

# Quantum Chemistry and Dynamics of Excited States

Methods and Applications

*Edited by*

*Leticia González*

Institute of Theoretical Chemistry, Faculty of Chemistry  
University of Vienna  
Austria

*Roland Lindh*

Department of Chemistry – BMC  
Uppsala University  
Sweden

**WILEY**

## 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
<b>3</b>	<b>Multi-Configurational Density Functional Theory: Progress and Challenges</b>	<b>47</b>
	<i>Erik Donovan Hedegård</i>	
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
<b>4</b>	<b>Equation-of-Motion Coupled-Cluster Models</b>	<b>77</b>
	<i>Monika Musiał</i>	
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
<b>5</b>	<b>The Algebraic-Diagrammatic Construction Scheme for the Polarization Propagator</b>	<b>109</b>
	<i>Andreas Dreuw</i>	
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
<b>6</b>	<b>Foundation of Multi-Configurational Quantum Chemistry</b>	<b>133</b>
	<i>Giovanni Li Manni, Kai Guther, Dongxia Ma, and Werner Dobrautz</i>	
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 <sub>2</sub> 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
<b>7</b>	<b>The Density Matrix Renormalization Group for Strong Correlation in Ground and Excited States</b>	<b>205</b>
	<i>Leon Freitag and Markus Reiher</i>	
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
<b>8</b>	<b>Excited-State Calculations with Quantum Monte Carlo</b>	<b>247</b>
	<i>Jonas Feldt and Claudia Filippi</i>	
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
<b>9</b>	<b>Multi-Reference Configuration Interaction</b>	<b>277</b>
	<i>Felix Plasser and Hans Lischka</i>	
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
	<b>Part II Nuclear Dynamics</b>	<b>355</b>
<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 <i>G</i> -Matrix Formalism	365
11.3.2.1	General Setup	366
11.3.2.2	Practical Computation of the <i>G</i> -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
<b>12</b>	<b>Multi-Configuration Time-Dependent Hartree Methods: From Quantum to Semiclassical and Quantum-Classical</b>	<b>383</b>
	<i>M. Bonfanti, G. A. Worth, and I. Burghardt</i>	
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

- 13 Gaussian Wave Packets and the DD-vMCG Approach 413**  
*Graham A. Worth and Benjamin Lasorne*
- 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
- 14 Full and *Ab Initio* Multiple Spawning 435**  
*Basile F. E. Curchod*
- 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 *Ab Initio* Multiple Spawning 447
    - 14.5.1 From Full- to *Ab Initio* Multiple Spawning 447
    - 14.5.2 Testing the Approximations of *Ab Initio* Multiple Spawning 449
    - 14.5.3 On-the-Fly *Ab Initio* Multiple Spawning 450
    - 14.5.4 *Ab Initio* Multiple Spawning versus Trajectory Surface Hopping 451
  - 14.6 Dissecting an *Ab Initio* Multiple Spawning Dynamics 454
    - 14.6.1 The Different Steps of an *Ab Initio* Multiple Spawning Dynamics 454
    - 14.6.2 Example of *Ab Initio* Multiple Spawning Dynamics – the Photo-Chemistry of Cyclohexadiene 455
  - 14.7 *In Silico* Photo-Chemistry with *Ab Initio* Multiple Spawning 459
  - 14.8 Summary 462
    - References 463
- 15 Ehrenfest Methods for Electron and Nuclear Dynamics 469**  
*Adam Kirrander and Morgane Vacher*
- 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
<b>20</b>	<b>Path-Integral Approaches to Non-Adiabatic Dynamics</b>	<b>629</b>
	<i>Maximilian A. C. Saller, Johan E. Runeson, and Jeremy O. Richardson</i>	
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
	<b>Index</b>	<b>655</b>