

Contents

1	Introduction to Photochemistry	1
1.1	What Is Photochemistry?	1
1.2	Light and Photons	2
1.2.1	Monochromatic Light	3
1.2.2	Nonmonochromatic Light: The Radiation Spectrum	4
1.2.3	Photons	5
1.3	Photochemistry Versus Thermal Chemistry	6
1.4	An Overview of Photochemical and Photophysical Processes	7
1.5	Quantum Yields	12
1.6	Photochemical Kinetics	14
1.6.1	Excitation Rate	15
1.6.2	Rates of Photochemical Reactions and Photophysical Processes	17
1.6.3	Photoisomerization with Thermal Direct and Reverse Reaction	20
1.6.4	Reversible Photoisomerization	22
	References	24
2	Molecular States	25
2.1	The Time-Dependent Schrödinger Equation	25
2.1.1	Observables	27
2.1.2	Stationary States	30
2.2	Molecular Dynamics and the Separation of Variables	31
2.2.1	Independent Variables	32
2.2.2	Separation of Translation and Rotation	33

2.3	The Born–Oppenheimer Approximation and Its Breakdown: The Nonadiabatic Couplings	36
2.3.1	Properties of Nonadiabatic Couplings	38
2.3.2	Validity of the BO Approximation	39
2.3.3	Time Evolution in the BO Framework	42
2.4	The Electrostatic Approximation: Spin and Magnetic Couplings	43
2.4.1	Singlet and Triplet Wavefunctions	44
2.4.2	Spin–Orbit Coupling	46
2.5	Vibrational and Rotational States	49
2.5.1	Rotational States	50
2.5.2	Vibrational States	52
2.6	Electronic States of Polyatomics and Photoreactivity	56
2.6.1	Molecular Orbitals	56
2.6.2	Excited States $\sigma \rightarrow \sigma^*$	58
2.6.3	Excited States $n \rightarrow \sigma^*$	61
2.6.4	Excited States $\pi \rightarrow \pi^*$	62
2.6.5	Excited States $n \rightarrow \pi^*$	64
2.6.6	Excited States of Conjugated Systems	65
2.6.7	Charge Transfer States	67
2.7	Unimolecular Photochemical Reactions in Organic Molecules	68
2.7.1	Photoisomerization of Alkenes	68
2.7.2	Electrocyclic Reactions	68
2.7.3	Sigmatropic Reactions	70
2.7.4	Photodissociation of Carbonyl Compounds	71
2.8	Solvent Effects on Absorption and Emission Spectra	73
2.9	Computational Note: The Determination of Electronic Excited States	75
	References	77
3	Electronic Excitation and Decay	79
3.1	Constant and Time-Dependent Perturbations	79
3.2	Light–Molecule Interaction	81
3.3	The Two-State Model: Rabi Oscillations	83
3.4	Time-Dependent Perturbation Theory	87
3.5	Excitation by a Continuous Wave	89
3.6	Spontaneous Emission	93
3.7	Vibrational Structure of Electronic Spectra	95
3.8	Excitation by Radiation Pulses	99
3.9	Spectrum and Autocorrelation Function	100
3.10	Predissociation and Fermi’s Golden Rule	104

3.11	Excited State Decay to a Quasi-continuum	110
3.12	Computational Note: Franck–Condon Factors and Coupling Matrix Elements	115
	References	118
4	Wavepacket Dynamics and Geometrical Relaxation	119
4.1	Franck–Condon Excitation	119
4.2	Vibrational Wavepacket Dynamics	121
4.3	Intramolecular Vibrational Energy Redistribution	129
4.4	Static Environmental Effects	132
4.5	Dynamic Environmental Effects	133
4.6	Computational Note: Quantum Wavepacket Dynamics and Classical Trajectories	137
	References	139
5	Fast Nonadiabatic Dynamics	141
5.1	Noncrossing Rule and Avoided Crossings	141
5.2	Diabatic States	144
5.3	Landau–Zener Rule	148
5.4	Conical Intersections	151
	5.4.1 Classification of Conical Intersections	153
	5.4.2 Branching Plane (Real Hamiltonian)	155
	5.4.3 Geometric Phase	156
	5.4.4 The Jahn–Teller Effect	162
	5.4.5 Complex Hamiltonian and Kramers Degeneracy	163
5.5	Computational Note: Methods for Nonadiabatic Dynamics	169
	5.5.1 Quantum Wavepacket Dynamics	169
	5.5.2 Nonadiabatic Classical Trajectories	172
	References	175
6	Charge and Energy Transfer Processes	179
6.1	Gas-Phase Collisions	179
6.2	Encounters in Solution	181
6.3	Electronic Energy Transfers	184
6.4	Localized Excitations and Energy Transfer Mechanisms	189
	6.4.1 Group Functions	190
	6.4.2 Triplet Sensitization and Singlet Fission	192
	6.4.3 Singlet-to-Singlet Excitation Energy Transfer: Dexter and Förster Mechanisms	194
	6.4.4 Exciton Coupling	198
6.5	Charge or Electron Transfer	202
6.6	Computational Note: Diabatic States for ET and CT Studies	207
	References	211

Appendix A: Physical Constants and Conversion Factors	215
Appendix B: Dirac's Notation and Operator Algebra	217
Appendix C: The Dirac δ Function and the Normalization of Continuum States	223
Appendix D: Two-State Eigenvector Problem	227
Appendix E: Orbital Localization and Orthogonality	229
Appendix F: The Harmonic Oscillator	233
Appendix G: Animations	237
Solutions	241
Index	259