

# CONTENTS

|                                                          |             |
|----------------------------------------------------------|-------------|
| <b>Series Preface</b> .....                              | <b>xi</b>   |
| <b>Preface to the First Edition</b> .....                | <b>xiii</b> |
| <b>Preface to the Second Edition</b> .....               | <b>xvii</b> |
| <b>0 Prerequisites</b> .....                             | <b>1</b>    |
| 0.1 What is a Chapter 0? .....                           | 3           |
| 0.2 Branches of Mechanics .....                          | 4           |
| 0.3 Vectors, Vector Fields and Vector Calculus .....     | 4           |
| 0.4 Vector Calculus .....                                | 7           |
| 0.5 Newton's Laws of Motion .....                        | 11          |
| 0.6 Basic Electrostatics .....                           | 13          |
| 0.7 The Schrödinger Equation .....                       | 16          |
| 0.8 Systems of Units .....                               | 20          |
| <b>1 Molecular Mechanics</b> .....                       | <b>24</b>   |
| 1.1 Vibrational Motion .....                             | 24          |
| 1.2 Normal Modes of Vibration .....                      | 28          |
| 1.3 The Quantum-Mechanical Treatment .....               | 29          |
| 1.4 The Taylor Expansion .....                           | 35          |
| 1.5 The Morse Potential .....                            | 36          |
| 1.6 More Advanced Empirical Potentials .....             | 37          |
| 1.7 Molecular Mechanics .....                            | 38          |
| 1.8 Professional Molecular Mechanics Force Fields .....  | 44          |
| 1.9 A Sample MM Calculation: Aspirin .....               | 46          |
| 1.10 The Graphical User Interface .....                  | 48          |
| 1.11 General Features of Potential Energy Surfaces ..... | 51          |
| 1.12 Other Properties .....                              | 56          |

|          |                                             |            |
|----------|---------------------------------------------|------------|
| 1.13     | Protein Docking                             | 56         |
| 1.14     | Unanswered Questions                        | 57         |
| <b>2</b> | <b>Dynamics</b>                             | <b>58</b>  |
| 2.1      | Equipartition of Energy                     | 59         |
| 2.2      | Ensembles                                   | 60         |
| 2.3      | The Boltzmann Distribution                  | 60         |
| 2.4      | Molecular Dynamics                          | 62         |
| 2.5      | Collection of Statistics                    | 64         |
| 2.6      | Simulation of Systems                       | 64         |
| 2.7      | The Monte Carlo Method                      | 69         |
| <b>3</b> | <b>The Hydrogen Molecule Ion</b>            | <b>72</b>  |
| 3.1      | The Born–Oppenheimer Approximation          | 73         |
| 3.2      | The LCAO Model                              | 76         |
| 3.3      | Integral Evaluation                         | 77         |
| 3.4      | Improving the Atomic Orbital                | 80         |
| 3.5      | More Advanced Calculations                  | 81         |
| 3.6      | Visualization                               | 82         |
| <b>4</b> | <b>The Hydrogen Molecule</b>                | <b>85</b>  |
| 4.1      | The Non-Interacting Electron Model          | 87         |
| 4.2      | The Valence Bond Model                      | 88         |
| 4.3      | Indistinguishability                        | 89         |
| 4.4      | Electron Spin                               | 91         |
| 4.5      | The Pauli Principle                         | 91         |
| 4.6      | The Dihydrogen Molecule                     | 92         |
| 4.7      | Configuration Interaction                   | 94         |
| 4.8      | The LCAO–Molecular Orbital Model            | 95         |
| 4.9      | Comparison of Simple VB AND LCAO Treatments | 97         |
| 4.10     | Slater Determinants                         | 97         |
| <b>5</b> | <b>The Electron Density</b>                 | <b>99</b>  |
| 5.1      | The General LCAO Case                       | 102        |
| 5.2      | Population Analysis                         | 103        |
| 5.3      | Density Functions                           | 106        |
| <b>6</b> | <b>The Hartree–Fock Model</b>               | <b>109</b> |
| 6.1      | The LCAO Procedure                          | 113        |
| 6.2      | The Electronic Energy                       | 117        |
| 6.3      | The Koopmans Theorem                        | 117        |
| 6.4      | Open-Shell Systems                          | 118        |
| 6.5      | Unrestricted Hartree–Fock Theory            | 120        |
| 6.6      | The $\hat{J}$ and $\hat{K}$ Operators       | 121        |

|           |                                                      |            |
|-----------|------------------------------------------------------|------------|
| <b>7</b>  | <b>The Hückel Model</b>                              | <b>122</b> |
| 7.1       | Examples                                             | 124        |
| 7.2       | Bond Lengths and the Hückel model                    | 126        |
| 7.3       | Molecular Mechanics of $\pi$ -Electron Systems       | 127        |
| 7.4       | Alternant Hydrocarbons                               | 127        |
| 7.5       | Treatment of Heteroatoms                             | 128        |
| 7.6       | Extended Hückel Theory                               | 129        |
| 7.7       | The Nightmare of the Inner Shells                    | 133        |
| 7.8       | But What <i>is</i> the Hückel Hamiltonian?           | 134        |
| <b>8</b>  | <b>Neglect of Differential Overlap Models</b>        | <b>135</b> |
| 8.1       | The $\pi$ -electron Zero Differential Overlap Models | 136        |
| 8.2       | The Identity of the Basis Functions                  | 143        |
| 8.3       | The 'All Valence Electron' NDO models                | 144        |
| <b>9</b>  | <b>Basis Sets</b>                                    | <b>154</b> |
| 9.1       | Hydrogenic Orbitals                                  | 155        |
| 9.2       | Slater's Rules                                       | 157        |
| 9.3       | Clementi and Raimondi                                | 158        |
| 9.4       | Gaussian Orbitals                                    | 161        |
| 9.5       | The STO/ $n$ G Philosophy                            | 164        |
| 9.6       | The STO/4–31G Story                                  | 167        |
| 9.7       | Extended Basis Sets                                  | 168        |
| 9.8       | Diffuse and Polarization Functions                   | 170        |
| 9.9       | Effective Core Potentials                            | 171        |
| <b>10</b> | <b><i>Ab Initio</i> Packages</b>                     | <b>173</b> |
| 10.1      | Level of Theory                                      | 174        |
| 10.2      | Geometry Input                                       | 174        |
| 10.3      | An <i>Ab Initio</i> HF–LCAO Calculation              | 178        |
| 10.4      | Visualization                                        | 184        |
| <b>11</b> | <b>Electron Correlation</b>                          | <b>186</b> |
| 11.1      | Configuration Interaction                            | 189        |
| 11.2      | Perturbation Theory                                  | 197        |
| 11.3      | Møller-Plesset Perturbation Theory                   | 199        |
| 11.4      | The Dineon Pair Potential                            | 201        |
| 11.5      | Multiconfiguration SCF                               | 203        |
| 11.6      | Quadratic Configuration Interaction                  | 206        |
| 11.7      | Resource Consumption                                 | 208        |
| <b>12</b> | <b>Slater's <math>X\alpha</math> Model</b>           | <b>209</b> |
| 12.1      | The Exchange Potential                               | 211        |
| 12.2      | The Drude Model                                      | 211        |

|           |                                                               |            |
|-----------|---------------------------------------------------------------|------------|
| 12.3      | Pauli's Model                                                 | 212        |
| 12.4      | The Thomas–Fermi Model                                        | 213        |
| 12.5      | The Atomic $X\alpha$ Model                                    | 214        |
| 12.6      | Slater's Multiple Scattering $X\alpha$ Method for Molecules   | 215        |
| <b>13</b> | <b>Density Functional Theory</b>                              | <b>218</b> |
| 13.1      | The Hohenberg–Kohn Theorem                                    | 221        |
| 13.2      | The Kohn–Sham Equations                                       | 224        |
| 13.3      | The Local Density Approximation                               | 225        |
| 13.4      | Beyond the Local Density Approximation                        | 225        |
| 13.5      | The Becke Exchange correction                                 | 225        |
| 13.6      | The Lee–Yang–Parr Correlation Potential                       | 226        |
| 13.7      | Quadrature                                                    | 226        |
| 13.8      | A Typical Implementation                                      | 227        |
| <b>14</b> | <b>Potential Energy Surfaces</b>                              | <b>230</b> |
| 14.1      | A Diatomic Molecule                                           | 231        |
| 14.2      | Characterizing points on a Potential Energy Surface           | 232        |
| 14.3      | Locating Stationary Points                                    | 234        |
| 14.4      | General Comments                                              | 238        |
| 14.5      | Steepest Descents                                             | 238        |
| 14.6      | The Fletcher–Reeves Algorithm                                 | 238        |
| 14.7      | The Hellman–Feynman Theorem                                   | 239        |
| 14.8      | The Coupled Hartree–Fock (CPHF) Model                         | 240        |
| 14.9      | Choice of Variables                                           | 241        |
| 14.10     | Normal Coordinates                                            | 245        |
| 14.11     | Searching for Transition States                               | 249        |
| 14.12     | Surface-Fitting                                               | 249        |
| <b>15</b> | <b>Dealing with the Solvent</b>                               | <b>252</b> |
| 15.1      | Langevin Dynamics                                             | 252        |
| 15.2      | The Solvent Box                                               | 253        |
| 15.3      | The Onsager Model                                             | 254        |
| 15.4      | Hybrid Quantum-Mechanical and Molecular<br>Mechanical Methods | 260        |
| <b>16</b> | <b>Primary Properties and their Derivatives</b>               | <b>265</b> |
| 16.1      | Electric Multipole Moments                                    | 266        |
| 16.2      | The Multipole Expansion                                       | 269        |
| 16.3      | Charge Distribution in an External Field                      | 271        |
| 16.4      | Implications of Brillouin's Theorem                           | 271        |
| 16.5      | Electric Dipole Moments                                       | 272        |
| 16.6      | Analytical Gradients                                          | 276        |
| 16.7      | Electric Quadrupole Moments                                   | 276        |

|           |                                                               |            |
|-----------|---------------------------------------------------------------|------------|
| 16.8      | Electric Field Gradients                                      | 277        |
| 16.9      | The Electrostatic Potential                                   | 279        |
| <b>17</b> | <b>Induced Properties</b>                                     | <b>282</b> |
| 17.1      | Induced Dipoles                                               | 282        |
| 17.2      | Energy of Charge Distribution in Field                        | 283        |
| 17.3      | Multipole Polarizabilities                                    | 284        |
| 17.4      | Polarizability Derivatives                                    | 285        |
| 17.5      | A Classical Model of Dipole Polarizability                    | 285        |
| 17.6      | Quantum-Mechanical Calculations of Static<br>Polarizabilities | 287        |
| 17.7      | Derivatives                                                   | 290        |
| 17.8      | Interaction Polarizabilities                                  | 292        |
| 17.9      | The Hamiltonian                                               | 294        |
| 17.10     | Magnetizabilities                                             | 296        |
| 17.11     | Gauge Invariance                                              | 296        |
| 17.12     | Non-Linear Optical Properties                                 | 298        |
| 17.13     | Time-Dependent Perturbation Theory                            | 298        |
| 17.14     | Time-Dependent Hartree–Fock Theory                            | 300        |
| <b>18</b> | <b>Miscellany</b>                                             | <b>302</b> |
| 18.1      | The Floating Spherical Gaussian (FSGO) Model                  | 302        |
| 18.2      | Hyperfine Interactions                                        | 304        |
| 18.3      | Atoms in Molecules                                            | 316        |
| 18.4      | Thermodynamic Quantities                                      | 319        |
|           | <b>References</b>                                             | <b>325</b> |
|           | <b>Index</b>                                                  | <b>331</b> |