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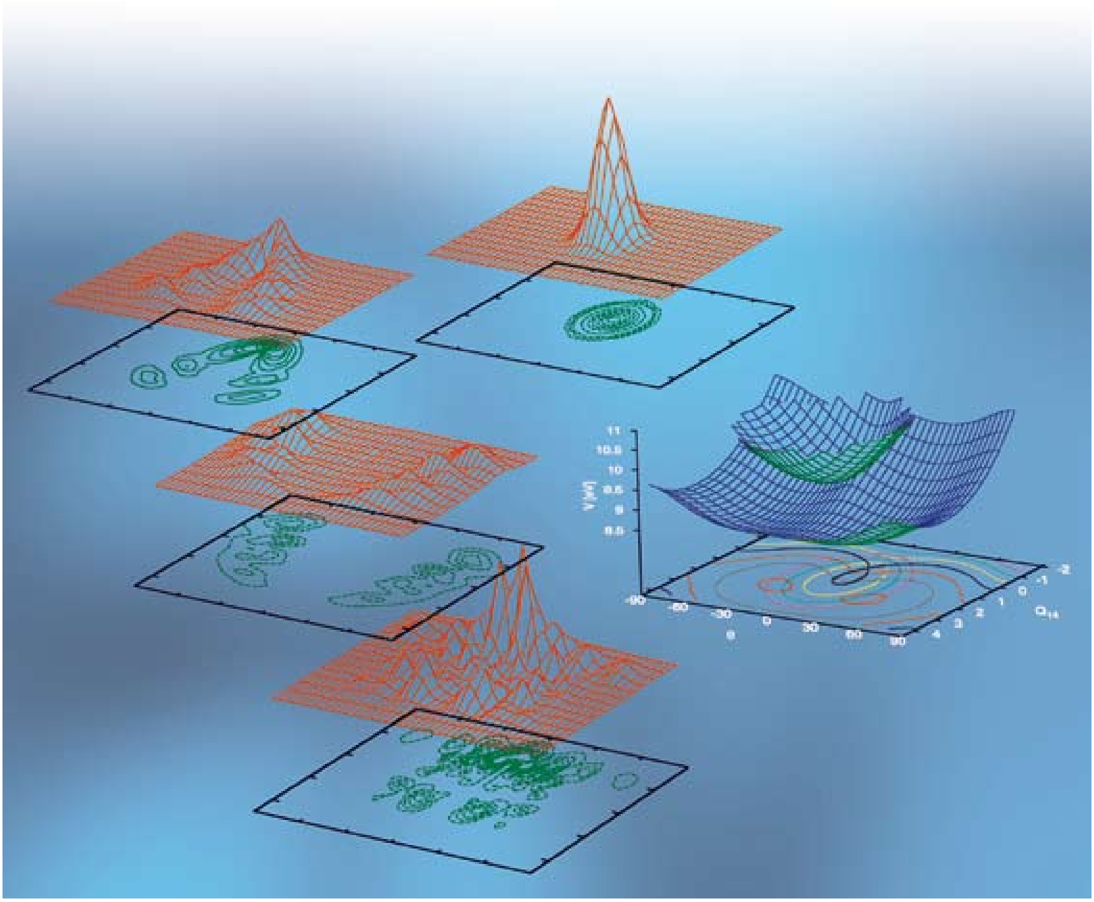
Multidimensional Quantum Dynamics

MCTDH Theory and Applications



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Multidimensional Quantum Dynamics: MCTDH Theory and Applications

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Contents

Part 1 **Introduction** *11*

1 **Introduction** *3*
The editors

Part 2 **Theory** *11*
The editors

2 **The road to MCTDH** *13*
2.1 The Standard Method *14*
2.2 Time Dependent Hartree *15*

3 **Basic MCTDH Theory** *19*
3.1 Wavefunction Ansatz and Equations of Motion *19*
3.2 The constraint operator *22*
3.3 Efficiency and Memory Requirements *24*
3.4 Multi-State Calculations *29*
3.5 Parameterized basis functions: G-MCTDH *30*

4 **Integration Schemes** *33*
4.1 The variable mean-field (VMF) integration scheme *33*
4.2 A simple constant mean-field (CMF) integration scheme *33*
4.3 Why CMF works *35*
4.4 Second-order CMF scheme *36*

5 **Preparation of the initial wavepacket** *39*
5.1 Initial wavepacket as Hartree product *39*
5.2 Eigenstates and operated wavefunctions *40*

6 **Analysis of the propagated wave packet** *41*
6.1 Run-time analysis of accuracy *41*

6.2 Spectra *43*
6.2.1 Photoabsorption Spectra *43*
6.2.2 Eigenvalues and Filter Diagonalization *46*
6.2.3 Time-Resolved Spectra *48*
6.3 Optimal Control *50*
6.4 State Populations *50*
6.5 Reaction Probabilities *52*

7 MCTDH for density operator *57*
7.1 Wavefunctions and density operators *57*
7.2 Type I density operators *58*
7.3 Type II density operators *60*
7.4 Properties of MCTDH density operator propagation *61*

8 Computing eigenstates by relaxation and improved relaxation *63*
8.1 Relaxation *63*
8.2 Improved relaxation *63*
8.3 Technical Details *66*

9 Iterative diagonalization of operators *69*
9.1 Operators defined by propagation *69*
9.2 A modified Lanczos scheme *70*
9.3 The state averaged MCTDH approach *71*

10 Correlation Discrete Variable Representation (CDVR) *73*
10.1 Introduction *73*
10.2 Time-dependent DVR *74*
10.3 Correlation DVR *76*
10.4 Symmetry Adapted CDVR *78*
10.5 Multidimensional CDVR *78*

11 Potential representations (POTFIT) *81*
11.1 Expansion in product basis sets *81*
11.2 Optimizing the coefficients *82*
11.3 Optimizing the basis *83*
11.4 The POTFIT algorithm *84*
11.5 Contraction over one particle *86*
11.6 Separable weights *86*
11.7 Non-separable weights *87*
11.8 Computational effort and memory request *88*

12 Kinetic energy operators *91*

12.1 Introduction *91*
12.2 Vector parameterization and properties of angular momenta *92*
12.2.1 Examples *93*
12.2.2 General formulation: *95*
12.3 A general expression of the KEO in standard polyspherical coordinates *98*
12.3.1 General expression: *98*
12.4 Examples *105*
12.4.1 Scattering systems: H_2+H_2 *106*
12.4.2 Semi-rigid molecules: HFCO *107*
12.5 Extensions: *108*
12.5.1 Separation into subsystems *108*
12.5.2 Constrained operators: *109*

Part 3 Extension to new areas *111*

13 Direct dynamics with quantum nuclei *113*
Benjamin Lasorne and Graham A. Worth
13.1 Introduction *113*
13.2 Variational multi-configurational Gaussian wavepackets *115*
13.2.1 Gaussian wavepacket *ansatz* *115*
13.2.2 Equations of motion *117*
13.2.3 Integration scheme *119*
13.2.4 Initial wavepacket *121*
13.2.5 Direct dynamics implementation *122*
13.3 Applications *124*
13.4 Conclusions *128*

14 Multilayer formulation of the multiconfiguration time-dependent Hartree theory *131*
Haobin Wang and Michael Thoss
14.1 Introduction *131*
14.2 From Conventional Wave Packet Propagation to ML-MCTDH Theory: A Variational Perspective *132*
14.2.1 Conventional Approach Based on Time-Independent Configurations *132*
14.2.2 The Multiconfiguration Time-Dependent Hartree Method *134*
14.2.3 The Multilayer Formulation of the MCTDH Theory *137*
14.3 Concluding remarks *145*

15 Shared Memory Parallelization of the Multi-Configuration Time-Dependent Hartree Method *149*

Michael Brill and Hans-Dieter Meyer
15.1 Motivation *149*
15.2 Shared memory parallelization of MCTDH *149*
15.2.1 Equations of motion and runtime distribution *150*
15.2.2 Parallelization of the MCTDH coefficients propagation *151*
15.2.3 Parallelization of the mean-field computation *152*
15.2.4 Parallelization of the SPFs propagation *153*
15.2.5 Parallelization scheme *153*
15.2.6 Load balancing and memory requirements *154*
15.3 Results and Conclusion *155*
15.3.1 Benchmark systems *155*
15.3.2 Amdahl's law *157*
15.3.3 Results *157*
15.3.4 Conclusion and Outlook *159*

16 Strongly driven few-fermion systems - MCTDHF *161*
Gerald Jordan and Armin Scrinzi
16.1 Equations of motion for indistinguishable particles *161*
16.1.1 Model system: laser-driven few-electron systems *162*
16.1.2 Spin *163*
16.2 Computation of operators *164*
16.2.1 $\mathcal{K}$ and mean field operators *164*
16.2.2 Spatial discretization *165*
16.2.3 One-particle operators *168*
16.2.4 Two-particle operators *169*
16.2.4.1 Representation of H on a coarse grid *169*
16.2.4.2 H-matrix representation *170*
16.3 Parallelization *171*
16.3.1 Application of the inverse overlap matrix $\mathcal{S}^{-1}$ *172*
16.3.2 Parallel computation of mean fields *173*
16.3.3 Dynamic load balancing *174*
16.4 Observables and transformations *174*
16.4.1 Orbital transformations *174*
16.4.2 Projections onto multi-particle states *175*
16.4.3 One- and two-particle expectation values *175*
16.4.4 All-particle observables *176*
16.4.5 Spectra *177*
16.5 Applications *178*
16.5.1 Ionization of linear molecules *178*
16.5.1.1 High harmonic spectra of molecules *179*
16.5.2 Cold fermionic atoms *182*

17 The multi-configurational time-dependent Hartree method for identical particles and mixtures thereof *185*
Ofir E. Alon, Alexej I. Streltsov, and Lorenz S. Cederbaum
17.1 Preliminary remarks *185*
17.2 Bosons or fermions: Unifying MCTDHB and MCTDHF *186*
17.2.1 Basic Ingredients *186*
17.2.2 Equations of motion with reduced density matrices *189*
17.3 Bose-Bose, Fermi-Fermi and Bose-Fermi mixtures: MCTDH-BB, MCTDH-FF, and MCTDH-BF *192*
17.3.1 Ingredients for mixtures *192*
17.3.2 Equations of motion with intra- and inter-species reduced density matrices *193*
17.4 Higher-order forces and reduced density matrices: Three-body interactions *196*
17.4.1 Ingredients for three-body interactions *196*
17.4.2 Equations of motion with three-body reduced density matrix *197*
17.5 Illustrative numerical examples for bosons: MCTDHB *198*
17.6 Discussion and perspectives *202*

Part 4 Applications ***207***

18 Multi-dimensional non-adiabatic dynamics *209*
Graham A. Worth, Horst Köppel, Etienne Gindensperger and Lorenz S. Cederbaum
18.1 Introduction *209*
18.2 The Vibronic Coupling Hamiltonian *210*
18.3 Combining the vibronic coupling model with MCTDH *213*
18.4 Examples *217*
18.4.1 Allene cation *217*
18.4.2 $Cr(CO)_5$ *219*
18.4.3 Benzene cation *221*
18.5 Effective Modes *223*
18.6 Summary *226*

19 MCTDH Calculation of Flux Correlation Functions: Rates and Reaction Probabilities for Polyatomic Chemical Reactions. *229*
Fermín Huarte-Larrañaga and Uwe Manthe
19.1 Introduction *229*
19.2 Flux correlation functions and the quantum transition state concept *231*
19.2.1 Thermal rates from flux correlation functions *231*

19.2.2 The thermal flux operator: properties and physical interpretation *233*
19.2.3 Calculation of N(E) and k(T) *235*
19.3 Rate constant calculations *237*
19.3.1 Propagating all F_T-eigenstates *237*
19.3.2 Statistical Sampling *237*
19.4 Application to polyatomic reactions *239*
19.5 The effect of rotation-vibration coupling on rate constants *242*
19.6 Concluding remarks and outlook *244*

20 Reactive and non-reactive scattering of molecules from surfaces *247*
Geert-Jan Kroes, Rob van Harrevelt, and Cédric Crespos
20.1 Introduction *247*
20.2 Theory *249*
20.3 Applications of the MCTDH method to molecule-surface scatterinag *252*
20.3.1 Rotationally and diffractionally inelastic scattering *252*
20.3.2 Dissociative chemisorption *253*
20.3.2.1 Dissociative chemisorption of H_2 on metal surfaces *253*
20.3.2.2 Dissociative chemisorption of N_2 on metal surfaces *259*
20.3.2.3 Dissociative chemisorption of CH_4 on Ni(111) *260*
20.3.3 Photodissociation of molecules on insulator surfaces *261*
20.3.4 Molecule-surface dynamics with dissipation *263*
20.4 Summary and outlook *266*

21 Intramolecular vibrational-energy redistribution and infrared spectroscopy *271*
Fabien Gatti and Christophe Iung
21.1 Introduction *271*
21.2 Local mode excitation of the CH stretch in fluoroform and in toluene *273*
21.3 Study of highly excited states in HFCO and DFCO *275*
21.4 Selective population of vibrational levels in H_2CS in the presence of an external field *281*
21.5 Cis-trans isomerization of HONO *283*
21.6 Conclusion *286*

22 Open System Quantum Dynamics with Discretized Environments *289*
Mathias Nest
22.1 Introduction *289*

22.2 The System-Bath Ansatz *291*
22.3 Static and Dynamic Effects of the Bath *293*
22.3.1 Static Effect: Lamb Shift *293*
22.3.2 Small Amplitude Motion *294*
22.3.3 Inelastic Surface Scattering: Adsorption *296*
22.4 Finite Temperatures *298*
22.4.1 Random Phase Wave Functions *298*
22.4.2 Inelastic Surface Scattering: Adsorption *299*
22.4.3 Initial Slip and Coupling to Photons *302*
22.5 Derivatives of MCTDH *304*
22.6 Summary and Outlook *305*

23 Proton transfer and hydrated proton in small water systems *307*
Oriol Vendrell and Hans-Dieter Meyer
23.1 Introduction *307*
23.2 Proton transfer along a chain of hydrogen-bonded water molecules *308*
23.2.1 Model for the simulation of a proton-wire *309*
23.2.2 Dynamics of a proton-wire *310*
23.3 Dynamics and Vibrational Spectroscopy of the Zundel cation *313*
23.3.1 Setup of the Hamiltonian Operator *313*
23.3.2 Representation of the Potential Energy Surface for $H_5O_2^+$ *316*
23.3.3 Ground Vibrational State and Eigenstates in the Low Frequency Domain *319*
23.3.4 Infrared Absorption Spectrum *322*
23.3.5 Analysis of the middle spectral region and dynamics of the cluster *325*
23.4 Conclusion *328*

24 Laser Driven Dynamics and Quantum Control of Molecular Wave Packets *329*
Oliver Kühn
24.1 Introduction *329*
24.2 Theory *330*
24.3 Applications *332*
24.3.1 Vibrational Ladder Climbing in a Heme-CO Model *332*
24.3.2 Hydrogen-bond Dynamics *339*
24.3.3 Predissociation Dynamics of Matrix-isolated Diatomics *342*
24.4 Summary *346*

25 Polyatomic dynamics of dissociative electron attachment to water using MCTDH *349*

Daniel J. Haxton, Thomas N. Rescigno, and C. William McCurdy
25.1 Dissociative electron attachment to water *351*
25.2 Time-dependent treatment of dissociative attachment within the Local Complex Potential model *352*
25.3 Coordinate systems *354*
25.4 Hamiltonians *356*
25.5 Choice of primitive basis and representation of the Hamiltonians *357*
25.6 Representation of potential energy functions using potfit *357*
25.7 Single-particle function (SPF) expansion and mode combinations *358*
25.8 Propagation and natural orbitals *359*
25.9 Analysis of flux to calculate cross sections *359*
25.9.1 Two-body breakup *360*
25.9.2 Three-body breakup *363*
25.10 Conclusion *366*
25.11 Acknowledgments *366*

26 Ultracold few-boson systems in traps *369*
Sascha Zöllner, Hans-Dieter Meyer, and Peter Schmelcher
26.1 Model *370*
26.2 Ground state: Crossover from weak to strong interactions *371*
26.3 Quantum dynamics: Correlated tunneling in double wells *375*

27 References *381*
Bibliography *381*

Part 1 Introduction

1
Introduction

The editors

Quantum dynamics simulations are now established as an essential tool for understanding experiments probing the nature of matter at the molecular level and on fundamental time-scales. This is a relatively recent development and for many years the methods of choice were based on time-independent calculations, describing a system in terms of its eigenfunctions and eigenvalues. This book is about the multi-configuration time-dependent Hartree method, commonly known by its acronym MCTDH, a method which has played a significant role in the upsurge of interest in time-dependent treatments by extending the range of applicability of what are often called wavepacket dynamics simulations.

The book will cover the theory of the method, highlighting the features that enable it to treat systems not accessible to other methods. Details in particular will be given on the implementation strategy required. Chapters will then detail extensions of the basic method to show how the theory provides a framework to treat systems outside the original aims and to combine different methods. In the final section examples of calculations are given. As the method is completely general, and has been applied to a range of problems, the result is a snapshot of the state-of-the-art in the study of molecular dynamics.

To describe a (non-relativistic) molecular system one needs to solve the Schrödinger equation, which in its time-dependent form reads

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi \quad . \tag{1.1}$$

Unfortunately this equation is impossible to solve for more than 2 particles, i.e the hydrogen atom and the field of theoretical chemistry is dominated by developments of methods, numerical and approximate, that provide solutions that can be used to treat atoms and molecules.

A key development in making this problem tractable is the separation of nuclear and electronic motion through the Born-Oppenheimer approximation [1–3]. This allows us to imagine our molecular system as a set of nuclei represented as point masses moving over a potential energy surface (PES) provided by the electrons: the electrons follow the much heavier nuclei, adjusting instantaneously as the nuclei change conformation. This approximation works extremely well. It does, however, break down in certain situations when two electronic configurations strongly mix with dependence on the nuclear conformation [4]. The nuclei then must be imagined as moving in a manifold of coupled electronic states, each associated with a potential energy surface.

The PES are obtained by solving the time-independent form of the Schrödinger equation applied only to the electrons and treating the nuclei as static point charges. This is the field of electronic structure theory, or quantum chemistry as it is often called. Quantum chemistry is a mature field of research with a number of general-purpose computer programs available such as Gaussian [5] and Molpro [6]. These programs are able to solve the electronic structure problem for a nuclear configuration using a range of methods. They can also provide an analysis of molecular properties at that molecular geometry.

Much of chemistry can be described by an analysis of the critical points on the PES: minima represent stable nuclear configurations and saddle-points transition states connecting them. In the field of photochemistry features such as conical intersections and avoided crossings where neighboring states interact are also important. The nuclear geometries and relative energies of these points can then be used to build up a picture of a reaction in molecular terms. Local analysis of these critical points can further provide information. For example frequencies related to vibrational spectra can be calculated from the Hessian matrix. These can all be provided by the quantum chemistry programs.

The field of molecular dynamics studies the motion between these critical points. This is chemistry at its fundamental level: how do nuclei move during molecular collisions and reactions, or in response to the absorption of a photon.

Molecular quantum dynamics, aiming to solve the time-dependent Schrödinger equation, is difficult and numerically demanding. Comparing it to quantum chemistry one may wonder why quantum dynamics cannot solve problems of similar size. Accurate computations of the electronic structure of molecules with more than 100 electrons are feasible whereas accurate dynamic calculations including 100 atoms are not (except for special simple cases).

One difference is that quantum chemistry is characterized by low quantum numbers. One is usually interested in the electronic ground state, or in the two or three lowest excited states. The molecular orbitals have a simple smooth form and can be well represented by Gaussian basis sets. In quantum dynamics, however, the wavefunction is much more structured and may contain highly oscillatory terms. Moreover, the density of states is rather high. There may be hundreds of eigenstates lying below a fundamental C-H or O-H stretch of a small polyatomic molecule (4 or 5 atoms, say). This high density of states, which is a consequence of the fact that nuclear masses are much larger than the electron mass, is one of the main sources of difficulties.

A second is that quantum chemistry is governed by the Coulomb potential, a rather structureless two-body interaction. Quantum dynamics, on the other hand, has to cope with complicated many-body potentials, which are not general but specific for the problem under investigation. The strong repulsion suffered by atoms which come close to each other may lead to a very strongly correlated motion. These differences explain why the techniques used in quantum chemistry and quantum dynamics are often similar in spirit but very different in detail.

The development of quantum dynamics simulations has been driven by research probing the fundamental properties of molecules. Historically, the first field of importance was scattering experiments using molecular beams. To study elementary reactions it is necessary to enable molecules to collide with known initial-states under controlled conditions and measure the products of the collision [7]. One way to achieve this experimentally is in scattering experiments using beams of molecules. In particular, crossed-molecular beam experiments, pioneered by Lee, Herschbach, Toennies and others, have provided a wealth of data in this field.

More recently, time-resolved spectroscopy driven by the development of pulsed lasers has also become important. The work of Zewail was key in the development of techniques to produce and apply pulses of the order of femtosecond duration [8]. This allows molecules to be followed on the timescale in which bonds vibrate and break. Early work studied bond breaking in molecules such as ICN and NaI, and bond vibration in I_2. The motion was evaluated in terms of a nuclear wavepacket moving over the potential surfaces. These “femtochemistry” experiments have now been applied to a wide variety of systems. A recent example of the detail produced by these techniques include a study of the retinal chromophore in the rhodopsin protein showing cis-trans isomerisation taking place over a picosecond [9].

Initial theoretical research focused on time-independent methods. Early research focused on understanding line spectra, for which the states must be known. The time-independent equation is easy to adapt to numerical solution using matrix diagonalisation methods. And, unless the Hamiltonian is explicitly time-dependent, even ostensibly dynamical problems can be described using the eigenfunctions and eigenvalues of the system.

Despite the early seminal work of McCullough and Wyatt [10, 11], which describes the H + H_2 exchange reaction in a time-dependent picture, time-dependent methods have really only become common in the last two decades and only recently has a text book on quantum mechanics been published which focuses on a time-dependent perspective [12]. These methods do, however, have advantages over time-independent ones. They are more intuitive, connecting directly with the motion of the system. They are able to treat continuum states in a more natural way, important in unbound systems. They are able to treat time-dependent Hamiltonians, important for including the effect of a laser pulse. They also provide a better starting point to approximate solutions.

The MCTDH method is one such approximate method. Its power lies in the fact that it uses a variational principle to derive equations of motion for a flexible wavefunction ansatz. The resulting evolution of the time-dependent basis functions means that the basis set remains optimally small, i.e. the wavefunction representation is very compact. Cheap, qualitative calculations are possible with a small number of functions, while increasing the basis set until convergence is reached with respect to the property of interest results in the numerically exact answer.

The present importance of quantum chemistry calculations in supporting general chemistry is in no small part due to the availability of computer programs usable by non-experts. Only a small handful of codes have been written implementing the MCTDH method. The main ones are the code developed by Manthe and co-workers in Bielefeld, the Las Cruces code developed by Wang, and the Heidelberg code developed by Meyer, Worth and co-workers [13]. The Heidelberg code in particular has the aim of being general and user-friendly. It is by no means yet possible for a non-expert to run quantum dynamics calculations, but it is now possible without the extensive coding for each new problem traditionally required.

MCTDH is of course only one method, if a very successful one, in the field and this book aims to be of interest to a wider audience than just the MCTDH community. The method does have limitations and for some calculations other approaches are to be preferred.[1] Many of the ideas developed here and the systems looked at are of general interest and we hope that some of them will be picked up by other communities.

In Part 2 of the book, the MCTDH theory will be reviewed. The background theory is dealt with briefly in Ch. 2, before the MCTDH method is looked at in detail in Ch. 3, focusing on the special features of the method. The various issues associated with quantum dynamics are then looked at. For example these include how to set up the initial wavepacket (Ch. 5) and how to analyze the results of a propagation in relation to experiments (Ch. 6). The choice of coordinates for a study plays a large role in how easy a calculation is and what information can be obtained. The subject of coordinates and obtaining the kinetic energy operator is addressed in Ch. 12. The efficient integration of

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1) For example, see recent review on the calculation of vibrational energies of polyatomic molecules, Ref. [14].

the equations of motion (Ch. 4) and evaluation of potential matrix elements (Chs. 10, 11) are also treated.

The MCTDH method is able to do more than just represent and propagate a nuclear wavefunction. It is also able to include thermal effects and environments using density operators. This is described in Ch.s 7 and 22. One can also obtain eigenvalues and eigenvectors of an operator taking advantage of the compact form of the MCTDH wavefunction. This can be done either by propagation in imaginary time (termed *relaxation*), or by iterative diagonalisation of the matrix representation of the operator. These methods are dealt with in Chs. 8 and 9. If only the eigenvalues are required the filter diagonalisation method presented in Ch. 6.2.2 is also possible. This uses the full power of the time-dependent formalism. If the operator is the Hamiltonian, the result is a solution of the time-independent Schrödinger equation. Another operator relevant for molecular dynamics studies is the thermal flux operator required in the calculation of rate constants. This topic is treated further in Ch. 19.

In Part 3, extensions to the basic method are looked at. These are all exciting developments moving quantum dynamics into new directions. Despite its power compared to standard grid-based quantum dynamics methods, MCTDH calculations are still unable to treat more than a few atoms explicitly: calculations with more than 20 DOF quickly become intractable. The multilayer approach of Ch. 14 promises to be able to treat 100s of particles in the MCTDH framework. Parallelization of the MCTDH algorithm to take advantage of modern computer architectures is also a must (Ch. 15).

A separate bottleneck to treating large systems is the need for a potential energy surface. Obtaining this function also becomes prohibitive for many atom systems. One approach is to use a model, as done in the vibronic coupling approach of Ch. 18, or the n-mode representation used in Ch. 23. Another is to use *direct dynamics* in which the PES is calculated on-the-fly by quantum chemistry calculations. This approach means that the PES is only generated where the system goes rather than globally, thus saving a huge effort. Its implementation is described in Ch. 13. Direct dynamics provides restrictions on the evolving basis functions as the PES is only known locally where it is calculated. A formulation of the MCTDH method, termed G-MCTDH, uses a Gaussian wavepacket basis which has the desired properties (Ch. 3.5). G-MCTDH also provides a framework to describe mixed methods such as quantum-semiclassical dynamics in which part of the system (the bath) is treated at a lower level level of theory to again allow larger calculations.

The original MCTDH method, like the vast majority of nuclear dynamics calculations, does not take into account the symmetry of particle exchange: it is assumed implicitly that all nuclei are distinguishable. The imposition of the correct symmetry for fermions leads to MCTDHF in Ch. 16. The method can now be used to describe electrons, and examples are given in Sec. 16.5 of the dynamics of these particles after the application of ultrashort, intense laser pulses. The bosonic version, MCTDHB, is discussed in Ch. 17, as is the formalism for the mixed case, MCTDHBF. The resulting theory here thus makes the MCTDH method complete.

In the final part of the book a number of applications are presented. These demonstrate the generality of the method and highlight systems of interest to quantum dynamics studies. Ch. 18 looks at calculating absorption spectra for polyatomic molecules, treating the non-adiabatic coupling between electronic states. The importance of being able to include enough modes is exemplified by calculations on the allene photo-electron spectrum. By including all 15-modes the assignment of the vibrational peaks was changed from previous work that had used only four modes.

Ch. 19 looks at calculating reaction rates. A convenient and efficient way to calculate the rate constant directly is offered by the flux-correlation approach of Miller and co-workers [15]. Combined with MCTDH, Manthe has been able to calculate accurate rate constants for a range of systems such as H + CH_4 in full dimensionality. Discrepancies with experimental data are due to errors in the potential surfaces and these calculations provide a tough test of these functions.

The topic of surface scattering is in Ch. 20, where it is shown that MCTDH is able to treat systems such as CH_4 and CH_3I absorbed onto a solid. The inclusion of all relevant modes is shown to be important for accurate results as reduced dimensionality studies can introduce artefacts by preventing certain motions. One approach used to include the huge number of modes of the substrate in these calculations is the density matrix formalism. How to treat general open systems using density matrices within the MCTDH framework is then further detailed in Ch. 22.

The topic of intramolecular vibrational-energy redistribution is looked at in Ch. 21. Understanding the flow of energy through a molecular system is a fundamental problem which naturally involves the coupling between many modes. The MCTDH method has been used to obtain detailed results in polyatomic systems such as HFCO, H_2CS and HONO.

Proton transfer, another ubiquitous mechanism in chemistry and biochemistry, is treated in Ch. 23. The results presented include the transfer of a proton along a "wire", and a full 15D simulation in which the IR-spectrum of the protonated water dimer – the Zundel cation – is assigned and explained.

The effect of a laser field are studied in Ch. 24, where the topic of quantum control is treated. Here, this is combined with the development of a general Cartesian Reaction Path Hamiltonian to treat a range of systems such as laser-driven proton-transfer and ladder climbing in CO bound to a heme molecule, and controlling predissociation of a diatomic molecule in a rare gas matrix.

The process of dissociative electron attachment in the water molecule is looked at in Ch. 25. This introduces the problems of complex potential energy surfaces and multiple product channels, and despite being only a triatomic system is a hard numerical problem to solve. The last chapter, Ch. 26, reports calculations on ultracold systems where quantum effects become very important for nuclei. Here, the MCTDH method is being applied to a new area in quantum dynamics, away from the traditional molecular dynamics for which it was conceived.