

Jan C. A. Boeyens

# Chemistry from First Principles



# Contents

<b>I A New Look at Old Theories</b>	<b>1</b>
<b>1 Historical Perspective</b>	<b>3</b>
<b>2 The Important Concepts</b>	<b>9</b>
2.1 The Principle of Relativity . . . . .	10
2.1.1 Relative Motion . . . . .	11
2.1.2 Lorentz Transformation . . . . .	12
2.1.3 General Relativity . . . . .	19
2.2 The Old Quantum Theory . . . . .	22
2.2.1 The Bohr Model . . . . .	22
2.2.2 The Sommerfeld Model . . . . .	27
2.3 Wave-Particle Duality . . . . .	31
2.3.1 Photoelectric Effect . . . . .	31
2.3.2 Compton Effect . . . . .	32
2.3.3 Electron Diffraction . . . . .	33
2.3.4 Wave Packets . . . . .	35
2.3.5 Matter Waves . . . . .	37
2.3.6 Historical Note . . . . .	39
2.4 Orbital Angular Momentum . . . . .	41
2.4.1 Laplace's Equation . . . . .	41
2.4.2 Angular Momentum . . . . .	45
2.4.3 Surface Harmonics . . . . .	47
2.5 The Quantum Theory . . . . .	48
2.5.1 The Uncertainty Principle . . . . .	49
2.5.2 The Measurement Problem . . . . .	49
2.5.3 The Quantum Limit . . . . .	50
2.5.4 Wave Mechanics . . . . .	52
2.5.5 Schrödinger's Equation . . . . .	54
2.5.6 Quantum Probability . . . . .	56
2.5.7 The Periodic Table . . . . .	57
2.6 Atomic Shape . . . . .	59

2.6.1	Chemical Affinity and Shape . . . . .	59
2.6.2	Orbiting Electrons . . . . .	60
2.6.3	Hybrid Orbitals . . . . .	61
2.6.4	Atomic Structure . . . . .	65
2.6.5	Compressed Atoms . . . . .	66
2.7	Chemical Bonding . . . . .	67
2.7.1	Classical Theory . . . . .	67
2.7.2	Quantum Theory . . . . .	68
2.7.3	Critique of the Model . . . . .	69
<b>3</b>	<b>The Quantum Quandary</b>	<b>73</b>
3.1	The Classical Background . . . . .	73
3.1.1	Hamilton-Jacobi Theory . . . . .	74
3.1.2	Periodic Systems . . . . .	81
3.1.3	Conclusion . . . . .	85
3.2	The Copenhagen Orthodoxy . . . . .	86
3.2.1	Matrix Mechanics . . . . .	86
3.2.2	The Interpretational Problem . . . . .	89
3.2.3	The Copenhagen Model . . . . .	90
3.3	The Schrödinger Interpretation . . . . .	94
3.3.1	The Negative Reaction . . . . .	95
3.3.2	The Positive Aspects . . . . .	98
3.3.3	The Wave Formalism . . . . .	101
3.3.4	Summary . . . . .	103
3.4	The Hydrodynamic Alternative . . . . .	104
3.4.1	Madelung's Model . . . . .	104
3.4.2	Refinements of the Model . . . . .	106
3.4.3	Implications of the Model . . . . .	107
3.5	Bohmian Mechanics . . . . .	109
3.5.1	Quantum Potential . . . . .	110
3.5.2	The Phase Factor . . . . .	113
3.5.3	Stationary States . . . . .	115
3.6	Atomic Theory . . . . .	116
3.6.1	The Virial Theorem . . . . .	116
3.6.2	Electronic Structure . . . . .	117
3.6.3	Compressive Activation . . . . .	118
3.7	Quantum Chemistry . . . . .	120
3.7.1	The <i>Ab-initio</i> Model . . . . .	122
3.7.2	The Hellmann-Feynman Theorem . . . . .	124
3.8	Density Functional Theory . . . . .	125

<b>II Alternative Theory</b>	<b>127</b>
<b>4 The Periodic Laws</b>	<b>129</b>
4.1 Introduction . . . . .	129
4.2 Nuclide Periodicity . . . . .	130
4.3 The Number Spiral . . . . .	132
4.4 Elemental Synthesis . . . . .	135
4.5 The Golden Parameter . . . . .	139
4.6 Periodic Table of the Elements . . . . .	140
4.6.1 Farey Fractions and Ford Circles . . . . .	141
4.7 Electron Spin . . . . .	144
4.7.1 Spherical Rotation . . . . .	144
4.7.2 Schrödinger's Equation and Spin . . . . .	146
4.7.3 The Spin Model . . . . .	149
4.7.4 Hund's Rule . . . . .	150
4.8 Nuclear Structure and Spin . . . . .	151
4.9 Nucleon Periodicity . . . . .	152
4.9.1 Farey and Ford Analysis . . . . .	153
4.10 Conclusion . . . . .	156
<b>5 Chemical Interaction</b>	<b>159</b>
5.1 The Valence State . . . . .	159
5.2 Electronegativity . . . . .	163
5.3 Covalent Interaction . . . . .	165
5.3.1 The Diatomic Energy Curve . . . . .	170
5.3.2 Generalized Covalence . . . . .	171
5.3.3 Bond Dissociation Energy . . . . .	174
5.3.4 The Quantum Model . . . . .	177
5.3.5 Screening and Bond Order . . . . .	179
5.4 Chemical Cohesion . . . . .	182
5.4.1 Interaction Theory . . . . .	183
5.4.2 Cohesive Interaction . . . . .	185
5.4.3 Conspectus . . . . .	196
<b>6 Structure Theory</b>	<b>203</b>
6.1 The Structure Hypothesis . . . . .	203
6.1.1 Mechanical Simulation . . . . .	205
6.1.2 Charge Density . . . . .	207
6.2 Angular Momentum and Shape . . . . .	207
6.2.1 Small Molecules . . . . .	208
6.2.2 Conformational Rigidity . . . . .	212

6.2.3	Molecular Chirality . . . . .	212
6.3	Molecular Modelling . . . . .	215
6.3.1	Free-electron Modelling . . . . .	215
6.3.2	The Jahn-Teller Model . . . . .	223
6.3.3	Molecular Mechanics . . . . .	224
6.4	Molecular Structure . . . . .	230
6.4.1	Charge and Momentum Density . . . . .	231
6.4.2	Crystallographic Analysis . . . . .	234
6.4.3	Molecules and Crystals . . . . .	239
6.4.4	Structural Formulae . . . . .	241
6.5	Emergent Structure . . . . .	243
6.5.1	Molecular Shape . . . . .	245
6.6	The Metaphysics . . . . .	246
<b>7</b>	<b>Chemical Change</b>	<b>249</b>
7.1	Thermodynamic Potentials . . . . .	249
7.2	Chemical Reactivity . . . . .	250
7.3	The Boltzmann Distribution . . . . .	253
7.4	Entropy . . . . .	254
7.5	Chemical Reaction . . . . .	255
7.5.1	Atomic Reactions . . . . .	257
7.6	Chemical Kinetics . . . . .	259
<b>8</b>	<b>The Central Science</b>	<b>261</b>
8.1	Introduction . . . . .	261
8.2	The Solar System . . . . .	262
8.2.1	Spiral Structure . . . . .	263
8.3	Chemical Science . . . . .	265
8.3.1	Where did Chemistry go wrong? . . . . .	266
8.3.2	Constructionism . . . . .	268
8.3.3	Emergent Chemical Properties . . . . .	269
8.4	General Chemistry . . . . .	270
8.4.1	Chemical Substance . . . . .	271
8.4.2	Electromagnetism . . . . .	272
8.4.3	Relativistic Effects . . . . .	273
8.4.4	Interaction Theory . . . . .	274
8.4.5	Quantum Effects . . . . .	275
8.4.6	The Wave Mechanics . . . . .	276
8.4.7	The Chemical Environment . . . . .	277
8.4.8	Covalence . . . . .	278
8.4.9	The Exclusion Principle . . . . .	279

8.4.10	The Common Model . . . . .	279
8.4.11	Molecular Structure . . . . .	280
8.4.12	Electron Spin . . . . .	281
8.4.13	Periodicity of Matter . . . . .	282
8.4.14	Nuclear Genesis . . . . .	285
8.4.15	Reaction Theory . . . . .	285
8.5	Chemical Cosmology . . . . .	288
8.5.1	Nuclear Synthesis . . . . .	289
8.5.2	Chirality of Space . . . . .	290
8.5.3	The Microwave Background . . . . .	291
8.5.4	Spectroscopic Red Shifts . . . . .	291
8.5.5	Conclusion . . . . .	291
	<b>Bibliography</b>	<b>293</b>
	<b>Index</b>	<b>299</b>