

## Contents

**Foreword** VII

**Acknowledgments** IX

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	Basics of Computational Chemistry	1
1.2	Aim of This Book	2
1.3	How to Use This Book	3
1.4	Structure of This Book	4
1.5	The Chapters	5
1.6	The Software	9
<b>2</b>	<b>Molecular Coordinates and Symmetry</b>	<b>11</b>
2.1	Aim	11
2.2	Theoretical Background	11
2.2.1	Cartesian and Internal Coordinates	11
2.2.2	The Z-Matrix	12
2.2.3	The Dihedral Angle	13
2.2.4	Symmetry	15
2.2.5	Symmetry Elements and Operations	16
2.2.6	Point Groups	17
2.3	Demonstration	19
2.3.1	Constructing a Z-Matrix	19
2.3.2	Determining Molecular Point Groups	20
2.4	Problems	22
2.5	Technical Details	23
2.6	Review and Summary	23
	References	23

<b>3</b>	<b>Vibrations of Diatomic Molecules: The Harmonic Approximation</b>	<b>25</b>
3.1	Aim	25
3.2	Theoretical Background	25
3.2.1	The Harmonic Approximation	25
3.2.2	The Reduced Mass	27
3.2.3	The Vibrational Frequencies	28
3.3	Demonstration	30
3.4	Problems	32
3.5	Technical Details	33
3.6	Review and Summary	34
	References	34
<b>4</b>	<b>Vibrations of Diatomic Molecules: The Schrödinger Equation</b>	<b>35</b>
4.1	Aim	35
4.2	Theoretical Background	35
4.2.1	Classical Versus Quantum Mechanics	35
4.2.2	The Stationary Schrödinger Equation	37
4.2.3	Solutions to the Schrödinger Equation	39
4.3	Demonstration	43
4.4	Problems	44
4.5	Technical Details	45
4.6	Review and Summary	45
	References	45
<b>5</b>	<b>Atomic Orbitals</b>	<b>47</b>
5.1	Aim	47
5.2	Theoretical Background	47
5.2.1	The Schrödinger Equation of the Atom	47
5.2.2	Atomic Orbitals	49
5.3	Demonstration	51
5.4	Problems	53
5.5	Technical Details	54
5.6	Review and Summary	54
	References	55
<b>6</b>	<b>Ionization Potentials and Electron Affinities of Atoms</b>	<b>57</b>
6.1	Aim	57
6.2	Theoretical Background	57
6.2.1	Ionization Potential and Electron Affinity	57
6.2.2	Slater Rules: Wavefunction and Binding Energies of Electrons in Atoms and Ions	59
6.2.3	Calculation of Ionization Potentials and Electron Affinities	61

6.3	Demonstration	62
6.4	Problems	64
6.5	Technical Details	65
6.6	Review and Summary	66
	References	66
<b>7</b>	<b>Hückel Molecular Orbital Theory: Stability of Conjugated Carbon <math>\pi</math> Systems</b>	<b>67</b>
7.1	Aim	67
7.2	Theoretical Background	67
7.2.1	Molecular Orbital Theory	68
7.2.2	The Hückel Postulates	70
7.2.3	Topology Matrices	71
7.2.4	Values for $\alpha$ and $\beta$	73
7.2.5	The Trap of Defining $x$	73
7.2.6	$\pi$ Electron Binding Energy	74
7.2.7	$\pi$ Electron Molecular Orbitals and Probability Density	74
7.3	Demonstration	75
7.3.1	Hückel Calculation of the Cyclopropenyl Cation	75
7.4	Problems	78
7.5	Technical Details	79
7.6	Review and Summary	80
	References	81
<b>8</b>	<b>Hückel Molecular Orbital Theory: Bond Order, Charge Order, and Molecular Orbitals</b>	<b>83</b>
8.1	Aim	83
8.2	Theoretical Background	83
8.2.1	Bond Order	83
8.2.2	Charge Order	84
8.3	Demonstration	85
8.3.1	Hückel Calculation of the Butadiene Molecule	85
8.4	Problems	88
8.5	Review and Summary	89
	References	90
<b>9</b>	<b>Geometry Optimization of a Diatomic Molecule</b>	<b>91</b>
9.1	Aim	91
9.2	Theoretical Background	91
9.2.1	The Potential Energy Surface	91
9.2.2	Forces in a Diatomic Molecule	93
9.2.3	The Steepest Descent Method	94
9.2.4	Hessian-Based Optimizers and the Newton–Raphson Method	95
9.2.5	Application to the Morse Potential	97

9.2.6	Global Versus Local Geometry Optimization	97
9.3	Demonstration	98
9.3.1	Optimizing CO With the Steepest Descent Method	98
9.3.2	Optimizing CO Using a Hessian-Based Newton–Raphson Optimizer	100
9.4	Problems	103
9.5	Technical Details	103
9.6	Review and Summary	104
	References	105
<b>10</b>	<b>The Electron Spin</b>	<b>107</b>
10.1	Aim	107
10.2	Theoretical Background	107
10.2.1	The Electron Spin	107
10.2.2	The Multiplicity	108
10.2.3	The Jahn–Teller Effect	108
10.3	Demonstration	109
10.4	Problems	110
10.5	Technical Details	111
10.6	Review and Summary	112
	References	112
<b>11</b>	<b>Vibrational Spectroscopy</b>	<b>113</b>
11.1	Aim	113
11.2	Theoretical Background	113
11.2.1	Analysis of Classical Vibrations Within the Harmonic Approximation	114
11.2.2	The Harmonic Oscillator Revisited	115
11.2.3	The Vibrational Modes	117
11.2.4	Intensities	119
11.3	Demonstration	120
11.3.1	The Vibrational Modes of a Linear Molecule	120
11.4	Problems	124
11.5	Technical Details	125
11.6	Review and Summary	126
	References	126
<b>12</b>	<b>Vibrational Spectroscopy and Character Tables – Advanced Topics</b>	<b>127</b>
12.1	Aim	127
12.2	Theoretical Background	127
12.2.1	The Hessian Matrix	127
12.2.2	Normal Modes	129
12.2.3	Symmetry in Normal Modes	130

12.2.4	Selection Rules	133
12.3	Demonstration	136
12.4	Problems	138
12.5	Review and Summary	140
	References	141
<b>13</b>	<b>Ionization Potential and Electron Affinities of Molecules</b>	<b>143</b>
13.1	Aim	143
13.2	Theoretical Background	143
13.2.1	Field of Application	143
13.2.2	Influence of Geometry	144
13.3	Demonstration	146
13.4	Problems	147
13.4.1	Technical Details	148
13.5	Review and Summary	148
	References	149
<b>14</b>	<b>Thermochemistry</b>	<b>151</b>
14.1	Aim	151
14.2	Theoretical Background	151
14.2.1	Calculating Thermodynamic Functions Using the Partition Function	152
14.2.2	Thermochemistry Within the Ideal-Gas Approximation	154
14.2.3	The Molecular Partition Function $q$	156
14.2.4	Calculating the Relative Abundance of Isomers in the Gas Phase	160
14.3	Demonstration	161
14.4	Problems	164
14.5	Review and Summary	165
	References	165
<b>15</b>	<b>Molecular Dynamics – Basic Concepts</b>	<b>167</b>
15.1	Aim	167
15.2	Theoretical Background	167
15.2.1	Computer Simulations in Chemistry	167
15.2.2	The Born–Oppenheimer Approximation	169
15.2.3	The Trajectory: Startup Conditions and Propagation of Atoms in Time	169
15.2.4	The Verlet Algorithm	170
15.2.5	The Velocity Verlet Algorithm	171
15.2.6	Conservation of Fundamental Physical Quantities: Energy, Momentum, and Angular Momentum	172
15.2.7	Numerical Considerations	173

15.2.8	Heat Bath: Thermostats	174
15.3	Demonstration	174
15.3.1	Classical Molecular Dynamics in a Spreadsheet	174
15.4	Problems	178
15.5	Review and Summary	178
	References	179
<b>16</b>	<b>Molecular Dynamics and Basic Thermodynamics</b>	<b>181</b>
16.1	Aim	181
16.2	Theoretical Background	181
16.2.1	Basic Thermodynamics: Ensembles	182
16.2.2	The Temperature and the Ergodic Theorem	183
16.2.3	The Connection to Real Macroscopic Systems	185
16.2.4	External Heat Baths – Thermostats	186
16.2.4.1	A Simple Scaling Thermostat	186
16.2.4.2	The Berendsen Thermostat	186
16.2.4.3	The Andersen Thermostat	187
16.2.4.4	The Nosé-Hoover Thermostat	187
16.2.5	Averages	188
16.3	Demonstration	188
16.4	Problems	194
16.5	Review and Summary	195
	References	196
<b>17</b>	<b>Molecular Dynamics – Simulated Annealing</b>	<b>197</b>
17.1	Aim	197
17.2	Theoretical Background	197
17.2.1	The Potential Energy Surface	199
17.2.2	Simulated Annealing	200
17.3	Demonstration	201
17.3.1	Inspecting Stationary Points With Simulated Annealing	201
17.3.2	Finding the Global Minimum of $\text{Al}_4^{2-}$ Using Simulated Annealing	203
17.4	Problems	205
17.5	Review and Summary	206
	References	207
	<b>Appendix</b>	
	<b>The Computational Chemistry Software Delivered with This Book</b>	<b>209</b>
A.1	Getting Started	210
A.1.1	Booting Directly the Live System	210
A.1.2	Booting as Virtual Machine	210
A.1.3	Running From a Pen Drive (USB Stick)	211

A.1.4	Configure Your Environment	213
A.2	A Brief Introduction to Linux	214
A.3	Character Tables for Chemically Important Point Groups	218
A.4	Computational Chemistry Software Delivered With This Book	219
A.4.1	Molden	219
A.4.2	deMon	219
A.4.3	CaGe	220
A.4.4	hueckel	222
A.4.5	THERMO Scripts	222
A.4.6	Xmgrace	223
A.4.7	GNUplot	223
	<b>Index</b>	<b>225</b>

