

Quantum And Classical Molecular Dynamics

Abstract: "In molecular dynamics applications there is a growing interest in so-called mixed quantum-classical models. These models describe most atoms of the molecular system by the means of classical mechanics but an important, small portion of the system by the means of quantum mechanics. A particularly extensively used model, the QCMD model, consists of a singularly perturbed Schrödinger equation nonlinearly coupled to a classical Newtonian equation of motion. This paper studies the singular limit of the QCMD model for finite dimensional Hilbert spaces. The main result states that this limit is given by the time-dependent Born-Oppenheimer model of quantum theory -- provided the Hamiltonian under consideration has a smooth spectral decomposition. This result is strongly related to the quantum adiabatic theorem. The proof uses the method of weak convergence by directly discussing the density matrix instead of the wave functions. This technique avoids the discussion of highly oscillatory phases. On the other hand, the limit of the QCMD model is of a different nature if the spectral decomposition of the Hamiltonian happens not to be smooth. We will present a generic example for which the limit set is not a unique trajectory of a limit dynamical system but rather a funnel consisting of infinitely many trajectories."

The study at the nanoscopic level of the polymeric systems is a keystone for a deeper understanding of their internal structure and properties, not only at nanometric scale but also at macroscopic level. The disciplines involved in this scientific field are diverse, including areas such as chemistry, physics, material science, biology and statistics among others. The aforementioned fields converge in a scientific and technologic central branch called nanotechnology. In the last decades, nanotechnology based on polymeric systems has aroused a great interest among the scientific community, as is clearly evidenced by the huge amount of scientific publications and applications developed within this area. However, the experimental complexity for the development of new devices and the economical limitations devoted to this end are barriers that let us think about the use of alternative approaches in this scientific field. In the face of this endeavors, the application of computer simulation methodologies to must be taken into account. The principal focus of this Thesis is the study at the atomic and molecular level of some polymeric systems through theoretical methodologies based on quantum and classical mechanics formalisms. Such methods allow us to support and understand some chemical and physical observables as well as to analyze and describe these systems at their structural level. Within the framework of the application of the atomic and molecular simulation methodologies, this Thesis could be divided mainly in three main research lines: Conducting Polymers, Polymeric Cation Exchange Membranes, and Dendrimers and Dendronized Polymers The first one focusses on evaluating the detection ability of different conducting polymers when

they interact with dopamine or morphine with the final aim of developing a sensor based on these materials. The examination of conducting polymers sensitivity to the analyte detection was carried out via inspection of their ability to form secondary interactions (i.e. weak and strong hydrogen bonds, p-stacking interactions), which was examined using quantum mechanical calculations. Second line is devoted to the application of atomistic molecular dynamics simulation for the investigation of the influence of the electric field strength and the temperature in the dynamical and structural properties of cationic exchange membranes. These investigations were focused on the analysis of hydronium transport mechanism, internal structural rearrangements of the membrane and the characteristics of the hydration shell surrounding the diffused hydronium ions. The last working line of this Thesis is centered on the study at electronic and atomic level of dendritic molecules and dendronized polymers through both quantum and classical mechanics formalisms. The structural properties and molecular interactions occurring in a particular class of dendronized polymers were analyzed. On one side, through a characterization of the inter and intramolecular non bonded interactions of two interacting polymer chains in an attempt to relate atomistic information to the rheological response of these large cylindrical-shape objects. On the other side, studying the internal structure and solvent absorption ability of these systems positively charged and comparing them with their neutral analogues. Finally, studies of both dendrimers and dendronized polymers based on all-thiophene dendrons through quantum mechanics and molecular dynamics were performed. The electronic properties of symmetric and unsymmetric all-thiophene dendrimers containing up to 45 thiophene rings in neutral and oxidized state was investigated. On the other hand, the internal organization of second and third generation macromonomers and dendronized polymers based on all-thiophene dendrons was studied using density functional theory calculations and classical molecular dynamics simulations, respectively.

The latest developments in quantum and classical molecular dynamics, related techniques, and their applications to several fields of science and engineering. Molecular simulations include a broad range of methodologies such as Monte Carlo, Brownian dynamics, lattice dynamics, and molecular dynamics (MD). Features of this book: • Presents advances in methodologies, introduces quantum methods and lists new techniques for classical MD • Deals with complex systems: biomolecules, aqueous solutions, ice and clathrates, liquid crystals, polymers • Provides chemical reactions, interfaces, catalysis, surface phenomena and solids Although the book is not formally divided into methods and applications, the chapters are arranged starting with those that discuss new algorithms, methods and techniques, followed by several important applications.

Addressing the need of chemistry, biology and engineering students to understand and perform their own molecular simulations, the author introduces the fundamentals of molecular modeling for a broad, practice-oriented audience and

presents versatile practical applications. The book presents a thorough overview of the underlying concepts. The theory group at AFRL/PRSP is engaged in an ongoing effort to develop, implement, and test the spectral theory of Schrodinger eigenstates for efficient construction of accurate many-body potential energy surfaces for HEDM systems such as atoms embedded in solid hydrogen. Because good experimental data is available for AlAr(sub N) clusters, they make an excellent test bed for the spectral theory and its computational implementation. We have used the spectral theory method to calculate the ground and low-lying excited states of AlAr(sub N) clusters, subsequently employing these in a sequence of quantum and classical Monte Carlo and classical molecular dynamics simulations to predict their structures, photoionization-induced fragmentation pathways, and optical absorption spectra. These simulations address the key issue of the degree of cluster fragmentation encountered following photoionization of the neutral clusters. The measured data refer to ion mass spectrometric signals of AlAr(sub N-M)(+) fragments detected subsequent to one-photon uv excitation followed by visible one-photon ionization of a distribution of non size-selected parent AlAr(sub N) clusters. Thus, the observed spectrum attributed to AlAr(sub N-M) is actually a superposition of spectra of all parent neutral clusters AlAr(sub N) which produce AlAr(sub N-M)(+) as one of the ionic fragments following the photoionization step.

The school held at Villa Marigola, Lerici, Italy, in July 1997 was very much an educational experiment aimed not just at teaching a new generation of students the latest developments in computer simulation methods and theory, but also at bringing together researchers from the condensed matter computer simulation community, the biophysical chemistry community and the quantum dynamics community to confront the shared problem: the development of methods to treat the dynamics of quantum condensed phase systems. This volume collects the lectures delivered there. Due to the focus of the school, the contributions divide along natural lines into two broad groups: (1) the most sophisticated forms of the art of computer simulation, including biased phase space sampling schemes, methods which address the multiplicity of time scales in condensed phase problems, and static equilibrium methods for treating quantum systems; (2) the contributions on quantum dynamics, including methods for mixing quantum and classical dynamics in condensed phase simulations and methods capable of treating all degrees of freedom quantum-mechanically. Contents:Barrier Crossing: Classical Theory of Rare but Important Events (D Chandler)Monte Carlo Simulations (D Frenkel)Molecular Dynamics Methods for the Enhanced Sampling of Phase Space (B J Berne)Constrained and Nonequilibrium Molecular Dynamics (G Ciccotti & M Ferrario)From Eyring to Kramers: Computation of Diffusive Barrier Crossing Rates (M J Ruiz-Montero)Monte Carlo Methods for Sampling of Rare Event States (W Janke)Proton Transfer in Ice (D Marx)Nudged Elastic Band Method for Finding Minimum Energy Paths of Transitions (H Jónsson et al.)RAW Quantum Transition State

Theory (G Mills et al.) Dynamics of Peptide Folding (R Elber et al.) Theoretical Studies of Activated Processes in Biological Ion Channels (B Roux & S Crouzy) The Semiclassical Initial Value Representation for Including Quantum Effects in Molecular Dynamics Simulations (W H Miller) Tunneling in the Condensed Phase: Barrier Crossing and Dynamical Control (N Makri) Feynman Path Centroid Methods for Condensed Phase Quantum Dynamics (G A Voth) Quantum Molecular Dynamics Using Wigner Representation (V S Filinov et al.) Nonadiabatic Molecular Dynamics Methods for Diffusion (D Laria et al.) and other papers Readership: Computational and statistical physicists.

Keywords: Quantum; Molecular Dynamics; Dynamics Reviews: "... this volume is a useful introduction to currently popular, and widely-used techniques in chemical and statistical physics. The authors are well-respected researchers in the field and the level is appropriate to graduate students and researchers." Journal of Statistical Physics

From March 30th to April 3rd, 1992, a NATO Advanced Research workshop entitled "Time Dependent Quantum Molecular Dynamics: Theory and Experiment" was held at Snowbird, Utah. The organizing committee consisted of J. BROECKHOVE (Antwerp, Belgium), L. CEDERBAUM (Heidelberg, Germany), L. LATHOUWERS (Antwerp, Belgium), N. OHRN (Gainesville, Florida) and J. SIMONS (Salt Lake City, Utah). Fifty-two participants from eleven different countries attended the meeting at which thirty-three talks and one poster session were held. Twenty-eight participants submitted contributions to the proceedings of the meeting, which are reproduced in this volume. The workshop brought together experts in different areas of molecular quantum dynamics, all adhering to the time dependent approach. The aim was to discuss and compare methods and applications. The familiarity of the audience with the concepts of time dependent approaches greatly facilitated topical discussions and probing towards new applications. A broad area of subject matter was covered including time resolved laser chemistry, intramolecular dynamics, photodissociation dynamics, reactive and inelastic collisions as well as new time dependent methodologies. This diversity in applications is reflected in the contributions included in this volume.

Abstract: "This paper presents an explicit and symplectic integrator called PICK-ABACK for quantum-classical molecular dynamics. This integration scheme is time reversible and unitary in the quantum part. We use the Lie formalism in order to construct a formal evolution operator which then is split using the Strang splitting yielding the symplectic discretization PICKABACK. Finally the new method is compared with a hybrid method in application to two examples: a collinear collision with a quantum oscillator and additionally a photodissociation process of a collinear ArHCl-molecule."

On May 21-24, 1997 the Second International Symposium on Algorithms for Macromolecular Modelling was held at the Konrad Zuse Zentrum in Berlin. The event brought together computational scientists in fields like biochemistry, biophysics, physical chemistry, or statistical physics and numerical analysts as well as computer scientists working on the advancement of algorithms, for a total of over 120 participants from 19 countries. In the course of the symposium, the speakers agreed to produce a representative volume that combines survey articles and original papers (all refereed) to give an impression of the present state of

the art of Molecular Dynamics. The 29 articles of the book reflect the main topics of the Berlin meeting which were i) Conformational Dynamics, ii) Thermodynamic Modelling, iii) Advanced Time-Stepping Algorithms, iv) Quantum-Classical Simulations and Fast Force Field and v) Fast Force Field Evaluation.

Molecular Dynamics From Classical to Quantum Methods Elsevier

Abstract: "In molecular dynamics applications there is a growing interest in mixed quantum-classical models. The article is concerned with the so-called QCMD model. This model describes most atoms of the molecular system by the means of classical mechanics but an important, small portion of the system by the means of a wavefunction. We review the conditions under which the QCMD model is known to approximate the full quantum dynamical evolution of the system. In most quantum-classical simulations the Born-Oppenheimer model (BO) is used. In this model, the wavefunction is adiabatically coupled to the classical motion which leads to serious approximation deficiencies with respect to non-adiabatic effects in the fully quantum dynamical description of the system. In contrast to the BO model, the QCMD model does include non-adiabatic processes, e.g., transitions between the energy levels of the quantum system. It is demonstrated that, in mildly non-adiabatic scenarios, so-called surface hopping extensions of QCMD simulations yield good approximations of the non-adiabatic effects in full quantum dynamics. The algorithmic strategy of such extensions of QCMD is explained and the crucial steps of its realization are discussed with special emphasis on the numerical problems caused by highly oscillatory phase effects."

Complex systems that bridge the traditional disciplines of physics, chemistry, biology, and materials science can be studied at an unprecedented level of detail using increasingly sophisticated theoretical methodology and high-speed computers. The aim of this book is to prepare burgeoning users and developers to become active participants in this exciting and rapidly advancing research area by uniting for the first time, in one monograph, the basic concepts of equilibrium and time-dependent statistical mechanics with the modern techniques used to solve the complex problems that arise in real-world applications. The book contains a detailed review of classical and quantum mechanics, in-depth discussions of the most commonly used ensembles simultaneously with modern computational techniques such as molecular dynamics and Monte Carlo, and important topics including free-energy calculations, linear-response theory, harmonic baths and the generalized Langevin equation, critical phenomena, and advanced conformational sampling methods. Burgeoning users and developers are thus provided firm grounding to become active participants in this exciting and rapidly advancing research area, while experienced practitioners will find the book to be a useful reference tool for the field.

The book provides a detailed account of how condensed-phase molecular dynamics are reflected in the line shapes of NMR spectra. The theories establishing connections between random, time-dependent molecular processes and lineshape effects are exposed in depth. Special emphasis is placed on the theoretical aspects, involving in particular intermolecular processes in solution, and molecular symmetry issues. The Liouville super-operator formalism is briefly introduced and used wherever it is beneficial for the transparency of presentation. The proposed formal descriptions of the discussed problems are sufficiently detailed to be implemented on a computer. Practical applications of

the theory in solid- and liquid-phase studies are illustrated with appropriate experimental examples, exposing the potential of the lineshape method in elucidating molecular dynamics NMR-observable molecular phenomena where quantization of the spatial nuclear degrees of freedom is crucial are addressed in the last part of the book. As an introduction to this exciting research field, selected aspects of the quantum mechanics of isolated systems undergoing rotational tunnelling are reviewed, together with some basic information about quantum systems interacting with their condensed environment. The quantum theory of rate processes evidenced in the NMR lineshapes of molecular rotors is presented, and illustrated with appropriate experimental examples from both solid- and liquid-phase spectra. In this context, the everlasting problem of the quantum-to-classical transition is discussed at a quantitative level. The book will be suitable for graduate students and new and practising researchers using NMR techniques.

Abstract: "It was revealed that the QCMD model is of canonical Hamiltonian form with symplectic structure, which implies the conservation of energy. An efficient and reliable integrator for transferring these properties to the discrete solution is the symplectic and explicit PICKABACK algorithm. The only drawback of this kind of integrator is the small stepsize in time induced by the splitting techniques used to discretize the quantum evolution operator. Recent investigations concerning Krylov iteration techniques result in alternative approaches which overcome this difficulty for a wide range of problems. By using iterative methods in the evaluation of the quantum time propagator, these techniques allow for the stepsize to adapt to the classical motion and the coupling between the classical and the quantum mechanical subsystem. This yields a drastic reduction of the numerical effort. The pros and cons of both approaches as well as the suitable applications are discussed in the last part."

Abstract: "The overall Hamiltonian structure of the Quantum-Classical Molecular Dynamics model makes -- analogously to classical molecular dynamics -- symplectic integration schemes the methods of choice for long-term simulations. This has already been demonstrated by the symplectic PICKABACK method [12]. However, this method requires a relatively small step-size due to the high-frequency quantum modes. Therefore, following related ideas from classical molecular dynamics, we investigate symplectic multiple-time-stepping methods and indicate various possibilities to overcome the step-size limitation of PICKABACK."

Quantum mechanics is a general theory of the motions, structures, properties, and behaviors of particles of atomic and subatomic dimensions. While quantum mechanics was created in the first third of the twentieth century by a handful of theoretical physicists working on a limited number of problems, it has further developed and is now applied by a great number of people working on a vast range of problems in wide areas of science and technology. Basic Molecular Quantum Mechanics introduces quantum mechanics by covering the fundamentals of quantum mechanics and some of its most important chemical applications: vibrational and rotational spectroscopy and electronic structure of atoms and molecules. Thoughtfully organized, the author builds up quantum mechanics systematically with each chapter preparing the student for the more advanced chapters and complex applications. Additional features include the following: This book presents rigorous and precise explanations of quantum mechanics and mathematical proofs. It contains qualitative discussions of key concepts with mathematics presented in the appendices. It provides problems and solutions at the end of each chapter to encourage understanding and application. This book is carefully written to emphasize its applications to chemistry and is a valuable resource for advanced undergraduates and beginning graduate students specializing in chemistry, in related fields such as chemical engineering and materials science, and in some areas of biology.

Free energy calculations are one of the most powerful tools within modern theoretical chemistry and are often used to make comparisons

with experimental results. Existing free energy calculations are typically performed for classical molecular dynamics simulations but there are certain systems where nuclear quantum effects play an integral role. Specifically, systems with light atoms or low temperatures are the most influenced by such nuclear quantum effects and the development of Feynman path integrals [1] has been effective in accurately describing the quantum nature of these nuclei [2-8]. The primary objective of this thesis is the development of a pair of methodologies to calculate free energies utilizing path integral molecular dynamics to account for nuclear quantum effects. Prior to the development of these free energy methodologies, this thesis presents a communication interface between the OpenMM and MMTK software packages that has been previously published [9]. This interface allows for users of MMTK to take advantage of the performance of OpenMM without major modifications to existing simulation scripts. Notably, the serial OpenMM integrator is shown to provide a 3x performance gain in comparison to a standard MMTK simulation while the GPU implementations of OpenMM provide over a 400x performance gain for larger systems with periodic boundary conditions. The first path integral free energy methodology of this thesis combines the existing umbrella sampling technique [10,11] with path integral molecular dynamics. This methodology has been previously published and proposes that the umbrella sampling biasing potential only needs to be applied to a single path integral bead [12]. Furthermore, this proposed methodology is successfully benchmarked for a pair of Lennard-Jones dimer systems before being applied to the more difficult water dimer. The free energy profiles obtained from simulation are then used to calculate a free energy difference of -12.90 ± 0.05 kJ/mol for the MB-Pol potential in comparison to the experimental dissociation energy of -13.2 ± 0.12 kJ/mol [13]. The second path integral free energy methodology introduces a constraint within the path integral molecular dynamics simulations as opposed to an umbrella sampling restraint. Specifically, this methodology applies a constraint to an individual path integral bead in a manner that is similar to the concept of thermodynamic integration for classical simulations [14]. Formal estimators for the derivative of the free energy have been developed by Louchtchenko et al. [15] and the results presented in this thesis analyze the effectiveness of these estimators for molecular dynamics simulations of Lennard-Jones and water dimers. Additionally, a new estimator is developed and the resulting free energy profiles are used to evaluate a free energy difference for the water dimer of -13.03 ± 0.14 kJ/mol, which is within the errors of the experimental dissociation energy [13]. Overall, this thesis provides a theoretical framework to study the free energy of weakly bound systems over a broad range of temperatures. It is important to note that these methodologies were insufficient below 25 K and it remains more practical to use reaction coordinates that are not distances at such temperatures. Nevertheless, the extension and application of these methodologies to more complicated systems remains an area of exciting development.

Ab initio molecular dynamics revolutionized the field of realistic computer simulation of complex molecular systems and processes, including chemical reactions, by unifying molecular dynamics and electronic structure theory. This book provides the first coherent presentation of this rapidly growing field, covering a vast range of methods and their applications, from basic theory to advanced methods. This fascinating text for graduate students and researchers contains systematic derivations of various ab initio molecular dynamics techniques to enable readers to understand and assess the merits and drawbacks of commonly used methods. It also discusses the special features of the widely used Car-Parrinello approach, correcting various misconceptions currently found in research literature. The book contains pseudo-code and program layout for typical plane wave electronic structure codes, allowing newcomers to the field to understand commonly used program packages and enabling developers to improve and add new features in their code.

Atomistic simulations of metals under irradiation are indispensable for understanding damage processes at time- and length-scales beyond the reach of experiment. Previously, such simulations have largely ignored the effect of electronic excitations on the atomic dynamics, even

though energy exchange between atoms and electrons can have significant effects on the extent and nature of radiation damage. This thesis presents the results of time-dependent tight-binding simulations of radiation damage, in which the evolution of a coupled system of energetic classical ions and quantum mechanical electrons is correctly described. The effects of electronic excitations in collision cascades and ion channeling are explored and a new model is presented, which makes possible the accurate reproduction of non-adiabatic electronic forces in large-scale classical molecular dynamics simulations of metals.

"The cornucopia of computational chemical techniques available nowadays facilitates meticulous analysis of a wide range of properties of multi-body systems of various sizes and states. The work featured in this thesis aims to elucidate the application of such computational techniques as classical molecular dynamics, (time-dependent) density functional theory, and nonadiabatic molecular dynamics, to investigation of key mechanisms of energy harvesting, featuring well-known electrolyte solutions along with novel nanoscale materials that can be potentially employed in photovoltaic devices. The first chapter outlines the motivation of the work, followed by a brief overview of the operation principles of the promising energy harvesting devices, description of the auspicious materials, and, finally, delineation of the computational approaches. The second chapter focuses on the fundamental theoretical concepts implemented in the computational techniques applied herein. The third chapter discusses the results of the calculations, and is comprised of three parts: (a) molecular dynamic simulation of electrolyte solutions; (b) (time-dependent) density functional theory investigation of structural and optical properties of small organic molecules; and (c) nonadiabatic molecular dynamics survey of photoinduced dynamics in carbon nanotube ensembles. The closing remarks are provided in the fourth chapter."--Page vi.

Incorporating quantum mechanics into an atomistic simulation necessarily involves solving the Schroedinger equation. Unfortunately, the computational expense associated with solving this equation scales miserably with the number of included quantum degrees of freedom (DOF). The situation is so dire, in fact, that a molecular dynamics (MD) simulation cannot include more than a small number of quantum DOFs before it becomes computationally intractable. Thus, if one were to simulate a relatively large system, such as one containing several hundred atoms or molecules, it would be unreasonable to attempt to include the effects of all of the electrons associated with all of the components of the system. The mixed quantum/classical (MQC) approach provides a way to circumvent this issue. It involves treating the vast majority of the system classically, which incurs minimal computational expense, and reserves the consideration of quantum mechanical effects for only the few degrees of freedom more directly involved in the chemical phenomenon being studied. For example, if one were to study the bonding of a single diatomic molecule in the gas phase, one could employ a MQC approach by treating the nuclei of the molecule's two atoms classically--including the deeply bound, low-energy electrons that change relatively little--and solving the Schroedinger equation only for the high energy electron(s) directly involved in the bonding of the classical cores. In such a way, one could study the bonding of this molecule in a rigorous fashion while treating only the directly related degrees of freedom quantum mechanically. Pseudopotentials are then responsible for dictating the interactions between the quantum and classical degrees of freedom. As these potentials are the sole link between the quantum and classical DOFs, their proper development is of the utmost importance. This Thesis is concerned primarily with my work on the development of novel, rigorous and dynamical pseudopotentials for use in mixed quantum/ classical simulations in the condensed phase. The pseudopotentials discussed within are constructed in an ab initio fashion, without the introduction of any empiricism, and are able to exactly reproduce the results of higher level, fully quantum mechanical Hartree-Fock calculations. A recurring theme in the following pages is overcoming the so-called frozen core approximation (FCA). This essentially comes down to creating pseudopotentials that

are able to respond in some way to the local molecular environment in a rigorous fashion. The various methods and discussions that are part of this document are presented in the context of two particular systems. The first is the sodium dimer cation molecule, which serves as a proof of concept for the development of coordinate-dependent pseudopotentials and is the subject of Chapters 2 and 3. Next, the hydrated electron —the excess electron in liquid--water is tackled in an effort to address the recent controversy concerning its true structure and is the subject of Chapters 4 and 5. In essence, the work in this Dissertation is concerned with finding new ways to overcome the problem of a lack of infinite computer processing power.

Quantum dynamics of molecules poses a variety of computational challenges that are presently at the forefront of research efforts in numerical analysis in a number of application areas: high-dimensional partial differential equations, multiple scales, highly oscillatory solutions, and geometric structures such as symplecticity and reversibility that are favourably preserved in discretizations. This text addresses such problems in quantum mechanics from the viewpoint of numerical analysis, illustrating them to a large extent on intermediate models between the Schrodinger equation of full many-body quantum dynamics and the Newtonian equations of classical molecular dynamics. The fruitful interplay between quantum dynamics and numerical analysis is emphasized.

Abstract: "This paper presents a mathematical derivation of a model for quantum-classical molecular dynamics (QCMD) as a partial classical limit of the full Schrödinger equation. This limit is achieved in two steps: separation of the full wavefunction and short wave asymptotics for its 'classical' part. Both steps can be rigorously justified under certain smallness assumptions. Moreover, the results imply that neither the time-dependent self-consistent field method nor mixed quantum-semi-classical models lead to better approximations than QCMD since they depend on the separation step, too. On the other hand, the theory leads to a characterization of the critical situations in which the models are in danger of largely deviating from the solution of the full Schrödinger equation. These critical situations are exemplified in an illustrative numerical simulation: the collinear collision of an Argon atom with a harmonic quantum oscillator."

The guidelines of this textbook are numerous example programs, flux diagrams, schemes, and figures presenting the obtained results. Step by step, the authors explain how steady state Monte Carlo Simulation (MCS) and time resolved, so-called kinetic or dynamic Monte Carlo Simulation (KMCS), schemes, respectively, can be set up. Furthermore, examples of classical Molecular Dynamics Simulations (MDS) are included. In addressing the same type of problem by way off all these methods, the different schemes can directly be compared. For the example programs, they have chosen problems related to the adsorption of gas-phase species on surfaces (i.e. mainly lattice models related to gas-surface adsorption dynamics). Furthermore, the growth of deposits on grid surfaces has been address including fractal growth phenomena.

An introduction to the rapidly evolving methodology of electronic excited states For academic researchers, postdocs, graduate and undergraduate students, Quantum Chemistry and Dynamics of Excited States: Methods and Applications reports the most updated and accurate theoretical techniques to treat electronic excited states. From methods to deal with stationary calculations through time-dependent simulations of molecular systems, this book serves as a guide for beginners in the field and knowledge seekers alike. Taking into account the most recent theory developments and representative applications, it also covers the often-overlooked gap between theoretical and computational chemistry. An

excellent reference for both researchers and students, *Excited States* provides essential knowledge on quantum chemistry, an in-depth overview of the latest developments, and theoretical techniques around the properties and nonadiabatic dynamics of chemical systems. Readers will learn: ? Essential theoretical techniques to describe the properties and dynamics of chemical systems ? Electronic Structure methods for stationary calculations ? Methods for electronic excited states from both a quantum chemical and time-dependent point of view ? A breakdown of the most recent developments in the past 30 years For those searching for a better understanding of excited states as they relate to chemistry, biochemistry, industrial chemistry, and beyond, *Quantum Chemistry and Dynamics of Excited States* provides a solid education in the necessary foundations and important theories of excited states in photochemistry and ultrafast phenomena.

We are using classical molecular dynamics and condensed phase electronic-structure methods to predict some of the thermophysical and mechanical properties that are needed as input to realistic mesoscale models for plastic-bonded explosives. The main materials studied to date are HMX, PETN, Estane copolymer, and bi(2,2-dinitropropyl) formal/acetal (BDNPF/A). Emphasis is placed on non-reactive properties and thermodynamic states relevant to cookoff and shock initiation phenomena. Both crystal and liquid-state properties are of interest. Typical simulation sizes and times are (almost equal to) 10² molecules and 2-10 ns, respectively. The overarching goal is to develop internally consistent model thermodynamic and elastic mechanical descriptions for the materials. Prioritization among the set of properties amenable to atomistic simulation is made based on ongoing interactions with mesoscale modelers at Los Alamos and elsewhere. Recent work will be summarized and our view of profitable directions for future research will be discussed, including preliminary results for large-scale molecular dynamics simulations of shock response of crystalline HMX.

Abstract: "In molecular dynamics applications there is a growing interest in including quantum effects for simulations of larger molecules. This paper is concerned with mixed quantum-classical models which are currently discussed: the so-called QCMD model with variants and the time-dependent Born-Oppenheimer approximation. All these models are known to approximate the full quantum dynamical evolution -- under different assumptions, however. We review the meaning of these assumptions and the scope of the approximation. In particular, we characterize those typical problematic situations where a mixed model might largely deviate from the full quantum evolution. One such situation of specific interest, a non-adiabatic excitation at certain energy level crossings, can promisingly be dealt with by a modification of the QCMD model that we suggest."

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