

## Contents

**List of Contributors** *xix*

**Preface** *xxiii*

|          |                                                                               |          |
|----------|-------------------------------------------------------------------------------|----------|
| <b>1</b> | <b>Motivation and Basic Concepts</b>                                          | <b>1</b> |
|          | <i>Sandra Gómez, Ignacio Fdez. Galván, Roland Lindh, and Leticia González</i> |          |
| 1.1      | Mission and Motivation                                                        | 1        |
| 1.2      | Atomic Units                                                                  | 4        |
| 1.3      | The Molecular Hamiltonian                                                     | 5        |
| 1.4      | Dirac or Bra-Ket Notation                                                     | 6        |
| 1.5      | Index Definitions                                                             | 7        |
| 1.6      | Second Quantization Formalism                                                 | 7        |
| 1.7      | Born–Oppenheimer Approximation and Potential Energy Surfaces                  | 9        |
| 1.8      | Adiabatic Versus Diabatic Representations                                     | 10       |
| 1.9      | Conical Intersections                                                         | 11       |
| 1.10     | Further Reading                                                               | 12       |
| 1.11     | Acknowledgments                                                               | 12       |

## **Part I Quantum Chemistry** **13**

|          |                                                                |           |
|----------|----------------------------------------------------------------|-----------|
| <b>2</b> | <b>Time-Dependent Density Functional Theory</b>                | <b>15</b> |
|          | <i>Miquel Huix-Rotllant, Nicolas Ferré, and Mario Barbatti</i> |           |
| 2.1      | Introduction                                                   | 15        |
| 2.2      | TDDFT Fundamentals                                             | 16        |
| 2.2.1    | The Runge–Gross Theorems                                       | 16        |
| 2.2.2    | The Time-Dependent Kohn–Sham Approach                          | 18        |
| 2.2.3    | Solutions of Time-Dependent Kohn–Sham Equations                | 19        |
| 2.2.3.1  | Real-Time TDDFT                                                | 19        |
| 2.2.3.2  | Linear-Response TDDFT                                          | 20        |
| 2.3      | Linear-Response TDDFT in Action                                | 22        |
| 2.3.1    | Vertical Excitations and Energy Surfaces                       | 22        |
| 2.3.1.1  | Vertical Excitations: How Good are They?                       | 23        |
| 2.3.1.2  | Reconstructed Energy Surfaces: How Good are They?              | 25        |
| 2.3.2    | Conical Intersections                                          | 28        |
| 2.3.3    | Coupling Terms and Auxiliary Wave Functions                    | 30        |

|         |                                                            |    |
|---------|------------------------------------------------------------|----|
| 2.3.3.1 | The Casida Ansatz                                          | 30 |
| 2.3.3.2 | Time-Derivative Non-Adiabatic Couplings                    | 31 |
| 2.3.4   | Non-Adiabatic Dynamics                                     | 32 |
| 2.4     | Excited States and Dynamics with TDDFT Variants and Beyond | 34 |
| 2.5     | Conclusions                                                | 35 |
|         | Acknowledgments                                            | 36 |
|         | References                                                 | 36 |

### **3 Multi-Configurational Density Functional Theory: Progress and Challenges 47**

*Erik Donovan Hedegård*

|         |                                                                               |    |
|---------|-------------------------------------------------------------------------------|----|
| 3.1     | Introduction                                                                  | 47 |
| 3.2     | Wave Function Theory                                                          | 50 |
| 3.3     | Kohn–Sham Density Functional Theory                                           | 50 |
| 3.3.1   | Density Functional Approximations                                             | 53 |
| 3.3.2   | Density Functional Theory for Excited States                                  | 54 |
| 3.3.2.1 | Issues Within the Time-Dependent Density Functional Theory Ansatz             | 55 |
| 3.3.2.2 | Self-Interaction Error                                                        | 55 |
| 3.3.2.3 | Degeneracies, Near-Degeneracies and the Symmetry Dilemma                      | 56 |
| 3.4     | Multi-Configurational Density Functional Theory                               | 57 |
| 3.4.1   | Semi-Empirical Multi-Configurational Density Functional Theory                | 57 |
| 3.4.2   | Multi-Configurational Density Functional Theory Based the On-Top Pair Density | 58 |
| 3.4.2.1 | Density Matrices and the On-Top Pair Density                                  | 59 |
| 3.4.2.2 | Energy Functional and Excited States with the On-Top Pair Density             | 60 |
| 3.4.3   | Multi-Configurational Density Functional Theory Based on Range-Separation     | 61 |
| 3.4.3.1 | Energy Functional and Excited States in Range-Separated Methods               | 62 |
| 3.4.3.2 | The Range-Separation Parameter in Excited State Calculations                  | 62 |
| 3.5     | Illustrative Examples                                                         | 64 |
| 3.5.1   | Excited States of Organic Molecules                                           | 64 |
| 3.5.2   | Excited States for a Transition Metal Complex                                 | 65 |
| 3.6     | Outlook                                                                       | 66 |
|         | Acknowledgments                                                               | 67 |
|         | References                                                                    | 67 |

### **4 Equation-of-Motion Coupled-Cluster Models 77**

*Monika Musiał*

|       |                                    |    |
|-------|------------------------------------|----|
| 4.1   | Introduction                       | 77 |
| 4.2   | Theoretical Background             | 79 |
| 4.2.1 | Coupled-Cluster Wave Function      | 79 |
| 4.2.2 | The Equation-of-Motion Approach    | 80 |
| 4.2.3 | Similarity-Transformed Hamiltonian | 81 |
| 4.2.4 | Davidson Diagonalization Algorithm | 82 |
| 4.3   | Excited States: EE-EOM-CC          | 84 |
| 4.3.1 | EE-EOM-CCSD Model                  | 84 |
| 4.3.2 | EE-EOM-CCSDT Model                 | 86 |
| 4.3.3 | EE-EOM-CC Results                  | 87 |
| 4.4   | Ionized States: IP-EOM-CC          | 89 |

|       |                                             |     |
|-------|---------------------------------------------|-----|
| 4.4.1 | IP-EOM-CCSD Model                           | 89  |
| 4.4.2 | IP-EOM-CCSDT Model                          | 89  |
| 4.4.3 | IP-EOM-CC Results                           | 90  |
| 4.5   | Electron-Attached States: EA-EOM-CC         | 91  |
| 4.5.1 | EA-EOM-CCSD Model                           | 92  |
| 4.5.2 | EA-EOM-CCSDT Model                          | 92  |
| 4.5.3 | EA-EOM-CC Results                           | 92  |
| 4.6   | Doubly-Ionized States: DIP-EOM-CC           | 94  |
| 4.6.1 | DIP-EOM-CCSD Model                          | 95  |
| 4.6.2 | DIP-EOM-CCSDT Model                         | 95  |
| 4.6.3 | DIP-EOM-CC Results                          | 96  |
| 4.7   | Doubly Electron-Attached States: DEA-EOM-CC | 97  |
| 4.7.1 | DEA-EOM-CCSD Model                          | 98  |
| 4.7.2 | DEA-EOM-CCSDT Model                         | 98  |
| 4.7.3 | DEA-EOM-CC Results                          | 98  |
| 4.8   | Size-Extensivity Issue in the EOM-CC Theory | 100 |
| 4.9   | Final Remarks                               | 102 |
|       | References                                  | 103 |

## 5 The Algebraic-Diagrammatic Construction Scheme for the Polarization Propagator 109

*Andreas Dreuw*

|       |                                                      |     |
|-------|------------------------------------------------------|-----|
| 5.1   | Original Derivation via Green's Functions            | 110 |
| 5.2   | The Intermediate State Representation                | 112 |
| 5.3   | Calculation of Excited State Properties and Analysis | 114 |
| 5.3.1 | Excited State Properties                             | 114 |
| 5.3.2 | Excited-State Wave Function and Density Analyses     | 116 |
| 5.4   | Properties and Limitations of ADC                    | 117 |
| 5.5   | Variants of EE-ADC                                   | 119 |
| 5.5.1 | Extended ADC(2)                                      | 119 |
| 5.5.2 | Unrestricted EE-ADC Schemes                          | 120 |
| 5.5.3 | Spin-Flip EE-ADC Schemes                             | 121 |
| 5.5.4 | Spin-Opposite-Scaled ADC Schemes                     | 122 |
| 5.5.5 | Core-Valence Separated (CVS) EE-ADC                  | 123 |
| 5.6   | Describing Molecular Photochemistry with ADC Methods | 125 |
| 5.6.1 | Potential Energy Surfaces                            | 125 |
| 5.6.2 | Environment Models within ADC                        | 126 |
| 5.7   | Brief Summary and Perspective                        | 126 |
|       | Bibliography                                         | 127 |

## 6 Foundation of Multi-Configurational Quantum Chemistry 133

*Giovanni Li Manni, Kai Guther, Dongxia Ma, and Werner Dobrautz*

|       |                                                    |     |
|-------|----------------------------------------------------|-----|
| 6.1   | Scaling Problem in FCI, CAS and RAS Wave Functions | 136 |
| 6.2   | Factorization and Coupling of Slater Determinants  | 138 |
| 6.2.1 | Slater Condon Rules                                | 140 |
| 6.3   | Configuration State Functions                      | 141 |
| 6.3.1 | The Unitary Group Approach (UGA)                   | 142 |

|         |                                                          |     |
|---------|----------------------------------------------------------|-----|
| 6.3.1.1 | Analogy between CSFs and Spherical Harmonics             | 143 |
| 6.3.1.2 | Gel'fand-Tsetlin Basis                                   | 143 |
| 6.3.1.3 | Paldus and Weyl Tables                                   | 145 |
| 6.3.1.4 | The Step-Vector                                          | 148 |
| 6.3.2   | The Graphical Unitary Group Approach (GUGA)              | 148 |
| 6.3.3   | Evaluation of Non-Vanishing Hamiltonian Matrix Elements  | 153 |
| 6.3.3.1 | One-Body Coupling Coefficients                           | 154 |
| 6.3.3.2 | Two-Body Matrix Elements                                 | 157 |
| 6.4     | Configuration Interaction Eigenvalue Problem             | 158 |
| 6.4.1   | Iterative Methods                                        | 159 |
| 6.4.1.1 | Lanczos Algorithm                                        | 159 |
| 6.4.1.2 | Davidson Algorithm                                       | 160 |
| 6.4.2   | Direct-CI Algorithm                                      | 162 |
| 6.5     | The CASSCF Method                                        | 165 |
| 6.5.1   | The MCSCF Parameterization                               | 167 |
| 6.5.2   | The MCSCF Gradient and Hessian                           | 169 |
| 6.5.3   | One-Step and Two-Step Procedures                         | 170 |
| 6.5.4   | Augmented Hessian Method                                 | 171 |
| 6.5.5   | Matrix form of the First and Second Derivatives in MCSCF | 171 |
| 6.5.6   | Quadratically Converging Method with Optimal Convergence | 175 |
| 6.5.7   | Orbital-CI Coupling Terms                                | 178 |
| 6.5.8   | Super-CI for the Orbital Optimization                    | 179 |
| 6.5.9   | Redundancy of Active Orbital Rotations                   | 181 |
| 6.6     | Restricted and Generalized Active Space Wave Functions   | 182 |
| 6.6.1   | GUGA Applied to CAS, RAS and GAS Wave Functions          | 184 |
| 6.6.2   | Redundancies in GASSCF Orbital Rotations                 | 186 |
| 6.6.3   | MCSCF Molecular Orbitals                                 | 187 |
| 6.6.4   | GASSCF Applied to the $Gd_2$ Molecule                    | 188 |
| 6.7     | Excited States                                           | 189 |
| 6.7.1   | Multi-State CI Solver                                    | 190 |
| 6.7.2   | State-Specific and State-Averaged MCSCF                  | 191 |
| 6.8     | Stochastic Multiconfigurational Approaches               | 191 |
| 6.8.1   | FCIQMC Working Equation                                  | 192 |
| 6.8.2   | Multi-Wave Function Approach for Excited States          | 196 |
| 6.8.3   | Sampling Reduced Density Matrices                        | 196 |
|         | Bibliography                                             | 198 |

## 7 The Density Matrix Renormalization Group for Strong Correlation in Ground and Excited States 205

*Leon Freitag and Markus Reiher*

|       |                                                                                  |     |
|-------|----------------------------------------------------------------------------------|-----|
| 7.1   | Introduction                                                                     | 205 |
| 7.2   | DMRG Theory                                                                      | 207 |
| 7.2.1 | Renormalization Group Formulation                                                | 207 |
| 7.2.2 | Matrix Product States and Matrix Product Operators                               | 210 |
| 7.2.3 | MPS-MPO Formulation of DMRG                                                      | 214 |
| 7.2.4 | Connection between the Renormalization Group and the MPS-MPO Formulation of DMRG | 217 |

|       |                                                                        |     |
|-------|------------------------------------------------------------------------|-----|
| 7.2.5 | Developments to Enhance DMRG Convergence and Performance               | 218 |
| 7.3   | DMRG and Orbital Entanglement                                          | 218 |
| 7.4   | DMRG in Practice                                                       | 220 |
| 7.4.1 | Calculating Excited States with DMRG                                   | 220 |
| 7.4.2 | Factors Affecting the DMRG Convergence and Accuracy                    | 220 |
| 7.4.3 | Post-DMRG Methods for Dynamic Correlation and Environment Effects      | 221 |
| 7.4.4 | Analytical Energy Gradients and Non-Adiabatic Coupling Matrix Elements | 222 |
| 7.4.5 | Tensor Network States                                                  | 224 |
| 7.5   | Applications in Quantum Chemistry                                      | 225 |
| 7.6   | Conclusions                                                            | 230 |
|       | Acknowledgment                                                         | 231 |
|       | References                                                             | 231 |

## 8 Excited-State Calculations with Quantum Monte Carlo 247

*Jonas Feldt and Claudia Filippi*

|       |                                                     |     |
|-------|-----------------------------------------------------|-----|
| 8.1   | Introduction                                        | 247 |
| 8.2   | Variational Monte Carlo                             | 249 |
| 8.3   | Diffusion Monte Carlo                               | 252 |
| 8.4   | Wave Functions and their Optimization               | 256 |
| 8.4.1 | Stochastic Reconfiguration Method                   | 258 |
| 8.4.2 | Linear Method                                       | 259 |
| 8.5   | Excited States                                      | 261 |
| 8.5.1 | Energy-Based Methods                                | 261 |
| 8.5.2 | Time-Dependent Linear-Response VMC                  | 263 |
| 8.5.3 | Variance-Based Methods                              | 264 |
| 8.6   | Applications to Excited States of Molecular Systems | 265 |
| 8.7   | Alternatives to Diffusion Monte Carlo               | 269 |
|       | Bibliography                                        | 270 |

## 9 Multi-Reference Configuration Interaction 277

*Felix Plasser and Hans Lischka*

|       |                                                         |     |
|-------|---------------------------------------------------------|-----|
| 9.1   | Introduction                                            | 277 |
| 9.2   | Basics                                                  | 278 |
| 9.2.1 | Configuration Interaction and the Variational Principle | 278 |
| 9.2.2 | The Size-Extensivity Problem of Truncated CI            | 280 |
| 9.2.3 | Multi-Reference Configuration Spaces                    | 282 |
| 9.2.4 | Many-Electron Basis Functions: Determinants and CSFs    | 286 |
| 9.2.5 | Workflow                                                | 287 |
| 9.3   | Types of MRCI                                           | 289 |
| 9.3.1 | Uncontracted and Contracted MRCI                        | 289 |
| 9.3.2 | MRCI with Extensivity Corrections                       | 291 |
| 9.3.3 | Types of Selection Schemes                              | 293 |
| 9.3.4 | Construction of Orbitals                                | 293 |
| 9.4   | Popular Implementations                                 | 294 |
| 9.5   | Conclusions                                             | 295 |
|       | References                                              | 295 |

|           |                                                                                             |            |
|-----------|---------------------------------------------------------------------------------------------|------------|
| <b>10</b> | <b>Multi-Configurational Reference Perturbation Theory with a CASSCF Reference Function</b> | <b>299</b> |
|           | <i>Roland Lindh and Ignacio Fdez. Galván</i>                                                |            |
| 10.1      | Rayleigh–Schrödinger Perturbation Theory                                                    | 300        |
| 10.1.1    | The Single-State Theory                                                                     | 300        |
| 10.1.1.1  | The Conventional Projectional Derivation                                                    | 300        |
| 10.1.1.2  | The Bi-Variational Approach                                                                 | 304        |
| 10.1.2    | Convergence Properties and Intruder States                                                  | 308        |
| 10.1.2.1  | Real and Imaginary Shift Techniques                                                         | 310        |
| 10.2      | Møller–Plesset Perturbation Theory                                                          | 313        |
| 10.2.1    | The Reference Function                                                                      | 314        |
| 10.2.2    | The Partitioning of the Hamiltonian                                                         | 315        |
| 10.2.3    | The First-Order Interacting Space and Second-Order Energy Correction                        | 316        |
| 10.3      | State-Specific Multi-Configurational Reference Perturbation Methods                         | 320        |
| 10.3.1    | The Generation of the Reference Hamiltonian                                                 | 321        |
| 10.3.2    | CAS-MP2 Theory                                                                              | 322        |
| 10.3.3    | CASPT2 Theory                                                                               | 323        |
| 10.3.3.1  | The Partitioning of the Hamiltonian                                                         | 324        |
| 10.3.3.2  | The First-Order Interacting Space                                                           | 325        |
| 10.3.3.3  | Other Active Space References                                                               | 328        |
| 10.3.3.4  | Benchmark Results                                                                           | 329        |
| 10.3.3.5  | IPEA Shift                                                                                  | 330        |
| 10.3.4    | MRMP2 Theory                                                                                | 331        |
| 10.3.4.1  | The Partitioning of the Hamiltonian                                                         | 331        |
| 10.3.4.2  | The First-Order Interacting Space                                                           | 332        |
| 10.3.5    | NEVPT2 Theory                                                                               | 333        |
| 10.3.5.1  | The Partitioning of the Hamiltonian                                                         | 333        |
| 10.3.5.2  | The First-Order Interacting Space                                                           | 335        |
| 10.3.6    | Performance Improvements                                                                    | 336        |
| 10.4      | Quasi-Degenerate Perturbation Theory                                                        | 338        |
| 10.5      | Multi-State Multi-Configurational Reference Perturbation Methods                            | 341        |
| 10.5.1    | Multi-State CASPT2 Theory                                                                   | 341        |
| 10.5.2    | Extended MS-CASPT2 Theory                                                                   | 342        |
| 10.6      | Summary and Outlook                                                                         | 343        |
|           | Acknowledgments                                                                             | 345        |
|           | References                                                                                  | 345        |
|           | Appendix                                                                                    | 350        |

## Part II Nuclear Dynamics 355

|           |                                                                        |            |
|-----------|------------------------------------------------------------------------|------------|
| <b>11</b> | <b>Exact Quantum Dynamics (Wave Packets) in Reduced Dimensionality</b> | <b>357</b> |
|           | <i>Sebastian Reiter, Daniel Keefer, and Regina de Vivie-Riedle</i>     |            |
| 11.1      | Introduction                                                           | 357        |
| 11.2      | Fundamentals of Molecular Quantum Dynamics                             | 358        |
| 11.2.1    | Wave Packet Dynamics                                                   | 358        |

|          |                                                                           |     |
|----------|---------------------------------------------------------------------------|-----|
| 11.2.2   | Time-Propagator Schemes                                                   | 360 |
| 11.2.3   | Excited State Wave Packet Dynamics                                        | 362 |
| 11.2.4   | Surfaces and Coupling Elements in Reactive Coordinates                    | 362 |
| 11.3     | Choice of Dynamical Coordinates and Hamiltonian in Reduced Dimensionality | 364 |
| 11.3.1   | Manual Selection by Chemical Intuition                                    | 364 |
| 11.3.2   | The G-Matrix Formalism                                                    | 365 |
| 11.3.2.1 | General Setup                                                             | 366 |
| 11.3.2.2 | Practical Computation of the G-Matrix Elements                            | 367 |
| 11.3.2.3 | Photorelaxation of Uracil in Linear Reactive Coordinates                  | 367 |
| 11.3.3   | Automatic Generation of Linear Coordinates                                | 369 |
| 11.3.3.1 | IRC Based Approach                                                        | 369 |
| 11.3.3.2 | Trajectory-Based Approach                                                 | 371 |
| 11.3.3.3 | Comparison of Both Techniques for Linear Subspaces                        | 372 |
| 11.3.4   | Automatic Generation of Non-Linear Coordinates                            | 374 |
| 11.4     | Summary and Further Remarks                                               | 378 |
|          | References                                                                | 379 |

## 12 Multi-Configuration Time-Dependent Hartree Methods: From Quantum to Semiclassical and Quantum-Classical 383

*M. Bonfanti, G. A. Worth, and I. Burghardt*

|          |                                                         |     |
|----------|---------------------------------------------------------|-----|
| 12.1     | Introduction                                            | 383 |
| 12.2     | Time-Dependent Variational Principle and MCTDH          | 385 |
| 12.2.1   | Variational Principle and Tangent Space Projections     | 385 |
| 12.2.2   | MCTDH: Variational Multi-Configurational Wave Functions | 386 |
| 12.2.2.1 | MCTDH Wave Function Ansatz                              | 386 |
| 12.2.2.2 | MCTDH Equations of Motion                               | 388 |
| 12.2.3   | ML-MCTDH: Hierarchical Representations                  | 389 |
| 12.3     | Gaussian-Based MCTDH                                    | 390 |
| 12.3.1   | G-MCTDH and vMCG                                        | 390 |
| 12.3.1.1 | G-MCTDH Wave Function Ansatz                            | 391 |
| 12.3.1.2 | G-MCTDH Equations of Motion                             | 392 |
| 12.3.1.3 | vMCG Equations of Motion                                | 393 |
| 12.3.2   | 2L-GMCTDH                                               | 394 |
| 12.3.2.1 | Wave Function Ansatz                                    | 394 |
| 12.3.2.2 | Equations of Motion                                     | 395 |
| 12.4     | Quantum-Classical Multi-Configurational Approaches      | 396 |
| 12.4.1   | Quantum-Classical Limit of G-MCTDH                      | 396 |
| 12.4.2   | Quantum-Classical Scheme with Finite-Width Wave Packets | 398 |
| 12.4.3   | Related Approaches                                      | 399 |
| 12.5     | How to use MCTDH & Co                                   | 399 |
| 12.6     | Synopsis and Application to Donor-Acceptor Complex      | 400 |
| 12.6.1   | Hamiltonian, Spectral Densities, and Potential Surfaces | 400 |
| 12.6.2   | Ultrafast Coherent Charge Transfer Dynamics             | 402 |
| 12.6.3   | Comparison of Methods                                   | 403 |
| 12.7     | Conclusions and Outlook                                 | 405 |
|          | Acknowledgments                                         | 406 |
|          | References                                              | 406 |

|           |                                                                                                |            |
|-----------|------------------------------------------------------------------------------------------------|------------|
| <b>13</b> | <b>Gaussian Wave Packets and the DD-vMCG Approach</b>                                          | <b>413</b> |
|           | <i>Graham A. Worth and Benjamin Lasorne</i>                                                    |            |
| 13.1      | Historical Background                                                                          | 413        |
| 13.2      | Basic Theory                                                                                   | 415        |
| 13.2.1    | Gaussian Wave Packets                                                                          | 415        |
| 13.2.2    | General Equations of Motion                                                                    | 418        |
| 13.2.2.1  | Coefficients and Parameters                                                                    | 418        |
| 13.2.2.2  | CX-Formalism                                                                                   | 419        |
| 13.2.2.3  | Nuclear and Electronic Degrees of Freedom                                                      | 420        |
| 13.2.3    | Variational Multi-Configurational Gaussian Approach                                            | 422        |
| 13.3      | Example Calculations                                                                           | 424        |
| 13.4      | Tunneling Dynamics: Salicylaldehyde                                                            | 425        |
| 13.5      | Non-Adiabatic Dynamics: The Butatriene Cation                                                  | 426        |
| 13.6      | Direct Non-Adiabatic Dynamics: Formamide                                                       | 428        |
| 13.7      | Summary                                                                                        | 431        |
| 13.8      | Practical Implementation                                                                       | 431        |
|           | Acknowledgments                                                                                | 431        |
|           | References                                                                                     | 431        |
| <b>14</b> | <b>Full and <i>Ab Initio</i> Multiple Spawning</b>                                             | <b>435</b> |
|           | <i>Basile F. E. Curchod</i>                                                                    |            |
| 14.1      | Introduction                                                                                   | 435        |
| 14.2      | Time-Dependent Molecular Schrödinger Equation in a Gaussian Basis                              | 436        |
| 14.2.1    | Central Equations of Motion                                                                    | 436        |
| 14.2.2    | Dynamics of the Trajectory Basis Functions                                                     | 439        |
| 14.3      | Full Multiple Spawning                                                                         | 440        |
| 14.3.1    | Full Multiple Spawning Equations                                                               | 440        |
| 14.3.2    | Spawning Algorithm                                                                             | 442        |
| 14.4      | Extending Full Multiple Spawning                                                               | 443        |
| 14.4.1    | External Field in Full Multiple Spawning                                                       | 444        |
| 14.4.2    | Spin-Orbit Coupling in Full Multiple Spawning                                                  | 445        |
| 14.5      | <i>Ab Initio</i> Multiple Spawning                                                             | 447        |
| 14.5.1    | From Full- to <i>Ab Initio</i> Multiple Spawning                                               | 447        |
| 14.5.2    | Testing the Approximations of <i>Ab Initio</i> Multiple Spawning                               | 449        |
| 14.5.3    | On-the-Fly <i>Ab Initio</i> Multiple Spawning                                                  | 450        |
| 14.5.4    | <i>Ab Initio</i> Multiple Spawning versus Trajectory Surface Hopping                           | 451        |
| 14.6      | Dissecting an <i>Ab Initio</i> Multiple Spawning Dynamics                                      | 454        |
| 14.6.1    | The Different Steps of an <i>Ab Initio</i> Multiple Spawning Dynamics                          | 454        |
| 14.6.2    | Example of <i>Ab Initio</i> Multiple Spawning Dynamics – the Photo-Chemistry of Cyclohexadiene | 455        |
| 14.7      | <i>In Silico</i> Photo-Chemistry with <i>Ab Initio</i> Multiple Spawning                       | 459        |
| 14.8      | Summary                                                                                        | 462        |
|           | References                                                                                     | 463        |
| <b>15</b> | <b>Ehrenfest Methods for Electron and Nuclear Dynamics</b>                                     | <b>469</b> |
|           | <i>Adam Kirrander and Morgane Vacher</i>                                                       |            |
| 15.1      | Introduction                                                                                   | 469        |
| 15.2      | Theory of the (Simple) Ehrenfest Method                                                        | 470        |

|           |                                                                                                   |            |
|-----------|---------------------------------------------------------------------------------------------------|------------|
| 15.2.1    | Wave Function Ansatz                                                                              | 471        |
| 15.2.2    | Equations of Motion                                                                               | 472        |
| 15.3      | Theory of the Multi-Configurational Ehrenfest Method                                              | 474        |
| 15.3.1    | Wave Function Ansatz                                                                              | 474        |
| 15.3.2    | Equations of Motion                                                                               | 476        |
| 15.3.3    | Computational Aspects                                                                             | 479        |
| 15.4      | Applications                                                                                      | 480        |
| 15.4.1    | Coupled Electron and Nuclear Dynamics Upon Sudden Ionization                                      | 481        |
| 15.4.2    | Ultrafast Scattering as a Probe of Nuclear Dynamics                                               | 485        |
| 15.5      | Conclusion                                                                                        | 490        |
|           | References                                                                                        | 491        |
| <b>16</b> | <b>Surface Hopping Molecular Dynamics</b>                                                         | <b>499</b> |
|           | <i>Sebastian Mai, Philipp Marquetand, and Leticia González</i>                                    |            |
| 16.1      | Introduction                                                                                      | 499        |
| 16.2      | Basics of Surface Hopping                                                                         | 500        |
| 16.2.1    | Advantages and Disadvantages                                                                      | 500        |
| 16.2.2    | General Algorithm                                                                                 | 501        |
| 16.3      | Surface Hopping Ingredients                                                                       | 503        |
| 16.3.1    | Nuclear Motion                                                                                    | 503        |
| 16.3.2    | Wave Function Propagation                                                                         | 504        |
| 16.3.3    | Decoherence                                                                                       | 505        |
| 16.3.4    | Surface Hopping Algorithm                                                                         | 507        |
| 16.3.5    | Kinetic Energy Adjustment and Frustrated Hops                                                     | 509        |
| 16.3.6    | Coupling Terms and Representations                                                                | 511        |
| 16.4      | Practical Remarks                                                                                 | 513        |
| 16.4.1    | Choice of the Electronic Structure Method                                                         | 513        |
| 16.4.2    | Initial Conditions                                                                                | 516        |
| 16.4.3    | Example Application and Trajectory Analysis                                                       | 518        |
| 16.5      | Popular Implementations                                                                           | 521        |
| 16.6      | Conclusion and Outlook                                                                            | 522        |
|           | Acknowledgments                                                                                   | 522        |
|           | References                                                                                        | 522        |
| <b>17</b> | <b>Exact Factorization of the Electron–Nuclear Wave Function: Theory and Applications</b>         | <b>531</b> |
|           | <i>Federica Agostini and E. K. U. Gross</i>                                                       |            |
| 17.1      | Introduction                                                                                      | 531        |
| 17.2      | The Time-Dependent Molecular Problem in the Exact-Factorization Formulation                       | 533        |
| 17.2.1    | Wave Function Ansatz                                                                              | 533        |
| 17.2.2    | Equations of Motion                                                                               | 535        |
| 17.3      | The Born–Oppenheimer Framework and the Exact Factorization                                        | 536        |
| 17.3.1    | One-Dimensional Case: Time-Dependent Potential Energy Surface                                     | 538        |
| 17.3.2    | Two-Dimensional Case: Time-Dependent Potential Energy Surface and Time-Dependent Vector Potential | 542        |
| 17.4      | Trajectory-Based Solution of the Exact-Factorization Equations                                    | 545        |
| 17.4.1    | CT-MQC: The Approximations                                                                        | 546        |
| 17.4.2    | CT-MQC: Photo-Induced Ring Opening in Oxirane                                                     | 549        |

|           |                                                                                           |            |
|-----------|-------------------------------------------------------------------------------------------|------------|
| 17.4.3    | CT-MQC: The Algorithm                                                                     | 551        |
| 17.5      | The Molecular Berry Phase                                                                 | 553        |
| 17.6      | Conclusions                                                                               | 556        |
|           | Acknowledgments                                                                           | 556        |
|           | References                                                                                | 556        |
| <b>18</b> | <b>Bohmian Approaches to Non-Adiabatic Molecular Dynamics</b>                             | <b>563</b> |
|           | <i>Guillermo Albareda and Ivano Tavernelli</i>                                            |            |
| 18.1      | Introduction                                                                              | 563        |
| 18.2      | A Practical Overview of Bohmian Mechanics                                                 | 565        |
| 18.2.1    | The Postulates                                                                            | 565        |
| 18.2.2    | Computation of Bohmian Trajectories                                                       | 566        |
| 18.2.2.1  | Trajectories from the Schrödinger Equation                                                | 566        |
| 18.2.2.2  | Trajectories from the Hamilton–Jacobi Equation                                            | 567        |
| 18.2.2.3  | Trajectories from a Complex Action                                                        | 568        |
| 18.2.3    | Computation of Expectation Values                                                         | 569        |
| 18.3      | The Born–Huang Picture of Molecular Dynamics                                              | 569        |
| 18.3.1    | The Molecular Schrödinger Equation in Position Space                                      | 569        |
| 18.3.2    | Schrödinger Equation in the Born–Huang Basis                                              | 570        |
| 18.3.2.1  | The Born–Oppenheimer Approximation: The Adiabatic Case                                    | 571        |
| 18.3.2.2  | Non-Adiabatic Dynamics                                                                    | 572        |
| 18.4      | BH-Based Approaches                                                                       | 573        |
| 18.4.1    | The Non-Adiabatic Bohmian Dynamics Equations (NABDY)                                      | 573        |
| 18.4.2    | Implementation in Molecular Dynamics: The Adiabatic Case                                  | 575        |
| 18.4.3    | The Approximate Quantum Potential Approach                                                | 577        |
| 18.5      | Non-BH Approaches                                                                         | 579        |
| 18.5.1    | The Conditional Wave Function Approach                                                    | 579        |
| 18.5.1.1  | Hermitian Conditional Wave Function Approach                                              | 581        |
| 18.5.2    | The Interacting Conditional Wave Function Approach                                        | 582        |
| 18.5.3    | Time-Dependent Quantum Monte Carlo                                                        | 585        |
| 18.6      | Conclusions                                                                               | 588        |
|           | References                                                                                | 589        |
| <b>19</b> | <b>Semiclassical Molecular Dynamics for Spectroscopic Calculations</b>                    | <b>595</b> |
|           | <i>Riccardo Conte and Michele Ceotto</i>                                                  |            |
| 19.1      | Introduction                                                                              | 595        |
| 19.2      | From Feynman’s Path Integral to van Vleck’s Semiclassical Propagator                      | 598        |
| 19.3      | The Semiclassical Initial Value Representation and the Heller–Herman–Kluk–Kay Formulation | 601        |
| 19.4      | A Derivation of the Heller–Herman–Kluk–Kay Propagator                                     | 603        |
| 19.5      | The Time-Averaging Filter                                                                 | 604        |
| 19.6      | The Multiple Coherent States SCIVR                                                        | 606        |
| 19.7      | The “Divide-and-Conquer” SCIVR                                                            | 610        |
| 19.8      | Mixed SCIVR Dynamics: Towards Semiclassical Spectroscopy in Condensed Phase               | 615        |
| 19.9      | Semiclassical Spectroscopy Workflow                                                       | 618        |
| 19.10     | A Taste of Semiclassical Spectroscopy                                                     | 619        |

|       |                         |     |
|-------|-------------------------|-----|
| 19.11 | Summary and Conclusions | 622 |
|       | Acknowledgments         | 624 |
|       | Bibliography            | 624 |

## **20 Path-Integral Approaches to Non-Adiabatic Dynamics 629**

*Maximilian A. C. Saller, Johan E. Runeson, and Jeremy O. Richardson*

|        |                                                  |     |
|--------|--------------------------------------------------|-----|
| 20.1   | Introduction                                     | 629 |
| 20.2   | Semiclassical Theory                             | 631 |
| 20.2.1 | Mapping Approach                                 | 631 |
| 20.2.2 | Linearized Semiclassical Dynamics                | 632 |
| 20.3   | Non-Equilibrium Dynamics                         | 633 |
| 20.3.1 | Spin-Boson Systems                               | 634 |
| 20.3.2 | Non-Equilibrium Correlation Functions            | 636 |
| 20.4   | Non-Adiabatic Path-Integral Theory               | 640 |
| 20.4.1 | Mean-Field Path-Integral Sampling                | 640 |
| 20.4.2 | Non-Adiabatic Ring-Polymer Molecular Dynamics    | 641 |
| 20.4.3 | Alleviation of the Negative Sign                 | 644 |
| 20.4.4 | Practical Implementation of Monte Carlo Sampling | 644 |
| 20.5   | Equilibrium Correlation Functions                | 646 |
| 20.6   | Conclusions                                      | 648 |
|        | Acknowledgments                                  | 649 |
|        | References                                       | 649 |

## **Index 655**