

Contents

Chapter 1 Electric Multipoles, Polarizabilities and Hyperpolarizabilities	1
<i>By David Pugh</i>	
1 Introduction	1
2 Perturbation of Molecules by Static Electric Fields: General Theory	2
2.1 Analytic Derivatives of the Energy	3
3 Frequency-Dependent Polarizabilities: General Theory	4
3.1 Time-Dependent Perturbation Theory: The Sum over States Method	5
3.1.1 Second Order Effects	6
3.1.2 Third Order Effects	7
3.2 Measurement of the Dynamic Hyperpolarizabilities	7
4 Methods of Calculation: Development from 1970 to 1998	7
4.1 Permanent Multipoles	8
4.2 Static Polarizabilities and Hyperpolarizabilities	8
4.3 Dynamic Response Functions	10
4.4 The First Hyperpolarizability of Organic Donor/ Acceptor Molecules	11
4.5 Calculations of the Second Hyperpolarizability	13
5 Review of Literature: 1998–May 1999	14
5.1 Dipole and Quadrupole Moments	14
5.2 Polarizabilities and Hyperpolarizabilities of Small Molecules	15
5.2.1 Diatomic Molecules	15
5.2.2 Butadiene	17
5.2.3 Static Polarizabilities and Hyperpolarizabilities by <i>ab initio</i> Methods	18
5.2.4 Dynamic Polarizabilities and Hyper- polarizabilities by <i>ab initio</i> Methods	19
5.2.5 Density Functional Calculations	19
5.2.6 Clusters and Small Homologous Series	20
5.2.7 Excited State Polarizabilities	21

5.3	Polarizabilities and Hyperpolarizabilities of Larger Molecules	21
5.3.1	<i>Ab initio</i> Calculations	21
5.3.2	Semi-Empirical Methods	22
5.3.3	Linear Conjugated Chains	24
5.3.4	Vibrational Polarization	26
5.3.5	Fullerenes	27
5.3.6	Solvent Effects, Crystal Fields	28
5.3.7	New Theoretical Developments	29
	References	30
Chapter 2	Atomic Structure Computations	38
	<i>By T.E. Simos</i>	
1	Introduction	38
2	Methods with Coefficients Dependent on the Frequency of the Problem	39
2.1	Exponential Multistep Methods	39
2.1.1	The Derivation of Exponentially-Fitted Methods for General Problems	40
2.1.2	Exponentially-Fitted Methods	41
2.1.3	Linear Multistep Methods	42
2.1.4	Predictor-Corrector Methods	44
2.1.5	New Insights in Exponentially-Fitted Methods	49
2.1.6	A New Tenth Algebraic Order Exponentially-Fitted Method	54
2.1.7	Open Problems in Exponentially Fitting	58
2.2	Bessel and Neumann Fitted Methods	58
2.3	Phase Fitted Methods	66
2.3.1	A New Phase Fitted Method	71
2.4	Numerical Illustrations for Exponentially-Fitted Methods and Phase Fitted Methods	73
2.4.1	The Resonance Problem: Woods-Saxon Potential	74
2.4.2	Modified Woods-Saxon Potential: Coulombian Potential	76
2.4.3	The Bound-States Problem	77
2.4.4	Remarks and Conclusion	77
3	Theory for Constructing Methods with Constant Coefficients for the Numerical Solution of Schrödinger Type Equations	84
3.1	Phase-lag Analysis for Symmetric Two-Step Methods	84
3.2	Phase-lag Analysis of General Symmetric $2k$ -Step, $k \in N$ Methods	85
3.3	Phase-lag Analysis of Dissipative (Non-Symmetric) Two-Step Methods	87
3.4	Phase-lag Analysis of the Runge-Kutta Methods	89

3.5	Phase-lag Analysis of the Runga-Kutta-Nyström Methods	91
4	Methods with Constant Coefficients	93
4.1	Implicit Methods	93
4.1.1	P-Stable Methods	93
4.1.2	Methods with Non-Empty Interval of Periodicity	104
4.2	Explicit Methods	110
4.2.1	Fourth Algebraic Order Methods	110
4.2.2	Sixth Algebraic Order Methods	110
4.2.3	Eighth Algebraic Order Methods	111
5	Variable-Step Methods	114
6	P-Stable Methods of High Exponential Order	117
7	Matrix Methods for the One-Dimensional Eigenvalue Schrödinger Equation	119
7.1	Methods of Discretization	119
7.1.1	Methods Which Lead to a Tridiagonal Form of the Matrix A	120
7.1.2	Methods Which Lead to a Pentadiagonal Form of the Matrix A	120
7.1.3	Methods Which Lead to a Heptadiagonal Form of the Matrix A	120
7.1.4	Numerov Discretization	120
7.1.5	Extended Numerov Form	120
7.1.6	An Improved Four-Step Method	121
7.1.7	An Improved Three-Step Method	121
7.1.8	An Improved Hybrid Four-Step Method	122
7.2	Discussion	123
8	Runga-Kutta and Runga-Kutta-Nyström Methods for Specific Schrödinger Equations	123
9	Two Dimensional Eigenvalue Schrödinger Equation	124
10	Numerical Illustrations for the Methods with Constant Coefficients and the Variable-Step Methods	125
10.1	Methods with Constant Coefficients	125
10.1.1	Remarks and Conclusion	126
10.2	Variable-Step Methods	127
10.2.1	Error Estimation	127
10.2.2	Coupled Differential Equations	128
10.3	Remarks and Conclusion	132
	Appendix	133
	References	140

Chapter 3 Atoms in Molecules 143

By P.L.A. Popelier, F.M. Aicken and S.E. O'Brien

1	Introduction	143
1.1	What Is AIM?	143

1.2	Scope	144
1.3	The Roots of AIM	146
1.4	The Development of AIM	147
1.5	Software	149
2	Theoretical	149
2.1	Open Systems	149
2.2	Molecular Similarity and QSAR	150
2.3	Electron Correlation	151
2.4	Transferability	151
2.5	Multipoles	152
2.6	Molecular Dynamics	152
2.7	Partitioning	153
3	The Laplacian	153
3.1	Alternative Wave Functions	153
3.2	Relation to Bohm Quantum Potential	154
3.3	Protonation	154
4	Electron Densities from High-resolution X-ray Diffraction	156
4.1	State of the Art	156
4.2	Comparison between Experimental and Theoretical Densities	156
4.3	Hydrogen Bonding	160
4.4	Organic Compounds	163
4.5	Transition Metal Compounds	166
4.6	Minerals	170
5	Chemical Bonding	171
5.1	Theory	171
5.2	Ligand Close Packing (LCP) Model	172
5.3	Hypervalency	172
5.4	Organic Compounds	173
5.5	Transition Metal Compounds	174
5.6	Minerals	177
5.7	Solid State	178
5.8	Compounds of Atmospheric Interest	178
5.9	Van der Waals Complexes	179
6	Hydrogen Bonding	179
6.1	Review	179
6.2	Relationships	180
6.3	Cooperative Effect	180
6.4	Bifurcated Hydrogen Bonds	182
6.5	Low-barrier Hydrogen Bonds	182
6.6	Dihydrogen Bonds	184
6.7	Very Strong Hydrogen Bonds	184
6.8	Organic Compounds	184
6.9	Biochemical Compounds	185
6.10	Compounds of Atmospheric Importance	187

7	Reactions	188
	7.1 Organic Compounds	188
	7.2 Inorganic Compounds	190
8	Conclusion	192
9	Disclaimer	192
	References	193
Chapter 4	Modelling Biological Systems	199
	<i>By R.I. Maurer and C.J. Reynolds</i>	
1	Introduction	199
2	G-Protein Coupled Receptors	200
3	Protein-Protein Docking	201
	3.1 Traditional Docking Approaches	201
	3.2 Sequence-based Approaches to Docking	202
4	Simulations on the Early Stages of Protein Folding	202
5	Simulations on DNA	205
	5.1 Particle Mesh Ewald	206
6	Free Energy Calculations	206
	6.1 Free Energy Calculations from a Single Reference Simulation	208
	6.2 Multimolecule Free Energy Methods	209
	6.3 Linear Response Method	210
	6.4 Free Energy Perturbation Methods with Quantum Energies	211
	6.5 Force Fields	211
7	Continuum Methods	212
	7.1 Parameter Dependence	213
	7.2 pK_a Calculations	214
	7.3 Binding Studies	216
	7.4 Protein Folding and Stability	217
	7.5 Solvation and Conformational Energies	219
	7.6 Redox Studies	220
	7.7 Additional Studies	221
8	Hybrid QM/MM Calculations	221
	8.1 Methodology Developments	222
	8.2 The Models	223
	8.3 The Link Atom Problem	226
	8.4 Miscellaneous Improvements	228
	8.5 The 'Onion' Approach	229
	8.6 Applications	230
	8.6.1 Nickel-Iron Hydrogenase	230
	8.6.2 β -Lactam Hydrolysis	230
	8.6.3 Bacteriorhodopsin	231
	8.6.4 The Bacterial Photosynthetic Reaction Centre	231
	8.6.5 Other Studies	232

9	Car-Parrinello Calculations	232
	Acknowledgement	233
	References	233
Chapter 5	Relativistic Pseudopotential Calculations, 1993–June 1999	239
	<i>By Pekka Pyykkö and Hermann Stoll</i>	
1	Methods	239
1.1	Introduction	239
1.2	Model Potentials	242
1.3	Shape-Consistent Pseudopotentials	246
1.4	DFT-Based Pseudopotentials	250
1.5	Soft-Core Pseudopotentials and Separability	252
1.6	Energy-Consistent Pseudopotentials	255
1.7	Core-Polarization Pseudopotentials	257
1.8	Concluding Remarks	259
2	Applications by Element	260
3	Some Applications by Subject	260
3.1	New Species	260
3.2	Metal-Ligand Interactions	260
3.3	Closed-Shell Interactions	260
3.4	Chemical Reactions and Homogeneous Catalysis	278
3.5	Chemisorption and Heterogeneous Catalysis	278
3.6	Other	278
	Acknowledgements	278
	References	278
Chapter 6	Density-Functional Theory	306
	<i>By Michael Springborg</i>	
1	Introduction	306
2	Fundamentals	307
2.1	Wavefunction-based Methods	308
2.2	Approximating the Schrödinger Equation	310
2.3	Density-functional Theory	312
2.4	Hybrid Methods	318
3	Structural Properties	319
3.1	Structure Optimization	320
3.2	Examples of Structure Optimizations	322
4	Vibrations	328
5	Relative Energies	329
5.1	Dissociation Energies	329
5.2	Comparing Isomers	330
6	Chemical Reactions	331
6.1	Transition States	331
6.2	Hardness, Softness and Other Descriptors	333

7	Weak Bonds	338
7.1	van der Waals Bonds	338
7.2	Hydrogen Bonds	338
8	The Total Electron Density	340
9	The Orbitals	340
10	Excitations	343
11	Spin Properties	346
11.1	NMR Chemical Shifts	346
11.2	Electron Spin	347
11.3	Electronic Spin-Spin Couplings	349
11.4	Nuclear Spin-Spin Couplings	350
12	Electrostatic Fields	350
13	Solvation	352
13.1	Dielectric Continuum	352
13.2	Point Charges	353
14	Solids	353
14.1	Band Structures	354
14.2	Applications	354
15	Liquids	356
16	Surfaces as Catalysts	357
17	Intermediate-sized Systems	358
18	Conclusions	359
	Acknowledgements	360
	References	361

Chapter 7 Many-body Perturbation Theory and Its Application to the Molecular Electronic Structure Problem **364**

By S. Wilson

1	Introduction	364
1.1	A Personal Note	368
2	Theoretical Apparatus and Practical Algorithms	369
2.1	Quantum Electrodynamics and Many-body Perturbation Theory	369
2.1.1	The N -Dependence of Perturbation Expansions	371
2.1.2	The Linked Diagram Theorem	377
2.2	Many-body Perturbation Theory	384
2.2.1	Closed-shell Molecules	388
2.2.2	Open-shell Molecules	400
2.3	Relativistic Many-body Perturbation Theory	400
2.3.1	The Dirac Spectrum in the Algebraic Expansion	403
2.3.2	Many-electron Relativistic Hamiltonians	406
2.3.3	The ‘No Virtual Pair’ Approximation	407
2.3.4	Quantum Electrodynamics and Virtual Pair Creation Processes	409

2.4	The Algebraic Approximation	409
2.4.1	Gaussian Basis Sets and Finite Nuclei	410
2.4.2	Even-tempered Basis Sets	410
2.4.3	Symmetric Sequences of Basis Sets	411
2.4.4	Universal Basis Sets	414
2.5	Higher Order Correlation Energy Components	416
2.5.1	Fourth Order Energy Components	416
2.5.2	Fifth Order Energy Components	420
2.5.3	Higher Order Energy Components	428
2.6	The Use of Multireference Functions in Perturbation Theory	429
2.7	Concurrent Computation Many-body Perturbation Theory (<i>ccMBPT</i>)	430
2.7.1	Parallel Computing and Its Impact	430
2.7.2	Concurrent Computation and Performance Modelling: <i>ccMBPT</i>	433
2.8	Analysis of Different Approaches to the Electron Correlation Problem in Molecules	438
2.8.1	Configuration Mixing	438
2.8.2	Coupled Electron Pair and Cluster Expansions	440
3	Applications of Many-body Perturbation Theory	441
3.1	Graphical User Interfaces	441
3.2	Universal Basis Sets and Direct <i>ccMBPT</i>	442
3.3	Finite Element Methods Applied to Many-body Perturbation Theory	443
4	Future Directions	444
	Acknowledgements	445
	References	445
Chapter 8 New Developments on the Quantum Theory of Large Molecules and Polymers		453
<i>By Janos J. Ladik</i>		
1	Introduction	453
2	The Treatment of Large Molecules Using Solid State Physical Methods Developed for Aperiodic Chains	454
2.1	The Negative Factor Counting Methods with Correlation and Methods to Calculate Effective Total Energy per Unit Cell of Disordered Chains	455
2.1.1	The Matrix Block Negative Factor Counting Method	455
2.1.2	The Inclusion of Correlation in the Calculation of Density of States of Disordered Chains	459
2.1.3	The Calculation of Effective Total Energy per Unit Cell	460
2.2	Application to Proteins and Nucleotide Base Stacks	461

2.3	Possible Application of the Negative Factor Counting Method to Large Molecules	463
3	Correlation Corrected Energy Band Structures of Different Periodic Polymers	464
3.1	Methods	464
3.1.1	Inverse Dyson Equation with MP2 Self Energy	464
3.1.2	Formulation of the Coupled Cluster Method for Quasi 1D Polymers	465
3.1.3	Analytic Energy Gradients	468
3.2	Examples of Correlation Corrected Band Structures of Quasi 1D Polymers	471
4	Application of First Principles Density Functional Theory (DFT) to Polymers	474
4.1	Methods	474
4.2	Examples of LDA Calculations on Polymers	476
5	Non-linear Optical Properties of Polymers	478
5.1	Theory of Non-linear Optical Properties of Quasi 1D Periodic Polymers	478
5.1.1	Solid State Physical Methods	478
5.1.2	Large Clusters and Extrapolated Oligomers	493
5.2	Results of Calculations of NLO Properties and Their Discussion	494
5.2.1	Solid State Physical Calculations	494
5.2.2	Extrapolated Oligomer Calculations	495
6	Conformational Solitons in DNA and Their Possible Role in Cancer Inhibition	496
	Acknowledgement	500
	References	500

