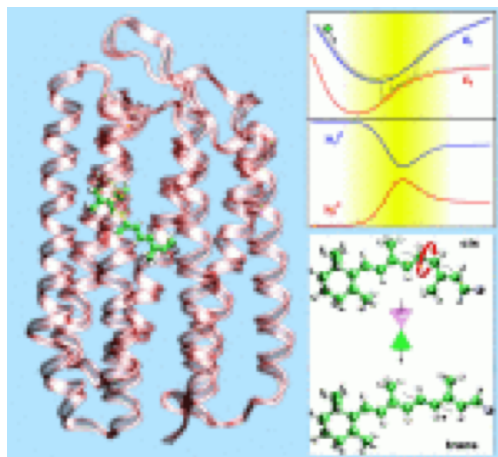


Ab initio simulations in photochemistry: bringing together
nonadiabatic dynamics and electronic structure theory



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May, 23rd 2007

1 Workshop details

1.1 Details

Timing

Number of days : 3

Start : 2007-05-23

End : 2007-05-25

Location of the activity

CECAM
46 allée d'Italie
69007 Lyon
France

1.2 Description

This workshop will address the challenge of simulating realistic photoactivated processes of interest in biology and materials science [1,2,3]. These phenomena usually involve non-adiabatic transitions among the electronic states of the system induced by the coupled motion of electronic and nuclear degrees of freedom. Consequently, their simulation requires both accurate ab initio calculations of the (many) electronic states of the system and of the couplings among them and the non-adiabatic time evolution of its components. Although several approaches have been developed recently to tackle these problems [4,5,6,7,8], the techniques currently available are generally either not efficient or not accurate enough to provide a reliable tool to study photophysical processes in complex systems (see proposal for further details).

The workshop will bring together experts from the fields of ab initio quantum chemistry and non-adiabatic dynamics calculations to provide an opportunity for the two communities to join forces and accelerate progress towards reliable theoretical studies of photoactivated phenomena. Current approaches to non-adiabatic ab initio molecular dynamics will be examined and compared to assess their strengths and weaknesses. Novel approaches will also be presented and their potential with respect to realistic applications assessed, both in terms of accuracy and efficiency.

Requested Support

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3 Participant List

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4 Presentation list

Ab initio nonadiabatic photodynamics using the on-the-fly surface-hopping program system NEWTON-X: the photostability of DNA base models, cis-trans photoisomerization of protonated Schiff bases and the excited-state proton transfer in 2-(2'-Hydroxyphenyl)benzothiazole

Hans Lischka

University of Vienna

Coauthor(s) : Mario Barbatti

Abstract

In this contribution the features of the newly developed surface-hopping program system NEWTON-X [1] are presented. The nonadiabatic dynamics is based on Tully's surface hopping approach. The program has been developed with the aim of 1) to create a flexible tool to be used in connection with a multitude of third-party electronic-structure program packages and 2) to provide the most common options for excited-state dynamics simulations. Currently, NEWTON-X is connected to COLUMBUS and TURBOMOLE. From COLUMBUS analytic MR-CISD and state-averaged MCSCF gradients for excited states and nonadiabatic coupling vectors are available, thus allowing full nonadiabatic dynamics. TURBOMOLE provides RI-CC2 and TDDFT analytic excited-state gradients. Links to other program systems are in preparation.

Three classes of photochemical problems are discussed. The first case treats the photodynamics of models for DNA bases and the reaction paths deduced from surface-hopping dynamics. The second set of examples deals with the cis-trans isomerization of protonated Schiff bases in the S₁ state. In particular, mechanical restrictions are applied at the chain ends in order to mimic environmental effects due to embedding into the protein structure. Finally, excited-state intramolecular proton transfer is discussed in 2-(2'-Hydroxyphenyl)benzothiazole (HBT). In the first two examples COLUMBUS has been used for the electronic structure calculations, whereas TURBOMOLE has been applied in the last case.

Key References

[1] M. Barbatti, G. Granucci, M. Persico, M. Ruckebauer, M. Vazdar, M. Eckert-Maksić and H. Lischka, *Journal of Photochemistry and Photobiology A*, in press.

Photochemistry of Visual Pigment Chromophore Models by ab Initio Molecular Dynamics

Oliver Weingart

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Coauthor(s) : Igor Schapiro and Volker Buss

Abstract

The photoreaction of retinal in rhodopsin is one of the fastest reactions devised by nature. The investigation of retinal photochemistry with *ab initio* methods requires an appropriate treatment of both, the excited state reaction and the adiabatic hopping event in order to obtain meaningful and interpretable results. Current computational limitations require a compromise between the accuracy in the description and the cost of the calculation. Our method replaces the accurate determination of the hopping event in a trajectory by two steps: (a) the determination of the first close approach of the S₁ and S₀ surfaces below a certain threshold and (b) the detection of a surface crossing along the trajectory. For both points the resulting photoproduct is projected. Instead of a calculated quantum yield we obtain the quantum yield range in which the reaction can take place [1,2]. In combination with effective routines to obtain gradients for state averaged wavefunctions this approach enables us to calculate molecular ensembles of retinal models consisting of up to five double bonds. These calculations give insight into mechanistic details of the photoreaction of retinal models in vacuo and in the protein environment.

Key References

- [1] Bond torsion affects the product distribution in the photoreaction of retinal model chromophores O. Weingart, I. Schapiro, V. Buss, J. Mol. Mod. 2006, 12(5), 713-721
[2] Photochemistry of Visual Pigment Chromophore Models by ab Initio Molecular Dynamics, O. Weingart, I. Schapiro, V. Buss, J. Phys. Chem. A 2007, in print

Excited State Dynamics of Conjugated Molecules

Peter Rossky

University of Texas at Austin

Coauthor(s) : Fabio Sterpone, Hyojoon Kim

Abstract

This talk will describe our developments of methods and initial results obtained for the electronic excited state dynamics of conjugated molecules. The methods are currently based on quite simple semi-empirical electronic structure methods coupled with molecular mechanics, but are implemented within a well defined non-adiabatic dynamics simulation scheme. Examples to be discussed include excited state intramolecular electron transfer in a solvated dye molecule, and excited state relaxation of conjugated oligomers of interest in the organic LED context.

Semiempirical and QM/MM methods for direct excited state dynamics.

Maurizio Persico

Universita'di Pisa

Coauthor(s) : Giovanni Granucci

Abstract

We have set up a new semiempirical method within the NDO approach, that is able to deal with excited states, bond breaking, and orbital degeneracies. The molecular orbitals are obtained by an SCF procedure with variable occupation numbers, and the electronic wavefunctions are of CI type. A QM/MM version of the method allows us to treat large systems, including cases in which the QM subsystem (chromophore and/or reacting center) interacts by covalent bonding with the MM one. Analytic gradients and nonadiabatic couplings can be computed, so the method is suitable to run excited state dynamics with "on the fly" calculation of the electronic quantities. In this way, we have run simulations of photochemical and photophysical processes, with the trajectory surface hopping or full multiple spawning approaches (the latter in collaboration with T. J. Martinez).

Key References

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Direct semiclassical simulation of photochemical processes with semiempirical wavefunctions.
J. Chem. Phys. 114, 10608-10615 (2001)

M. Persico, G. Granucci, S. Inglesse, T. Laino, A. Toniolo,
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Theoret. Chem. Acc. 93, 270-279 (2004)

C. Ciminelli, G. Granucci, M. Persico,

The photoisomerization mechanism of azobenzene: a semiclassical simulation of nonadiabatic dynamics.

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M. Barbatti, G. Granucci, M. Persico, H. Lischka,
Semiempirical molecular dynamics investigation of the excited state lifetime of ethylene.

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Photodissociation of formic acid. A trajectory surface hopping study.

Chem. Phys. Lett. 412, 35-40 (2005)

C. Ciminelli, G. Granucci, M. Persico,
Are azobenzenophanes rotation-restricted?

J. Chem. Phys. 123, 174317/1-10 (2005)

A. Toniolo, C. Ciminelli, M. Persico, T. J. Martínez,
Simulation of the photodynamics of azobenzene on its first excited state: comparison of full multiple spawning and surface hopping treatments.

J. Chem. Phys. 123, 234308/1-10 (2005)

Surface hopping algorithms: internal consistency and quantum decoherence.

Maurizio Persico

Universita'di Pisa

Coauthor(s) : Giovanni Granucci

Abstract

We address the problem of internal consistency in trajectory surface hopping methods, i.e. the requirement that the fraction of trajectories running on each electronic state equals the probabilities computed by the electronic time-dependent Schroedinger equation, after averaging over all trajectories. We derive a formula for the hopping probability in Tully's "fewest switches" spirit, that would yield a rigorously consistent treatment. We show the relationship of Tully's widely used surface hopping algorithm with the "exact" prescription, that cannot be applied when running each trajectory independently. We also bring out the connection of the consistency problem with the coherent propagation of the electronic wavefunction, and the artefacts caused by coherent Rabi-like oscillations of the state probabilities in weak coupling regimes. A real molecule (azobenzene) and two ad hoc models serve as examples to illustrate the above theoretical arguments. Following a proposal by Truhlar's group, we apply a decoherence correction to the state probabilities, in conjunction with Tully's algorithm, and we obtain satisfactory results in terms of internal consistency and of agreement with the outcomes of quantum wavepacket calculations.

Key References

G. Granucci, M. Persico
A critical appraisal of the fewest switches algorithm for surface hopping.
J. Chem. Phys., accepted

G. Granucci, M. Persico,
Excited state dynamics with the direct trajectory surface hopping method: azobenzene and its derivatives as a case study.
Theoret. Chem. Acc., in press, available online

Photochemistry with ab initio quantum molecular dynamics: from molecules to clusters

Petr Slavicek

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Abstract

Ab initio quantum molecular dynamics represents a synthesis of quantum molecular dynamics (answering the question what the nuclei are doing) and ab initio quantum chemistry (answering a question what the electrons are doing). While full quantum dynamics is apparently impractical/impossible to use, various semiclassical techniques have been suggested. Full multiple spawning (FMS) method is one possible route connecting the worlds of quantum dynamics and quantum chemistry.

In this presentation, various examples of ab initio simulations in photochemistry will be shown. In particular, photochemistry of atmospherically relevant molecules (nitrophenols, acetone) and biologically important molecules (glycine). Importance of the dynamical point of view will be emphasized. In the next part, photochemistry of molecular complexes will be studied (hydrogen halides on ice nanoparticles, complexes of aromatic heteromolecules).

Several methodological aspects of ab initio quantum simulations, e.g. time extension, will also be discussed.

Assessment of Time-Dependent Density-Functional Theory (TDDFT) for Con- and Disrotatory CC Ring-Opening in Oxirane

Mark Casida

Univ. of Grenoble

Coauthor(s) : F. Cordova, L. Joubert Doriol, A. Ipatov, C. Filippi, and A. Vela

Abstract

The success of Car-Parrinello (CP) density-functional theory (DFT) molecular dynamics calculations for thermochemical reactions has generated interest in the extension of CP calculations to photochemical reactions through the use of time-dependent DFT (TDDFT).

Although TDDFT is a formally rigorous way to obtain excitation energies, practical calculations involve the use of approximate functionals and "corrections" intended to approximate expected features of exact TDDFT.

We have investigated some variants on TDDFT methodology for the rather idealized reaction of symmetric (Woodward-Hoffmann) CC ring opening of oxirane and recommend using the Tamm-Dancoff approximation and avoiding the use of hybrid functionals when seeking to calculate global features of potential energy surfaces.

Key References

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[CIC06] M.E. Casida, A. Ipatov, and F. Cordova, in *Time-Dependent Density-Functional Theory*, edited by M.A.L. Marques, C. Ullrich, F. Nogueira, A. Rubio, and E.K.U. Gross, *Lecture Notes in Physics*

(Springer: Berlin, 2006), p. 243. "Linear-Response Time-Dependent Density-Functional Theory for Open-Shell Molecules"

[CJI+07] F. Cordova, L. Joubert Doriol, A. Ipatov, M.E. Casida, C. Filippi, and A. Vela, *in preparation*. "Assessment of Time-Dependent Density-Functional Theory for Con- and Disrotatory CC Ring-Opening in Oxirane"

CASSCF/CASPT2 Potential Energy Hypersurfaces and the Photochemistry of Biochromophores: Reaction Paths, Conical Intersections, and the Role of the Correlation Energy

Luis Serrano-Andres

University of Valencia

Abstract

From a theoretical chemist perspective to get insight in a field like photobiology implies computing the dynamics of the photochemical process on lowest potential energy surfaces of biochromophores. The initial step is clearly to obtain an accurate representation of the potential energy surface of the excited state by performing electronic structure calculations, a challenging objective in itself because it requires the use of advanced and computationally expensive quantum-chemical methods and strategies able to include in a balanced way differential electronic correlation effects on the various electronic states hypersurfaces. The dynamic path of the initially absorbed energy can then be followed along the complex topology of the hypersurface through favorable reaction paths, energy barriers, minima, and surface crossings, in a sequence of nonadiabatic and adiabatic processes which control the fate of the energy. In the present report, ab initio CASSCF/CASPT2 calculations on electronic states hypersurfaces of different biomolecules will illustrate the role of conical intersections in the ultrafast photochemistry of such systems, stressing the need of using highly correlated quantum chemical methods to get accurate reaction profiles, energy gaps, and transition probabilities. Examples include the ultrafast deactivation of excited DNA nucleobase monomers, excimer formation, photoreactivity and charge transfer in pi-stacked DNA nucleobase dimers, electron transfer in photosynthetic porphyrin-quinone pairs, and triplet state populations in DNA nucleobases, furocoumarines, and flavins.

Key References

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Diabatic dynamics with ROKS

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Coauthor(s) : Konstantina Damianos, Stephan Grimm, Christel Nonnenberg

Abstract

Restricted Open-Shell Kohn-Sham (ROKS) theory is a single-configuration method. Due to its simple structure it can be applied to the on-the-fly excited-state simulation of relatively large molecular systems. The single-configuration approximation bears the further advantage that the system conserves its orbital symmetry during a simulation. We propose to use this feature for efficient diabatic simulations of the photoreactions of large molecules.

Dynamics at Conical Intersections: Applications to Photochemistry and Photobiology

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Abstract

The QM (CASSCF)/MM (GROMACS) treatment of photochemical dynamics will be illustrated by application to photostability and photoswitching in the protein environment. A CASSCF approach with QM dynamics will be illustrated for channel 3 benzene. Finally the second order treatment of conical intersections will be discussed with application to the photochemistry of benzene

Understanding ultrafast photodynamics with ab initio multiple spawning and time-dependent density functional theory

Benjamin Levine

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Coauthor(s) : Benjamin G. Levine, Chaehyuk Ko, and Todd J. Martinez

Ultrafast nonadiabatic dynamics using vibronic-coupling models and multiconfigurational methods: from conjugated molecules to semiconducting polymers

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Coauthor(s) : H. Tamura, G. A. Worth, E. R. Bittner

Abstract

In this talk, we address the characterization of photochemical processes by a combination of diabatic vibronic-coupling models and multiconfigurational wavepacket propagation methods. These methods include, in particular, the G-MCTDH (Gaussian-based Multi-Configuration Time-Dependent Hartree) variant [1] of the MCTDH scheme; this method uses a variationally optimized Gaussian basis and is suitable for on-the-fly dynamics calculations [2]. Applications

include the ultrafast photochemistry of semiconducting polymer systems, as illustrated by our recent analysis of the exciton decay at donor-acceptor polymer heterojunctions [3]. This analysis is based upon an explicit 24-mode electron-phonon model, parameterized by semi-empirical and TDDFT calculations. A hierarchical effective-mode representation [3,4] as applied to a TFB:F8BT heterojunction highlights (i) the dominance of the high-frequency C=C stretch modes in the coupling to the electronic subsystem and (ii) the key role of the low-frequency ring-torsional modes in mediating the ultrafast nonadiabatic dynamics.

Key References

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Group theory approach to quantum-classical dynamics

Federica Agostini

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Coauthor(s) : Caprara Sergio, Ciccotti Giovanni

Abstract

The derivation of quantum-classical equations of motion, describing the dynamics of a classical bath coupled to a small number of quantum degrees of freedom, is still an open problem.

In this talk, we analyse a new approach to the quantum-classical problem, recently proposed by V. V. Kisil [1]. Quantum and classical mechanics

are formulated within the Heisenberg group, which allows to obtain the second as a straightforward limit of the first.

The representation theory of the group is the starting point to propose an ansatz for mixed quantum-classical Lie brackets generating time evolution of observables.

In the attempt to provide a physical interpretation of the results proposed in [1] and to apply quantum-classical equations of motion in a molecular dynamics simulation, we found a way to show [2] the purely classical nature of the supposedly quantum-classical equations derived by Kisil.

The ansatz proposed by Kisil is not useful for any application in a quantum-classical problem but we think that the representation theory of the Heisenberg group could be a powerful mean to produce some interesting kind of quantum-classical equations.

Key References

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- [2] Agostini F., Caprara S., Ciccotti G. 'Do we have a consistent quantum-classical dynamics?' Europhys. Lett. 78 (2007), 30001.

Towards Multi-Component TDDFT for the complete system of electrons and nuclei

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Coauthor(s) : E.K.U. Gross

Environmental decoherence and linearization for nonadiabatic dynamics

David Coker

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Abstract

We discuss the nonadiabatic dynamics of a quantum subsystem coupled to a local environment which is in turn coupled to a bath. The bath causes decoherence of the local environment resulting in the reliability of a low order expansion of the forward and backward propagators in terms of mean and differences between forward and backward paths of the local environment. This leads to a linearized classical-like nonadiabatic dynamics for the local environmental variables coupled to transitions between quantum subsystem states. The approach is explored in applications to model test problems and a realistic model of vibrational dephasing and relaxation in condensed phases.

Proton Transfer in Polar Molecule Nanoclusters

Raymond Kapral

University of Toronto

Coauthor(s) : Hyojoon Kim and Gabriel Hanna

Abstract

The calculation of quantum reaction rates in condensed phase systems from the perspective of quantum-classical Liouville dynamics will be considered. An application to proton transfer in polar molecule nanoclusters will be described. Proton transfer takes place in a molecular complex which is dissolved in a polar molecule cluster. The results of simulations of nonadiabatic reaction rates using a surface-hopping scheme based on quantum-classical Liouville dynamics will be presented. The dynamic and structural factors that influence the rate and reaction mechanism will be discussed and compared with those for bulk systems.

Ab initio excited state MD study of photochemical processes in gas phase and solution using TDDFT

Ivano Tavernelli

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Coauthor(s) : Enrico Tapavicza and Ursula Rothlisberger

Abstract

Photochemical processes are ubiquitous in chemistry and biology. Recently, the study of excited state structure and dynamics of large molecules was made possible by the development of time-dependent DFT (TDDFT) [1-2]. Our computational approach is based on the implementation of TDDFT in the ab initio MD code CPMD, and allows the description of solvation effects through the coupling with a classically described environment (QM/MM). Both real-time propagation and linear response approximations of the TDDFT equations are used for the calculation of excited states properties of molecules in gas phase and solution. Non-adiabatic effects are treated using either the Landau-Zener approximation or a more sophisticated Tully's type algorithm [3]. In the talk, I will also discuss the implementation of the linearized path integral approach (LAND-map [4]) for the evaluation of quantum time correlation functions using DFT/TDDFT surfaces.

Key References

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Theoretical Investigation on the excited-state deactivation mechanism of organic photoscreeners

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Abstract

The photophysics of intramolecular hydrogen bonds in aromatic systems is of particular interest, since it appears to play an essential role for the functionality of so-called photoscreeners and photostabilizers, which are in wide technical use for the protection of organic polymers (and human skin) against degradation by the UV components of sunlight [1]. These organic compounds absorb UV photons with a large cross section and convert the photon energy into heat, without undergoing destructive photochemical reactions. The essential mechanism is ultrafast radiationless decay of the photoexcited singlet state to the electronic ground state. This process is called internal conversion. It converts the potentially dangerous energy of the UV photon into vibrational energy (heat) which is subsequently dissipated into the environment.

While there is rather broad consensus on the essential role of the barrierless excited-state hydrogen transfer (ESIHT) process in organic photostabilizers, the specific mechanisms which are responsible for the ultrafast deactivation of the excited singlet state in these compounds are still largely unknown.

This presentation reports results of calculations of reaction paths and the corresponding energy profiles in excited electronic states of selected organic photostabilizers and photoscreeners using ab initio methods. 2-(2'-hydroxyphenyl)benzotriazole (TIN-H) and salicylic acid (SA) are considered as examples of the former systems, while 5,6-dihydroxyindole (DHI), one of the elementary building blocks of eumelanin, represents the latter. Hydrogen transfer along the intramolecular hydrogen bond and torsion of the hydrogen accepting molecular moiety are identified as the most relevant photochemical reaction coordinates. These reaction paths lead to conical intersection with the electronic ground state and provide a pathway for ultrafast radiationless deactivation [2,3,4].

Key References

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- [4] A.L. Sobolewski and W. Domcke, ChemPhysChem, 2007, 8, 756.

Electron transfer in dye sensitized solar cells

Florian Schiffmann

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Abstract

Of particular interest in dye sensitized solar cells (DSSC) are the electron transfer (ET) processes at the dye/semiconductor interface. Studies have been performed on the ultrafast, nonadiabatic, ET from the dye into the semiconductor. We aim at the back ET reaction, which is assumed to proceed in the adiabatic regime and can be treated with Marcus theory of electron transfer. It is now well known how to calculate the reorganization energy and the free energy within the context of ab initio molecular dynamics [1]. Considerably more difficult is the calculation of the diabatic electronic coupling matrix element using DFT. In order to calculate this parameter we employ the method developed by Wu and Van Voorhis [2] using constrained density functional theory. We combined this approach with density derived atomic point charges (DDAPC) [3] to put a constrained on charge or

spin. With this method it is possible to compute from first principles all parameters of ET in the framework of Marcus theory.

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Nonadiabatic Hybrid QM/MM Molecular Dynamics

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Abstract

The nonadiabatic extension to ab initio molecular dynamics (AIMD) recently developed by Doltsinis and Marx [1,2] makes feasible the study of photoactivated processes in comparatively large systems containing up to a few hundred atoms (e.g. [3,4]). Based on density functional theory this approach couples the Kohn-Sham electronic ground state to the restricted open-shell Kohn-Sham (ROKS) first excited singlet state using Tully's surface hopping method. To extend the applicability of nonadiabatic AIMD to large condensed phase systems consisting of several thousands of atoms, we have connected this method to classical (force field) MD using the CPMD/GROMOS interface developed by Laio et al. [5]. This enables us to describe light-induced phenomena on a much increased length scale, treating only the chromophore quantum-mechanically and the complex environment classically.

In terms of applications the focus of our interest is on polymeric materials containing the azobenzene moiety; these are of increasing interest because of their photoswitchable macroscopic properties due to the light-induced E-Z isomerisation of the central nitrogen double bond [6].

Our new nonadiabatic QM/MM approach is currently being applied to study photoisomerisation in liquid azobenzene as a first step towards modelling optically active materials. In the MM part we use an especially adapted force field which we have optimized for the simulation of azobenzene compounds [7].

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