
Contents

1	Thermodynamics	1
1.1	Ideal Gas	2
1.2	Kinetic Model of Gases	3
1.2.1	Pressure and Temperature	4
1.2.2	Distribution of Velocities	6
1.2.3	Mean Free Path	9
1.3	Van der Waals Equation	13
1.4	Mathematical Tools	16
1.4.1	Exact Differential	17
1.4.2	Fundamental Theorem of Calculus	20
1.4.3	Line Integral	21
1.5	Thermodynamic Systems	23
1.6	Heat and Work	24
1.6.1	Mechanical Work	25
1.7	First Law	26
1.7.1	Heat Capacities	28
1.7.2	Calorimeter	29
1.7.3	Standard States	30
1.8	Reversible Heat Engine	31
1.8.1	Carnot's Heat Engine	33
1.8.2	Absolute Temperature	33
1.9	Entropy and the Second Law	35
1.10	Irreversible Processes	38
1.10.1	Heat Flow	38
1.10.2	Gas Expansion	39
1.10.3	Diffusion of Matter	40
1.10.4	Chemical Reaction	41
1.11	Chemical Potential	42
1.11.1	Gibbs–Duhem Equation	43
1.11.2	Ideal Gas	44
1.11.3	Real Gases	45
1.11.4	Liquid Solutions	46
1.11.5	Pure Liquids and Solids	47

1.12	Gibbs Energy	47
1.12.1	Chemical Potential and Gibbs Energy of Formation	48
1.12.2	Gibbs–Helmholtz Equation.	50
1.13	Chemical Equilibrium	51
1.14	Gibbs Phase Rule.	52
1.15	Helmholtz Energy	54
1.16	Surface Tension	55
1.16.1	Liquid Droplet in Air	55
1.16.2	Capillary Action	56
1.17	Membrane Potential	58
1.18	Electrochemical Cell.	61
1.18.1	Nernst Equation	62
	Notes	65
	<i>Mathematica</i> Codes	69
	Glossary	75
	Exercises	81
	References	82
	Further Reading.	82
2	Chemical Kinetics	83
2.1	Rate of a Chemical Reaction	84
2.2	Experimental Rate Equation.	86
2.2.1	First-Order Reactions	87
2.2.2	Second-Order Reactions.	88
2.2.3	Zeroth-Order Reactions	89
2.3	Effect of Temperature Change	89
2.4	Elementary Reactions	91
2.5	Complex Reactions.	92
2.6	Extremely Fast Reactions	94
2.6.1	Neutralization Reaction in Water	96
2.7	Chemical Oscillations	96
2.7.1	Brusselator.	97
	Notes	102
	<i>Mathematica</i> Codes	106
	Glossary	108
	Exercises	110
	References	111
	Further Reading.	111
3	The Schrödinger Equation	113
3.1	Operators	114
3.1.1	Eigenvalues and Eigenfunctions	115
3.1.2	One-Dimensional Schrödinger Equation.	115
3.1.3	Hermitian Operators	117

3.1.4	Important Theorems	118
3.1.5	Dirac Notation	121
3.2	Harmonic Oscillator	121
3.2.1	Reduced Mass	122
3.2.2	Classical Treatment	123
3.2.3	Quantum-Mechanical Treatment	124
3.2.4	Morse Potential	127
3.3	Spherical Coordinates	128
3.4	Angular Momentum	130
3.4.1	Orbital Angular Momentum	131
3.4.2	Spin	133
3.5	Hydrogen Atom	134
3.6	Antisymmetry Principle	137
3.7	Variational Method	141
3.8	Born–Oppenheimer Approximation	143
3.9	Hartree–Fock Method	146
3.9.1	Slater-Type Orbitals	148
3.9.2	Hartree–Fock Equations	149
3.9.3	Hartree–Fock–Roothaan Equations	150
3.9.4	Correlation Energy	151
3.10	Density Functional Theory	152
3.10.1	Electron Probability Density	152
3.10.2	External Potential	152
3.10.3	Functional Derivative	153
3.10.4	Hohenberg–Kohn Theorems	156
3.10.5	Kohn–Sham Method	157
3.10.6	Overview	160
3.11	Perturbation Theory	161
3.11.1	Nondegenerate Energy Level	162
3.11.2	Variational Perturbation Method	164
3.11.3	Degenerate Energy Level	166
3.12	Time-Dependent Perturbation Theory	168
3.12.1	Time-Dependent Schrödinger Equation	168
3.12.2	Time-Dependent Perturbation	169
3.13	Absorption and Emission of Radiation	172
3.13.1	Spontaneous Emission of Radiation	175
3.14	Raman Scattering	176
3.14.1	Classical Treatment	177
3.14.2	Quantum-Mechanical Treatment	178
3.15	Molecular Calculations	181
3.15.1	Computational Methods	181
3.15.2	Gaussian-Type Functions	182
3.15.3	Standard Basis Sets	185

Notes	186
<i>Mathematica</i> Codes	190
Glossary	200
Exercises	203
References	205
Further Reading	205
4 Molecular Symmetry	207
4.1 Symmetry Operations	207
4.2 Point Groups	210
4.3 Matrix Representations	214
4.4 Character Tables	218
4.5 Selection Rules	222
4.6 Molecular Vibrations	224
<i>Mathematica</i> Codes	232
Glossary	238
Exercises	240
Further Reading	241
5 Molecular Structure	243
5.1 Electron Probability Density	244
5.2 Electrostatic Potential	245
5.3 Mulliken Population Analysis	249
5.3.1 Density Matrix	249
5.3.2 Minimal Basis Set Calculation for CH ₄	251
5.4 Natural Bond Orbitals	254
5.4.1 Hybrid Atomic Orbitals	254
5.4.2 Natural Bond Orbitals for CH ₄	257
5.4.3 Natural Bond Orbitals for H ₂ C=CH ₂	258
5.4.4 Natural Bond Orbitals for HC≡CH	259
5.4.5 CH Hybrids in CH ₄ , H ₂ C=CH ₂ and HC≡CH	260
5.4.6 Molecular Geometries and Electrostatic Potentials	261
5.5 Potential Energy Surfaces	262
5.5.1 Intrinsic Reaction Coordinate	264
5.6 Molecular Conformations	266
5.6.1 Ethane	266
5.6.2 1,2-Dichloroethane	269
5.6.3 Boltzmann Distribution	270
5.7 Chiral Molecules	272
<i>Mathematica</i> Codes	277
Glossary	281
Exercises	284
References	284
Further Reading	285

6 Crystals	287
6.1 Packing Disks and Spheres	287
6.1.1 Disks	287
6.1.2 Spheres	289
6.1.3 Hexagonal Close Packing	291
6.1.4 Cubic Close Packing	292
6.1.5 Packing Densities	292
6.1.6 Occupying Interstices	295
6.2 Translation Symmetries	297
6.2.1 2D Bravais Lattices	297
6.2.2 3D Bravais Lattices	301
6.3 Crystal Structures	304
6.3.1 Metals	304
6.3.2 Lattice Energy	304
6.3.3 Cesium Chloride and Sodium Chloride	305
6.3.4 Diamond and Zinc Blende	306
6.4 X-Ray Diffraction	308
6.5 Electrons in Solids	310
6.6 Semiconductors	312
<i>Mathematica</i> Codes	315
Glossary	327
Exercises	328
References	329
Further Reading	329
7 Water	331
7.1 Molecular Geometry	332
7.2 Enthalpy of Formation	333
7.3 Atomic Charges	333
7.4 Dipole Moment	334
7.4.1 Electric Multipoles	334
7.4.2 Point Dipole	336
7.4.3 Electric Field Streamlines	337
7.4.4 H ₂ O Dipole and Quadrupole	338
7.5 Molecular Orbitals	339
7.5.1 Natural Bond Orbitals	341
7.6 Molecular Vibrations	342
7.7 Intermolecular Interactions	344
7.7.1 Electrostatic Interaction	344
7.7.2 Induction	346
7.7.3 Dispersion	347
7.8 Hydrogen Bond	349
7.8.1 The Water Dimer	351

7.9	Ice I _h	353
7.9.1	Gas Hydrates	354
7.10	Liquid Water	355
7.11	Phase Diagram	357
7.12	Water as Solvent	359
7.12.1	Electric Permittivity	359
7.13	Simple Nonpolar Solutes	361
7.13.1	Ostwald Coefficient	362
7.13.2	Hydrophobic Interaction	365
7.14	Ionic Solutions	366
7.15	Amphipathic Molecules	370
7.15.1	Sodium Decanoate Micelles	373
7.16	Acids and Bases	375
7.16.1	Autoionization of Water	376
7.16.2	Acid Ionization Constant	377
7.16.3	Lewis Acids and Bases	380
7.17	Standard Electrode Potentials	381
	<i>Mathematica</i> Codes	385
	Glossary	394
	Exercises	395
	References	397
	Further Reading	398
	Erratum to: Molecular Physical Chemistry	E1
	Appendix	399
	Answers to Exercises	403
	Index	449



<http://www.springer.com/978-3-319-41092-0>

Molecular Physical Chemistry

A Computer-based Approach using Mathematica® and
Gaussian

Teixeira-Dias, J.J.C.

2017, XVI, 457 p. 270 illus., 17 illus. in color., Hardcover

ISBN: 978-3-319-41092-0