

Contents

Foreword	V
Preface	VII
Preface to the second edition	X
Part A The Definition of the Model	1
1 Elementary Quantum Chemistry	3
1.1 The Schrödinger Equation	3
1.2 The Variational Principle	6
1.3 The Hartree-Fock Approximation	8
1.4 The Restricted and Unrestricted Hartree-Fock Models	13
1.5 Electron Correlation	14
2 Electron Density and Hole Functions	19
2.1 The Electron Density	19
2.2 The Pair Density	20
2.3 Fermi and Coulomb Holes	24
2.3.1 The Fermi Hole	25
2.3.2 The Coulomb Hole	27
3 The Electron Density as Basic Variable: Early Attempts	29
3.1 Does it Make Sense?	29
3.2 The Thomas-Fermi Model	30
3.3 Slater's Approximation of Hartree-Fock Exchange	31
4 The Hohenberg-Kohn Theorems	33
4.1 The First Hohenberg-Kohn Theorem: Proof of Existence	33
4.2 The Second Hohenberg-Kohn Theorem: Variational Principle	36
4.3 The Constrained-Search Approach	37
4.4 Do We Know the Ground State Wave Function in Density Functional Theory?	39
4.5 Discussion	39

5	The Kohn-Sham Approach	41
5.1	Orbitals and the Non-Interacting Reference System	41
5.2	The Kohn-Sham Equations	43
5.3	Discussion	47
5.3.1	The Kohn-Sham Potential is Local	47
5.3.2	The Exchange-Correlation Energy in the Kohn-Sham and Hartree-Fock Schemes	48
5.3.3	Do the Kohn-Sham Orbitals Mean Anything?	49
5.3.4	Is the Kohn-Sham Approach a Single Determinant Method?	50
5.3.5	The Unrestricted Kohn-Sham Formalism	52
5.3.6	On Degeneracy, Ensembles and other Oddities	55
5.3.7	Excited States and the Multiplet Problem	59
6	The Quest for Approximate Exchange-Correlation Functionals	65
6.1	Is There a Systematic Strategy?	65
6.2	The Adiabatic Connection	67
6.3	From Holes to Functionals	69
6.4	The Local Density and Local Spin-Density Approximations	70
6.5	The Generalized Gradient Approximation	75
6.6	Hybrid Functionals	78
6.7	Self-Interaction	85
6.8	Asymptotic Behavior of Exchange-Correlation Potentials	88
6.9	Discussion	89
7	The Basic Machinery of Density Functional Programs	93
7.1	Introduction of a Basis: The LCAO Ansatz in the Kohn-Sham Equations	93
7.2	Basis Sets	97
7.3	The Calculation of the Coulomb Term	102
7.4	Numerical Quadrature Techniques to Handle the Exchange-Correlation Potential	105
7.5	Grid-Free Techniques to Handle the Exchange-Correlation Potential	110
7.6	Towards Linear Scaling Kohn-Sham Theory	113
Part B	The Performance of the Model	117
8	Molecular Structures and Vibrational Frequencies	119
8.1	Molecular Structures	119
8.1.1	Molecular Structures of Covalently Bound Main Group Elements	119
8.1.2	Molecular Structures of Transition Metal Complexes	127
8.2	Vibrational Frequencies	130
8.2.1	Vibrational Frequencies of Main Group Compounds	131
8.2.2	Vibrational Frequencies of Transition Metal Complexes	135

9	Relative Energies and Thermochemistry	137
9.1	Atomization Energies	137
9.2	Atomic Energies	149
9.3	Bond Strengths in Transition Metal Complexes	157
9.4	Ionization Energies	163
9.5	Electron Affinities	166
9.6	Electronic Excitation Energies and the Singlet/Triplet Splitting in Carbenes	168
10	Electric Properties	177
10.1	Population Analysis	178
10.2	Dipole Moments	180
10.3	Polarizabilities	183
10.4	Hyperpolarizabilities	188
10.5	Infrared and Raman Intensities	191
11	Magnetic Properties	197
11.1	Theoretical Background	198
11.2	NMR Chemical Shifts	201
11.3	NMR Nuclear Spin-Spin Coupling Constants	209
11.4	ESR g -Tensors	211
11.5	Hyperfine Coupling Constants	211
11.6	Summary	214
12	Hydrogen Bonds and Weakly Bound Systems	217
12.1	The Water Dimer – A Worked Example	221
12.2	Larger Water Clusters	230
12.3	Other Hydrogen Bonded Systems	232
12.4	The Dispersion Energy Problem	236
13	Chemical Reactivity: Exploration of Potential Energy Surfaces	239
13.1	First Example: Pericyclic Reactions	240
13.1.1	Electrocyclic Ring Opening of Cyclobutene	241
13.1.2	Cycloaddition of Ethylene to Butadiene	243
13.2	Second Example: The S_N2 Reaction at Saturated Carbon	247
13.3	Third Example: Proton Transfer and Hydrogen Abstraction Reactions	249
13.3.1	Proton Transfer in Malonaldehyde Enol	249
13.3.2	A Hydrogen Abstraction Reaction	252
13.4	Fourth Example: H_2 Activation by FeO^+ in the Gas Phase	255
Bibliography		265
Index		295