

Contents

Chapter 1 Many-body Perturbation Theory of Molecules	1
<i>By S. Wilson</i>	
1 Introduction	1
2 The Many-body Perturbation Theory	4
General Remarks	4
The Partitioning Technique	4
Lennard-Jones Brillouin Wigner Perturbation Theory	5
Rayleigh–Schrödinger Perturbation Theory	7
The Many-body Perturbation Theory	7
Diagrammatic Conventions	9
Diagrammatic Perturbation Theory	12
Generalizations	13
3 The Algebraic Approximation	15
General Remarks	15
The Algebraic Approximation	15
Universal Basis Sets	16
Basis Set Truncation	18
4 Truncation of the Many-body Perturbation Expansion	19
General Remarks	19
Padé Approximants and Perturbation Expansions	20
Scaling of the Zero-order Hamiltonian	22
Modified Potentials	22
Upper Bounds to Total Energies	23
Fourth-order and Higher-order Terms	23
Quasi-degeneracy Effects	30
Comparison with Other Methods	31
5 Computational Aspects	34
General Remarks	34
Third-order Many-body Perturbative Calculations	34
Higher-order Terms	36
Bubble Diagrams	37
Vector Processing Computers	39
6 Some Applications	40
General Remarks	40

Application to Li_2 , N_2	41
Potential Energy Curves	42
Triple-excitations and Quadruple-excitations	43
Molecular Properties	44
7 Concluding Remarks	45
General Remarks	45
Some Other Aspects	45
Final Comments	47
Chapter 2 The Electronic Structure of Polymers	49
<i>By J. Ladik and S. Suhai</i>	
1 Introduction	49
2 Hartree-Fock LCAO Crystal Orbital Method	51
<i>Ab initio</i> Closed Shell Formalism	51
DODS Crystal Orbital Method	53
Truncation of Infinite Lattice Sums	54
Calculation of Wannier Functions	56
3 Excited States and Correlation Effects in Polymers	57
Intermediate Exciton Theory of Excited States	57
More General Treatments of Electron Correlation in Polymers	59
4 Semi-empirical Crystal Orbital Methods	61
5 Disorder Effects in the Electronic Structure of Polymers	63
Application of Dean's Negative Eigenvalue Theorem to Aperiodic Polymers	64
Treatment of Point Defects in Polymers	65
6 Illustrative Examples	65
Polyacetylenes (Polyenes)	65
Infinite Stacks of TCNQ and TTF Molecules	77
Periodic DNA Models	80
Periodic Protein Models	83
Impurity and Aperiodicity Effects in Polymers	84
Chapter 3 Electron Density Description of Atoms and Molecules	92
<i>By N. H. March</i>	
1 Introduction	92
2 Density-Potential Relation of Thomas-Fermi Statistical Theory	92
Self-consistent Fields for Heavy Positive Atomic Ions	93

3 Variation Principle and Chemical Potential of TF Theory	95
Kinetic Energy Density of Electron Cloud	96
Euler Equation for Density	96
4 Energy Relations for Heavy Positive Atomic Ions	97
Total Energy for Heavy Neutral Atoms	97
Comparison with Bare Coulomb Field	98
Scaling of Energies of Positive Ions	99
5 Relation of TF Theory to $1/Z$ Expansion	100
6 Inhomogeneity and Exchange Corrections to TF Theory	102
Origin of Corrections to TF Neutral Atom Energy	103
Chemical Potential and Energy Relations	105
7 Ionic Binding Energies, Ionization Potentials, and Electron Affinity	105
8 Kinetic Energies Calculated from Density Gradient Expansion	108
Relation between Total Energy and Sum of One-electron Energies	110
9 Density and Potential Distribution in Molecules	111
Central Field Model of Tetrahedral and Octahedral Molecules	112
10 Energy Relations for Molecules at Equilibrium	114
Adoption of Central Field Model at Equilibrium	114
Test of Energy Relations on Small Molecules	115
Regularities in Nuclear–Nuclear Potential Energy	116
11 Teller’s Theorem, Chemical Potential, and Molecular Binding	119
12 Form of Energy of Homonuclear Diatomic Molecules	120
Coulomb Field Scaling for Diatomic Molecules	120
Proposed Scaling in Self-consistent Field Theory	121
13 Can the Total Energy of a Molecule be Represented as the Sum of Orbital Energies?	123
Density Gradient Corrections	124
Basis for the Derivation of Walsh’s Rules	124
14 Density Description of Molecular Vibrations	127
Localized Models of Electron Density in Molecules	127
Point Charge Model of XY_2 Linear Symmetric Molecules	129
15 Inclusion of Correlation in Density Theory	131
Gradient Correction to Local Exchange and Correlation Energy	132

16 Electronegativity and Chemical Potential	133
Equivalence of Chemical Potential and Sanderson's Electronegativity	134
Electron Migration in a Model Heteronuclear Diatomic Molecule	134
Electronegativity Equalization in Bond Charge Model of Diatomic Molecules	135
Simple Charge Transfer Model for Electronegativity Neutralization	138
Total Energy, Sum of Orbital Energies, and Electronegativity	139
17 Wave Function Calculations and Density Functional Theory	142
First Row Diatomic Molecules	143
Alkali Dimers	148
Iron-series Dimers	151
18 Topology of Molecular Charge Distributions	158
Theory of Topological Dynamics of Molecular Systems	159
Topological Definition of Atoms, Bonds, and Structure	159
19 Summary and Future Directions	160
Appendix 1	
Some Results on the Chemical Potential for Electrons Moving Independently in a Harmonic Well and in a Pure Coulomb Field	164
Bare Coulomb Field	167
Appendix 2	
Hohenberg–Kohn and Two Other Density Theorems	168
Appendix 3	
One-body Potential in He and H ₂	169
Appendix 4	
Electron Correlation, Including Spin Density Description	171
Spin Density Description	172
Appendix 5	
Exact Differential Equation for Particle Density for N Particles Moving in One-dimensional Harmonic Oscillator Potential	173
Author Index	175