
Contents

Preface to the First Edition	xv
Preface to the Second Edition	xix
1 Introduction	1
1.1 Fundamental Issues	2
1.2 Describing the System	3
1.3 Fundamental Forces	4
1.4 The Dynamical Equation	5
1.5 Solving the Dynamical Equation	8
1.6 Separation of Variables	8
1.6.1 Separating space and time variables	10
1.6.2 Separating nuclear and electronic variables	10
1.6.3 Separating variables in general	11
1.7 Classical Mechanics	12
1.7.1 The Sun–Earth system	12
1.7.2 The solar system	13
1.8 Quantum Mechanics	14
1.8.1 A hydrogen-like atom	14
1.8.2 The helium atom	17
1.9 Chemistry	19
References	21
2 Force Field Methods	22
2.1 Introduction	22
2.2 The Force Field Energy	24
2.2.1 The stretch energy	25
2.2.2 The bending energy	27
2.2.3 The out-of-plane bending energy	30
2.2.4 The torsional energy	30
2.2.5 The van der Waals energy	34
2.2.6 The electrostatic energy: charges and dipoles	40
2.2.7 The electrostatic energy: multipoles and polarizabilities	43

2.2.8	Cross terms	47
2.2.9	Small rings and conjugated systems	48
2.2.10	Comparing energies of structurally different molecules	50
2.3	Force Field Parameterization	51
2.3.1	Parameter reductions in force fields	57
2.3.2	Force fields for metal coordination compounds	58
2.3.3	Universal force fields	62
2.4	Differences in Force Fields	62
2.5	Computational Considerations	65
2.6	Validation of Force Fields	67
2.7	Practical Considerations	69
2.8	Advantages and Limitations of Force Field Methods	69
2.9	Transition Structure Modelling	70
2.9.1	Modelling the TS as a minimum energy structure	70
2.9.2	Modelling the TS as a minimum energy structure on the reactant/ product energy seam	71
2.9.3	Modelling the reactive energy surface by interacting force field functions or by geometry-dependent parameters	73
2.10	Hybrid Force Field Electronic Structure Methods	74
	References	77
3	Electronic Structure Methods: Independent-Particle Models	80
3.1	The Adiabatic and Born–Oppenheimer Approximations	82
3.2	Self-Consistent Field Theory	86
3.3	The Energy of a Slater Determinant	87
3.4	Koopmans’ Theorem	92
3.5	The Basis Set Approximation	93
3.6	An Alternative Formulation of the Variational Problem	98
3.7	Restricted and Unrestricted Hartree–Fock	99
3.8	SCF Techniques	100
3.8.1	SCF convergence	101
3.8.2	Use of symmetry	104
3.8.3	Ensuring that the HF energy is a minimum, and the correct minimum	105
3.8.4	Initial guess orbitals	107
3.8.5	Direct SCF	108
3.8.6	Reduced scaling techniques	110
3.9	Periodic Systems	113
3.10	Semi-Empirical Methods	115
3.10.1	Neglect of Diatomic Differential Overlap Approximation (NDDO)	116
3.10.2	Intermediate Neglect of Differential Overlap Approximation (INDO)	117
3.10.3	Complete Neglect of Differential Overlap Approximation (CNDO)	117
3.11	Parameterization	118
3.11.1	Modified Intermediate Neglect of Differential Overlap (MINDO)	119
3.11.2	Modified NDDO models	119
3.11.3	Modified Neglect of Diatomic Overlap (MNDO)	121
3.11.4	Austin Model 1 (AM1)	121
3.11.5	Modified Neglect of Diatomic Overlap, Parametric Method Number 3 (PM3)	122
3.11.6	Parametric Method number 5 (PM5) and PDDG/PM3 methods	123

3.11.7	The MNDO/d and AM1/d methods	124
3.11.8	Semi Ab initio Method 1	124
3.12	Performance of Semi-Empirical Methods	125
3.13	Hückel Theory	127
3.13.1	Extended Hückel theory	127
3.13.2	Simple Hückel theory	128
3.14	Limitations and Advantages of Semi-Empirical Methods	129
	References	131
4	Electron Correlation Methods	133
4.1	Excited Slater Determinants	135
4.2	Configuration Interaction	137
4.2.1	CI Matrix elements	138
4.2.2	Size of the CI matrix	141
4.2.3	Truncated CI methods	143
4.2.4	Direct CI methods	144
4.3	Illustrating how CI Accounts for Electron Correlation, and the RHF Dissociation Problem	145
4.4	The UHF Dissociation, and the Spin Contamination Problem	148
4.5	Size Consistency and Size Extensivity	153
4.6	Multi-Configuration Self-Consistent Field	153
4.7	Multi-Reference Configuration Interaction	158
4.8	Many-Body Perturbation Theory	159
4.8.1	Møller–Plesset perturbation theory	162
4.8.2	Unrestricted and projected Møller–Plesset methods	168
4.9	Coupled Cluster	169
4.9.1	Truncated coupled cluster methods	172
4.10	Connections between Coupled Cluster, Configuration Interaction and Perturbation Theory	174
4.10.1	Illustrating correlation methods for the beryllium atom	177
4.11	Methods Involving the Interelectronic Distance	178
4.12	Direct Methods	181
4.13	Localized Orbital Methods	182
4.14	Summary of Electron Correlation Methods	183
4.15	Excited States	186
4.16	Quantum Monte Carlo Methods	187
	References	189
5	Basis Sets	192
5.1	Slater and Gaussian Type Orbitals	192
5.2	Classification of Basis Sets	194
5.3	Even- and Well-Tempered Basis Sets	198
5.4	Contracted Basis Sets	200
5.4.1	Pople style basis sets	202
5.4.2	Dunning–Huzinaga basis sets	204
5.4.3	MINI, MIDI and MAXI basis sets	205
5.4.4	Ahlrichs type basis sets	205
5.4.5	Atomic natural orbital basis sets	205
5.4.6	Correlation consistent basis sets	206

5.4.7	Polarization consistent basis sets	207
5.4.8	Basis set extrapolation	208
5.5	Plane Wave Basis Functions	211
5.6	Recent Developments and Computational Issues	212
5.7	Composite Extrapolation Procedures	213
5.8	Isogyric and Isodesmic Reactions	221
5.9	Effective Core Potentials	222
5.10	Basis Set Superposition Errors	225
5.11	Pseudospectral Methods	227
	References	229
6	Density Functional Methods	232
6.1	Orbital-Free Density Functional Theory	233
6.2	Kohn-Sham Theory	235
6.3	Reduced Density Matrix Methods	236
6.4	Exchange and Correlation Holes	240
6.5	Exchange-Correlation Functionals	243
6.5.1	Local Density Approximation	246
6.5.2	Gradient-corrected methods	248
6.5.3	Higher order gradient or meta-GGA methods	250
6.5.4	Hybrid or hyper-GGA methods	252
6.5.5	Generalized random phase methods	253
6.5.6	Functionals overview	254
6.6	Performance and Properties of Density Functional Methods	255
6.7	DFT Problems	258
6.8	Computational Considerations	260
6.9	Final Considerations	263
	References	264
7	Valence Bond Methods	268
7.1	Classical Valence Bond Theory	269
7.2	Spin-Coupled Valence Bond Theory	270
7.3	Generalized Valence Bond Theory	275
	References	276
8	Relativistic Methods	277
8.1	The Dirac Equation	278
8.2	Connections Between the Dirac and Schrödinger Equations	280
8.2.1	Including electric potentials	280
8.2.2	Including both electric and magnetic potentials	282
8.3	Many-Particle Systems	284
8.4	Four-Component Calculations	287
8.5	Relativistic Effects	289
	References	292
9	Wave Function Analysis	293
9.1	Population Analysis Based on Basis Functions	293
9.2	Population Analysis Based on the Electrostatic Potential	296

9.3	Population Analysis Based on the Electron Density	299
9.3.1	Atoms In Molecules	299
9.3.2	Voronoi, Hirshfeld and Stewart atomic charges	303
9.3.3	Generalized atomic polar tensor charges	304
9.4	Localized Orbitals	304
9.4.1	Computational considerations	306
9.5	Natural Orbitals	308
9.6	Natural Atomic Orbital and Natural Bond Orbital Analysis	309
9.7	Computational Considerations	311
9.8	Examples	312
	References	313
10	Molecular Properties	315
10.1	Examples of Molecular Properties	316
10.1.1	External electric field	316
10.1.2	External magnetic field	318
10.1.3	Internal magnetic moments	318
10.1.4	Geometry change	319
10.1.5	Mixed derivatives	319
10.2	Perturbation Methods	321
10.3	Derivative Techniques	321
10.4	Lagrangian Techniques	324
10.5	Coupled Perturbed Hartree–Fock	325
10.6	Electric Field Perturbation	329
10.6.1	External electric field	329
10.6.2	Internal electric field	329
10.7	Magnetic Field Perturbation	329
10.7.1	External magnetic field	331
10.7.2	Nuclear spin	332
10.7.3	Electron spin	333
10.7.4	Classical terms	333
10.7.5	Relativistic terms	334
10.7.6	Magnetic properties	334
10.7.7	Gauge dependence of magnetic properties	338
10.8	Geometry Perturbations	339
10.9	Response and Propagator Methods	343
10.10	Property Basis Sets	348
	References	349
11	Illustrating the Concepts	350
11.1	Geometry Convergence	350
11.1.1	Ab Initio methods	350
11.1.2	Density functional methods	353
11.2	Total Energy Convergence	354
11.3	Dipole Moment Convergence	356
11.3.1	Ab Initio methods	356
11.3.2	Density functional methods	357
11.4	Vibrational Frequency Convergence	358
11.4.1	Ab Initio methods	358
11.4.2	Density functional methods	360

11.5	Bond Dissociation Curves	361
	11.5.1 Basis set effect at the Hartree-Fock level	361
	11.5.2 Performance of different types of wave function	363
	11.5.3 Density functional methods	369
11.6	Angle Bending Curves	370
11.7	Problematic Systems	370
	11.7.1 The geometry of FOOF	371
	11.7.2 The dipole moment of CO	372
	11.7.3 The vibrational frequencies of O ₃	373
11.8	Relative Energies of C ₄ H ₆ Isomers	374
	References	378
12	Optimization Techniques	380
12.1	Optimizing Quadratic Functions	381
12.2	Optimizing General Functions: Finding Minima	383
	12.2.1 Steepest descent	383
	12.2.2 Conjugate gradient methods	384
	12.2.3 Newton-Raphson methods	385
	12.2.4 Step control	386
	12.2.5 Obtaining the Hessian	387
	12.2.6 Storing and diagonalizing the Hessian	388
	12.2.7 Extrapolations: the GDIIIS method	389
12.3	Choice of Coordinates	390
12.4	Optimizing General Functions: Finding Saddle Points (Transition Structures)	394
	12.4.1 One-structure interpolation methods: coordinate driving, linear and quadratic synchronous transit, and sphere optimization	394
	12.4.2 Two-structure interpolation methods: saddle, line-then-plane, ridge and step-and-slide optimizations	397
	12.4.3 Multi-structure interpolation methods: chain, locally updated planes, self-penalty walk, conjugate peak refinement and nudged elastic band	398
	12.4.4 Characteristics of interpolation methods	401
	12.4.5 Local methods: gradient norm minimization	402
	12.4.6 Local methods: Newton-Raphson	403
	12.4.7 Local methods: the dimer method	405
	12.4.8 Coordinates for TS searches	405
	12.4.9 Characteristics of local methods	406
	12.4.10 Dynamic methods	406
12.5	Constrained Optimization Problems	407
12.6	Conformational Sampling and the Global Minimum Problem	409
	12.6.1 Stochastic and Monte Carlo methods	411
	12.6.2 Molecular dynamics	412
	12.6.3 Simulated annealing	413
	12.6.4 Genetic algorithms	413
	12.6.5 Diffusion methods	414
	12.6.6 Distance geometry methods	414
12.7	Molecular Docking	415
12.8	Intrinsic Reaction Coordinate Methods	416
	References	419

13	Statistical Mechanics and Transition State Theory	421
13.1	Transition State Theory	421
13.2	Rice–Ramsperger–Kassel–Marcus Theory	424
13.3	Dynamical Effects	425
13.4	Statistical Mechanics	426
13.5	The Ideal Gas, Rigid-Rotor Harmonic-Oscillator Approximation	429
13.5.1	Translational degrees of freedom	430
13.5.2	Rotational degrees of freedom	430
13.5.3	Vibrational degrees of freedom	431
13.5.4	Electronic degrees of freedom	433
13.5.5	Enthalpy and entropy contributions	433
13.6	Condensed Phases	439
	References	443
14	Simulation Techniques	445
14.1	Monte Carlo Methods	448
14.1.1	Generating non-natural ensembles	450
14.2	Time-Dependent Methods	450
14.2.1	Molecular dynamics methods	451
14.2.2	Generating non-natural ensembles	454
14.2.3	Langevin methods	455
14.2.4	Direct methods	455
14.2.5	Extended Lagrange techniques (Car–Parrinello methods)	457
14.2.6	Quantum methods using potential energy surfaces	459
14.2.7	Reaction path methods	460
14.2.8	Non-Born–Oppenheimer methods	463
14.2.9	Constrained sampling methods	463
14.3	Periodic Boundary Conditions	464
14.4	Extracting Information from Simulations	468
14.5	Free Energy Methods	472
14.5.1	Thermodynamic perturbation methods	472
14.5.2	Thermodynamic integration methods	473
14.6	Solvation Models	475
14.7	Continuum Solvation Models	476
14.7.1	Poisson–Boltzmann methods	478
14.7.2	Born/Onsager/Kirkwood models	480
14.7.3	Self-consistent reaction field models	481
	References	484
15	Qualitative Theories	487
15.1	Frontier Molecular Orbital Theory	487
15.2	Concepts from Density Functional Theory	492
15.3	Qualitative Molecular Orbital Theory	494
15.4	Woodward–Hoffmann Rules	497
15.5	The Bell–Evans–Polanyi Principle/Hammond Postulate/Marcus Theory	506
15.6	More O’Ferrall–Jencks Diagrams	510
	References	512

16	Mathematical Methods	514
16.1	Numbers, Vectors, Matrices and Tensors	514
16.2	Change of Coordinate System	520
16.2.1	Examples of changing the coordinate system	525
16.2.2	Vibrational normal coordinates	526
16.2.3	Energy of a Slater determinant	528
16.2.4	Energy of a CI wave function	529
16.2.5	Computational Consideration	529
16.3	Coordinates, Functions, Functionals, Operators and Superoperators	530
16.3.1	Differential operators	531
16.4	Normalization, Orthogonalization and Projection	532
16.5	Differential Equations	535
16.5.1	Simple first-order differential equations	535
16.5.2	Less simple first-order differential equations	536
16.5.3	Simple second-order differential equations	536
16.5.4	Less simple second-order differential equations	537
16.5.5	Second-order differential equations depending on the function itself	537
16.6	Approximating Functions	538
16.6.1	Taylor expansion	539
16.6.2	Basis set expansion	541
16.7	Fourier and Laplace Transformations	541
16.8	Surfaces	543
	References	546
17	Statistics and QSAR	547
17.1	Introduction	547
17.2	Elementary Statistical Measures	549
17.3	Correlation Between Two Sets of Data	550
17.4	Correlation between Many Sets of Data	553
17.4.1	Multiple-descriptor data sets and quality analysis	553
17.4.2	Multiple linear regression	555
17.4.3	Principal component and partial least squares analysis	556
17.4.4	Illustrative example	558
17.5	Quantitative Structure–Activity Relationships (QSAR)	559
	References	561
18	Concluding Remarks	562
	Appendix A	565
	Notation	565
	Appendix B	570
	B.1 The Variational Principle	570
	B.2 The Hohenberg–Kohn Theorems	571
	B.3 The Adiabatic Connection Formula	572
	Reference	573

CONTENTS

xiii

Appendix C	574
Atomic Units	574
Appendix D	575
Z-Matrix Construction	575
Index	583