
7.1.1	Estimating the Energy of the Helium Atom.	59
7.2	Direct Integration	63
7.2.1	Many-electron Atoms Using Density Functional Theory	67
	References	69
<b>8</b>	<b>Methods for Molecules, Clusters, and Nanocrystals</b>	71
8.1	The H <sub>2</sub> Molecule: Heitler–London Theory	71
8.2	General Basis	76
8.2.1	Plane Wave Basis	79
8.2.2	Plane Waves Applied to Localized Systems	87
8.3	Solving the Eigenvalue Problem	89
8.3.1	An Example Using the Power Method	92
	References	95
<b>9</b>	<b>Engineering Quantum Mechanics</b>	97
9.1	Computational Considerations	97
9.2	Finite Difference Methods	99
9.2.1	Special Diagonalization Methods: Subspace Filtering	101
	References	104
<b>10</b>	<b>Atoms</b>	107
10.1	Energy levels	107
10.2	Ionization Energies	108
10.3	Hund's Rules	110
10.4	Excited State Energies and Optical Absorption	113
10.5	Polarizability	122
	References	124
<b>11</b>	<b>Molecules</b>	125
11.1	Interacting Atoms	125
11.2	Molecular Orbitals: Simplified	125
11.3	Molecular Orbitals: Not Simplified	130
11.4	Total Energy of a Molecule from the Kohn–Sham Equations	132
11.5	Optical Excitations	137
11.5.1	Time-dependent Density Functional Theory	138
11.6	Polarizability	140
11.7	The Vibrational Stark Effect in Molecules	140
	References	150
<b>12</b>	<b>Atomic Clusters</b>	153
12.1	Defining a Cluster	153

12.2	The Structure of a Cluster	154
12.2.1	Using Simulated Annealing for Structural Properties	155
12.2.2	Genetic Algorithms	159
12.2.3	Other Methods for Determining Structural Properties	162
12.3	Electronic Properties of a Cluster	164
12.3.1	The Electronic Polarizability of Clusters	164
12.3.2	The Optical Properties of Clusters	166
12.4	The Role of Temperature on Excited-state Properties	167
12.4.1	Magnetic Clusters of Iron	169
	References	174
<b>13</b>	<b>Nanocrystals</b>	<b>177</b>
13.1	Semiconductor Nanocrystals: Silicon	179
13.1.1	Intrinsic Properties	179
13.1.1.1	Electronic Properties	179
13.1.1.2	Effective Mass Theory	184
13.1.1.3	Vibrational Properties	187
13.1.1.4	Example of Vibrational Modes for Si Nanocrystals	188
13.1.2	Extrinsic Properties of Silicon Nanocrystals	190
13.1.2.1	Example of Phosphorus-Doped Silicon Nanocrystals	191
	References	197
<b>A</b>	<b>Units</b>	<b>199</b>
<b>B</b>	<b>A Working Electronic Structure Code</b>	<b>203</b>
	References	206
	<b>Index</b>	<b>207</b>

