

CONTENTS

| | |
|---|-----------|
| List of Symbols | xiv |
| 1. ATOMS IN CHEMISTRY | 1 |
| 1.1 Atoms and the molecular structure hypothesis | 1 |
| 1.2 Necessary criteria for a theory of atoms in molecules | 2 |
| 1.3 The role of the charge density | 5 |
| E1.1 Density matrices | 11 |
| 2. ATOMS AND THE TOPOLOGY OF THE CHARGE DENSITY | 13 |
| 2.1 Introduction | 13 |
| 2.2 Topological properties of the charge density | 14 |
| 2.2.1 The dominant form in the charge density | 14 |
| 2.2.2 Critical points and their classification | 16 |
| 2.2.3 Critical points of molecular charge distributions | 19 |
| 2.3 Gradient vector field of the charge density | 22 |
| 2.3.1 Trajectories of the gradient vector field | 22 |
| 2.3.2 Phase portraits of the gradient vector field | 25 |
| 2.4 Elements of molecular structure | 28 |
| 2.4.1 Equivalence of the topological and quantum definitions of an atom | 28 |
| 2.4.2 Chemical bonds and molecular graphs | 32 |
| 2.4.3 Rings and cages | 35 |
| E2.1 Local properties of ρ and associated theorems | 40 |
| E2.1.1 Local maxima in ρ | 40 |
| E2.1.2 Theorems concerning the properties of ρ | 45 |
| E2.2 Mathematical properties of ρ at a critical point | 47 |
| E2.2.1 Eigenvalues and eigenvectors of Hessian of ρ | 47 |
| E2.2.2 Analytical expression for a trajectory in the vicinity of a critical point | 49 |
| 3. MOLECULAR STRUCTURE AND ITS CHANGE | 53 |
| 3.1 The notion of structure in chemistry | 53 |
| 3.2 The definition of molecular structure | 54 |
| 3.2.1 The equivalence relation—a qualitative discussion | 54 |
| 3.2.2 Changes in structure | 58 |
| 3.2.3 Structure diagrams | 64 |
| 3.2.4 Bonds and structure | 70 |
| 3.3 A theory of molecular structure | 87 |
| 3.3.1 A coming together of mathematics and chemistry | 87 |
| 3.3.2 The equivalence relation and structural stability | 88 |

| | | |
|-------|--|-----|
| 3.3.3 | Stable and unstable intersections of lines and surfaces in R^3 | 91 |
| 3.3.4 | Criteria for structural stability | 94 |
| 3.4 | Comparison of a structure diagram with other partitionings of R^Q | 95 |
| 3.4.1 | Relation between topological and energetic stabilities of molecular structures | 95 |
| 3.4.2 | Structural homeomorphism between ρ and the nuclear potential | 97 |
| 3.4.3 | The mechanics of ρ in the one-electron case | 101 |
| 3.5 | Summary | 102 |
| E3.1 | Summary of set theoretic language | 103 |
| E3.2 | Natural coordinate system for an atomic basin | 103 |
| 4. | MATHEMATICAL MODELS OF STRUCTURAL CHANGE | 110 |
| 4.1 | Introduction | 110 |
| 4.2 | Catastrophe theory | 111 |
| 4.2.1 | Isolating the unstable piece of a critical point | 111 |
| 4.2.2 | Elementary catastrophes | 112 |
| 4.3 | Catastrophes in molecular structures | 113 |
| 4.3.1 | Opening a ring structure—the fold catastrophe | 113 |
| 4.3.2 | A general analysis of three-centre systems | 115 |
| 4.3.3 | Formation of a cage structure | 121 |
| 5. | THE QUANTUM ATOM | 130 |
| 5.1 | Chemistry and quantum mechanics | 130 |
| 5.1.1 | From Lewis to quantum mechanical models | 130 |
| 5.1.2 | The role of the charge density in defining structure | 132 |
| 5.2 | Need for a quantum definition of an atom | 133 |
| 5.2.1 | Observational basis for a quantum atom | 133 |
| 5.2.2 | Observables and their properties for a total system | 137 |
| 5.3 | Need for a subsystem variation principle | 146 |
| 5.3.1 | Schrödinger's derivation of wave mechanics | 150 |
| 5.3.2 | The variational definition of a subsystem and its properties | 154 |
| E5.1 | The variation of Hamiltonian-based functionals | 161 |
| E5.2 | Vectors, tensors, and dyadics | 164 |
| E5.3 | Divergence of a vector and Gauss's theorem | 166 |
| 6. | THE MECHANICS OF AN ATOM IN A MOLECULE | 169 |
| 6.1 | An atomic view of the properties of matter | 169 |
| 6.1.1 | The charge and current densities | 169 |
| 6.1.2 | Variational derivation of the atomic force law | 172 |

CONTENTS

xi

| | | |
|-------|--|---------|
| 6.1.3 | The atomic virial theorem | 175 |
| 6.1.4 | Correspondence between local and subsystem mechanics | 178 |
| 6.2 | Atomic properties | 179 |
| 6.2.1 | Single-particle basis for atomic properties | 179 |
| 6.2.2 | Definition of atomic properties | 180 |
| 6.3 | Energy of an atom in a molecule | 185 |
| 6.3.1 | Physical constraints on partitioning the energy | 185 |
| 6.3.2 | The virial and the partitioning of an energy of interaction | 185 |
| 6.3.3 | The electronic energy of an atom | 189 |
| 6.3.4 | Potential energy contributions to an atomic energy | 191 |
| 6.4 | Properties of atoms in molecules | 195 |
| 6.4.1 | Properties determined by the electronic charge density | 196 |
| 6.4.2 | Transferability of atomic properties | 209 |
| 6.4.3 | The origin of strain energy in cyclic hydrocarbon molecules | 219 |
| 6.4.4 | Origin of rotation and inversion barriers | 221 |
| 6.4.5 | Perfect transferability—an unattainable limit | 235 |
| 6.5 | The hypervirial theorem and the definition of bond properties | 238 |
| 6.5.1 | An atomic property expressed as a sum of bond contributions | 239 |
| 6.5.2 | Surface integrals proportional to the energy | 240 |
| | | |
| 7. | CHEMICAL MODELS AND THE LAPLACIAN OF THE CHARGE DENSITY | 248 |
| 7.1 | The physical basis of the Lewis electron pair model | 248 |
| 7.1.1 | The electron pair at any cost | 248 |
| 7.1.2 | Are electrons localized in pairs? | 249 |
| 7.1.3 | Properties of the Laplacian of the charge density | 252 |
| 7.1.4 | The valence shell charge concentration (VSCC) | 258 |
| 7.1.5 | Bonded and non-bonded charge concentrations | 260 |
| 7.2 | A physical basis for the VSEPR model of molecular geometry | 265 |
| 7.2.1 | Résumé of the VSEPR model | 265 |
| 7.2.2 | Valence-shell charge concentrations with four maxima | 266 |
| 7.2.3 | Valence-shell charge concentrations with five and six maxima | 268 |
| 7.2.4 | Effects of charge transfer on the properties of the VSCC | 274 |
| 7.2.5 | Summary | 275 |
| 7.3 | The Laplacian of ρ and chemical reactivity | 275 |
| 7.3.1 | The Laplacian and the local energy of ρ | 275 |
| 7.3.2 | Lewis acid–base reactions | 277 |
| 7.4 | The characterization of atomic interactions | 288 |
| 7.4.1 | Definition of atomic interactions | 288 |
| 7.4.2 | Classification of atomic interactions | 290 |
| 7.4.3 | Hydrogen bonds and van der Waals molecules | 302 |
| 7.4.4 | Intermediate interactions | 307 |
| 7.5 | Atomic interactions in bound and unbound states | 315 |
| 7.5.1 | The electrostatic theorem and chemical binding | 315 |

| | | |
|-----------|--|------------|
| 7.5.2 | The virial theorem and chemical bonding | 322 |
| 7.5.3 | A summary | 331 |
| E7.1 | The pair density and the localization of electrons | 332 |
| E7.2 | Local charge concentrations and partial localization of the Fermi hole | 343 |
| 8. | THE ACTION PRINCIPLE FOR A QUANTUM SUBSYSTEM | 352 |
| 8.1 | A common basis for classical and quantum mechanics | 352 |
| 8.1.1 | Introduction | 352 |
| 8.1.2 | State vectors, state functions, and transformation functions | 353 |
| 8.1.3 | Unitary transformations | 359 |
| 8.1.4 | Canonical transformations and classical mechanics | 361 |
| 8.2 | The quantum action principle | 369 |
| 8.2.1 | The principle of stationary action | 369 |
| 8.2.2 | Applying the principle of stationary action | 371 |
| 8.3 | Atomic action principle | 376 |
| 8.3.1 | Properties of the quantum mechanical Lagrangian | 376 |
| 8.3.2 | Atomic action and Lagrangian integrals | 378 |
| 8.3.3 | Variation of the atomic action integral | 380 |
| 8.3.4 | Principle of stationary action in the Schrödinger representation | 382 |
| 8.3.5 | Atomic statement of the principle of stationary action | 384 |
| 8.3.6 | Examples of unitary transformations | 391 |
| 8.4 | Variational basis for atomic properties | 393 |
| 8.4.1 | Variational derivation of the atomic force law | 393 |
| 8.4.2 | Differential force law | 396 |
| 8.4.3 | Variational derivation of the atomic virial theorem | 398 |
| 8.4.4 | Local virial relationship | 401 |
| 8.4.5 | Summary of the atomic variation principle | 402 |
| 8.5 | Atoms in an electromagnetic field | 403 |
| 8.5.1 | The Lagrangian and Hamiltonian | 403 |
| 8.5.2 | Definition of an atom in an external field | 406 |
| 8.5.3 | Atomic force and virial theorems in the presence of external fields | 410 |
| 8.5.4 | Atomic contributions to molecular polarizability and susceptibility | 416 |
| 8.6 | The action principle—in the past and in the future | 422 |
| | APPENDIX | 427 |
| | Table A1 Units | 427 |
| | Table A2 Contour values for maps of the electronic charge density and of the Laplacian distribution function | 427 |

| | | |
|----------|--|------|
| Table A3 | Properties of ρ at $(3, -1)$ critical point together with bonded and non bonded radii for ground-state diatomic molecules | 428 |
| Table A4 | Atomic charges, moments, and volumes of ground-state diatomic molecules | 430 |
| Table A5 | Radii of isolated ground-state spherical atoms and ions | 432 |
| INDEX | | 433 |
| | position vector of critical point \mathbf{r}_c | x |
| | the space and spin coordinates of a set of electrons | x |
| | position vector of the nucleus \mathbf{r}_N | x |
| | electronic position vector with origin at nucleus of atom \mathbf{r} | x |
| | volume element for a single electron | xi |
| | coordinates with respect to coordinates of an electron | xii |
| | nuclear coordinates \mathbf{R} | xii |
| | a point in \mathbb{R}^6 defining a molecular geometry, the set of nuclear coordinates | xii |
| | coordinates | xii |
| | position vector of nucleus \mathbf{r}_N | xii |
| | Schrödinger's constant $\hbar^2/2m$ eqn (E.58) | xii |
| | Schrödinger's constant $\hbar^2/2m$ eqn (E.58) | xii |
| | stationary state energy E_n | xii |
| | region with respect to nuclear coordinates | xii |
| | a summation over all electronic spin coordinates and the integration over the space coordinates of all electrons but one | xiii |
| | Hamiltonian eqn (E.5.1) and (E.5.2) eqn (E.5.1) and (E.5.2) eqn (E.5.1) and (E.5.2) | xiii |
| | integral over surface of atom Ω | xiii |
| | Lagrange integral eqn (E.7.7) | xiii |
| | Hamiltonian energy integral | xiii |
| | Vectors and dyadics | xiii |
| | atomic action integral eqn (E.11.1) | xiii |
| | the vector in x, y, z directions | xiii |
| | vector with components A_x, A_y, A_z eqn (E.2.11) | xiii |
| | scalar product of \mathbf{A} and \mathbf{B} eqn (E.2.12) | xiii |
| | vector product of \mathbf{A} and \mathbf{B} | xiii |
| | dyadic with nine components, eqn (E.2.14) | xiii |
| | charge density and related quantities | xiii |
| | Lagrange function operator | xiii |
| | electronic charge density $\rho(\mathbf{r}, t)$ | xiii |
| | value of $\rho(\mathbf{r}, t)$ at fixed \mathbf{r} and t | xiii |
| | value of $\rho(\mathbf{r}, t)$ at a fixed distance r | xiii |
| | density of a spinless fermion system | xiii |
| | position vector of nucleus \mathbf{r}_N eqn (E.5.1) eqn (E.5.1) | xiii |
| | path parameter of trajectory s | xiii |
| | unit vector normal to surface \mathbf{n} | xiii |
| | eigenvalue of the Hessian matrix at a critical point | xiii |