

## Contents

	<b>Preface</b>	<i>xi</i>
<b>1</b>	<b>Introduction</b>	<b>1</b>
<b>2</b>	<b>Quantum Mechanics</b>	<b>11</b>
2.1	Fundamentals	11
2.1.1	Postulates of Quantum Mechanics	11
2.1.2	Lagrangian and Hamiltonian Formalisms	11
2.1.3	Wave Functions and Operators	18
2.2	Time Evolution of Wave Functions	22
2.3	Time Evolution of Expectation Values	25
2.4	Variational Principle	27
	Further Reading	29
<b>3</b>	<b>Particles and Fields</b>	<b>31</b>
3.1	Microscopic Maxwell's Equations	32
3.1.1	General Considerations	32
3.1.2	The Stationary Case	34
3.1.3	The General Case	38
3.1.4	Electromagnetic Potentials and Gauge Freedom	39
3.1.5	Electromagnetic Waves and Polarization	41
3.1.6	Electrodynamics: Relativistic and Nonrelativistic Formulations	45
3.2	Particles in Electromagnetic Fields	48
3.2.1	The Classical Mechanical Hamiltonian	48
3.2.2	The Quantum-Mechanical Hamiltonian	52
3.3	Electric and Magnetic Multipoles	57
3.3.1	Multipolar Gauge	57
3.3.2	Multipole Expansions	59
3.3.3	The Electric Dipole Approximation and Beyond	63
3.3.4	Origin Dependence of Electric and Magnetic Multipoles	64
3.3.5	Electric Multipoles	65
3.3.5.1	General Versus Traceless Forms	65
3.3.5.2	What We Can Learn from Symmetry	68
3.3.6	Magnetic Multipoles	69
3.3.7	Electric Dipole Radiation	70

3.4	Macroscopic Maxwell's Equations	72
3.4.1	Spatial Averaging	72
3.4.2	Polarization and Magnetization	73
3.4.3	Maxwell's Equations in Matter	77
3.4.4	Constitutive Relations	79
3.5	Linear Media	81
3.5.1	Boundary Conditions	82
3.5.2	Polarization in Linear Media	86
3.5.3	Electromagnetic Waves in a Linear Medium	92
3.5.4	Frequency Dependence of the Permittivity	96
3.5.4.1	Kramers–Kronig Relations	97
3.5.4.2	Relaxation in the Debye Model	98
3.5.4.3	Resonances in the Lorentz Model	101
3.5.4.4	Refraction and Absorption	105
3.5.5	Rotational Averages	107
3.5.6	A Note About Dimensions, Units, and Magnitudes	110
	Further Reading	111
<b>4</b>	<b>Symmetry</b>	<b>113</b>
4.1	Fundamentals	113
4.1.1	Symmetry Operations and Groups	113
4.1.2	Group Representation	117
4.2	Time Symmetries	120
4.3	Spatial Symmetries	125
4.3.1	Spatial Inversion	125
4.3.2	Rotations	127
	Further Reading	134
<b>5</b>	<b>Exact-State Response Theory</b>	<b>135</b>
5.1	Responses in Two-Level System	135
5.2	Molecular Electric Properties	145
5.3	Reference-State Parameterizations	151
5.4	Equations of Motion	156
5.4.1	Time Evolution of Projection Amplitudes	157
5.4.2	Time Evolution of Rotation Amplitudes	159
5.5	Response Functions	163
5.5.1	First-Order Properties	166
5.5.2	Second-Order Properties	166
5.5.3	Third-Order Properties	169
5.5.4	Fourth-Order Properties	174
5.5.5	Higher-Order Properties	179
5.6	Dispersion	179
5.7	Oscillator Strength and Sum Rules	183
5.8	Absorption	185
5.9	Residue Analysis	190
5.10	Relaxation	194
5.10.1	Density Operator	195

5.10.2	Liouville Equation	196
5.10.3	Density Matrix from Perturbation Theory	200
5.10.4	Linear Response Functions from the Density Matrix	201
5.10.5	Nonlinear Response Functions from the Density Matrix	204
5.10.6	Relaxation in Wave Function Theory	204
5.10.7	Absorption Cross Section	207
5.10.8	Einstein Coefficients	210
	Further Reading	211
<b>6</b>	<b>Electronic and Nuclear Contributions to Molecular Properties</b>	<b>213</b>
6.1	Born–Oppenheimer Approximation	213
6.2	Separation of Response Functions	216
6.3	Molecular Vibrations and Normal Coordinates	221
6.4	Perturbation Theory for Vibrational Wave Functions	225
6.5	Zero-Point Vibrational Contributions to Properties	227
6.5.1	First-Order Anharmonic Contributions	227
6.5.2	Importance of Zero-Point Vibrational Corrections	231
6.5.3	Temperature Effects	234
6.6	Pure Vibrational Contributions to Properties	235
6.6.1	Perturbation Theory Approach	235
6.6.2	Pure Vibrational Effects from an Analysis of the Electric-Field Dependence of the Molecular Geometry	238
6.7	Adiabatic Vibronic Theory for Electronic Excitation Processes	244
6.7.1	Franck–Condon Integrals	248
6.7.2	Vibronic Effects in a Diatomic System	250
6.7.3	Linear Coupling Model	252
6.7.4	Herzberg–Teller Corrections and Vibronically Induced Transitions	252
	Further Reading	253
<b>7</b>	<b>Approximate Electronic State Response Theory</b>	<b>255</b>
7.1	Reference State Parameterizations	255
7.1.1	Single Determinant	255
7.1.2	Configuration Interaction	263
7.1.3	Multiconfiguration Self-Consistent Field	266
7.1.4	Coupled Cluster	268
7.2	Equations of Motion	271
7.2.1	Ehrenfest Theorem	271
7.2.2	Quasi-Energy Derivatives	275
7.3	Response Functions	276
7.3.1	Single Determinant Approaches	276
7.3.2	Configuration Interaction	281
7.3.3	Multiconfiguration Self-Consistent Field	281
7.3.4	Matrix Structure in the SCE, CI, and MCSCF Approximations	281
7.3.5	Coupled Cluster	285
7.4	Residue Analysis	288
7.5	Relaxation	291
	Further Reading	293

<b>8</b>	<b>Response Functions and Spectroscopies</b>	<b>295</b>
8.1	Nuclear Interactions	296
8.1.1	Nuclear Charge Distribution	296
8.1.2	Hyperfine Structure	301
8.1.2.1	Nuclear Magnetic Dipole Moment	301
8.1.2.2	Nuclear Electric Quadrupole Moment	305
8.2	Zeeman Interaction and Electron Paramagnetic Resonance	310
8.3	Polarizabilities	317
8.3.1	Linear Polarizability	317
8.3.1.1	Weak Intermolecular Forces	321
8.3.2	Nonlinear Polarizabilities	325
8.4	Magnetizability	326
8.4.1	The Origin Dependence of the Magnetizability	328
8.4.2	Magnetizabilities from Magnetically Induced Currents	331
8.4.3	Isotropic Magnetizabilities and Pascal's Rule	332
8.5	Electronic Absorption and Emission Spectroscopies	335
8.5.1	Visible and Ultraviolet Absorption	338
8.5.2	Fluorescence Spectroscopy	343
8.5.3	Phosphorescence	344
8.5.4	Multiphoton Absorption	347
8.5.4.1	Multiphoton Absorption Cross Sections	348
8.5.4.2	Few-State Models for Two-Photon Absorption Cross Section	350
8.5.4.3	General Multiphoton Absorption Processes	351
8.5.5	X-ray Absorption	354
8.5.5.1	Core-Excited States	355
8.5.5.2	Field Polarization	358
8.5.5.3	Static Exchange Approximation	360
8.5.5.4	Complex or Damped Response Theory	362
8.6	Birefringences and Dichroisms	364
8.6.1	Natural Optical Activity	366
8.6.2	Electronic Circular Dichroism	372
8.6.3	Nonlinear Birefringences	375
8.6.3.1	Magnetic Circular Dichroism	376
8.6.3.2	Electric Field Gradient-Induced Birefringence	379
8.7	Vibrational Spectroscopies	381
8.7.1	Infrared Absorption	381
8.7.1.1	Double-Harmonic Approximation	381
8.7.1.2	Anharmonic Corrections	383
8.7.2	Vibrational Circular Dichroism	384
8.7.3	Raman Scattering	388
8.7.3.1	Raman Scattering from a Classical Point of View	388
8.7.3.2	Raman Scattering from a Quantum Mechanical Point of View	392
8.7.4	Vibrational Raman Optical Activity	402
8.8	Nuclear Magnetic Resonance	408
8.8.1	The NMR Experiment	408
8.8.2	NMR Parameters	413
	Further Reading	417

## Appendices

- A**    **Abbreviations**    419
- B**    **Units**    421
- C**    **Second Quantization**    423
- C.1    Creation and Annihilation Operators    423
- C.2    Fock Space    425
- C.3    The Number Operator    426
- C.4    The Electronic Hamiltonian on Second-Quantized Form    427
- C.5    Spin in Second Quantization    429
- D**    **Fourier Transforms**    431
- E**    **Operator Algebra**    435
- F**    **Spin Matrix Algebra**    439
- G**    **Angular Momentum Algebra**    441
- H**    **Variational Perturbation Theory**    445
- I**    **Two-Level Atom**    451
- I.1    Rabi Oscillations    452
- I.2    Time-Dependent Perturbation Theory    454
- I.3    The Quasi-energy Approach    455
- Index**    457