MO 4: Quantum Chemistry and Molecular Dynamics I

Time: Monday 14:00–16:00　　　　　　　　　　　　　　　　Location: F 102

Invited Talk　　　　　　　　　MO 4.1　Mon 14:00　F 102
Quantum Molecular Dynamics studied with the Multiconfiguration Time-Dependent Hartree (MCTDH) method — •Hans-Dieter Meyer — Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg

The Multiconfiguration Time-Dependent Hartree (MCTDH) method and its multilayer (ML) extension are briefly introduced. The power and the limitations of the MCTDH and ML-MCTDH approaches are discussed. We then will discuss applications of the MCTDH method. 1) IR-spectrum of the Zundel cation, $H_5O_2^+$. The main features of the IR-spectrum are explained and assigned. 2) Tunneling splitting of the proton transfer in malonaldehyde. 3) Photoelectron spectra of naphthalene and antracene, i.e. a study of the vibronic dynamics of naphthalene and antracene cations.

All these studies are full-dimensional ones. The first two studies, which are 15D and 21D, respectively, involve the ground state BO-PES only. However, they employ general potential fits provided by the Bowman group. The first step is hence to employ the n-mode representation to represent the PES in a useful form.

The following examples treat nonadiabatic vibronic dynamics on 6 coupled electronic surfaces. The Hamiltonian used is a model one, namely the well known Vibronic Coupling Hamiltonian (VCH)-model. The studied systems, naphthalene and antracene, are of rather high dimensionality, 48D and 66D. Here ML-MCTDH could show its impressive performance.

MO 4.2　Mon 14:30　F 102
Exact factorization of the time-dependent electron-nuclear wavefunction — •Ali Abedi[1,2], Federica Agostini[1,2], Yasumitsu Suzuki[1,2], and E. K. U. Gross[1,2] — [1]Max-Planck Institut fuer Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany — [2]European Theoretical Spectroscopy Facility (ETSF)

Non-adiabatic couplings between electronic and nuclear motion play a prominent role in many photo-induced processes. As a first step towards a full ab-initio treatment of the coupled electron-nuclear dynamics, we deduce an exact decomposition of the electronic and nuclear degrees of freedom and derive a set of coupled equations of motion for the electrons and nuclei that describe the evolution of the complete electron-nuclear system. These exact equations lead to a rigorous definition of time-dependent potential energy surfaces as well as time-dependent vector potentials. Employing a 1D model-system, we show that the TDPES exhibits a dynamical step that bridges between piecewise adiabatic shapes. We analytically investigate the position of steps and the nature of the switching between the adiabatic pieces of the TDPES.

MO 4.3　Mon 14:45　F 102
Exact factorization of the time-dependent electron-nuclear wave-function: A mixed quantum-classical study — •Federica Agostini, Ali Abedi, Seung Kyu Min, and Eberhard Gross — Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

The solution of the time-dependent Schroedinger equation for a system of interacting electrons and nuclei can be written as a single correlated product of the electronic and nuclear wave-functions. In [1], coupled evolution equations for the two components of the full wavefunction have been derived and it has been proven that they are exactly equivalent to the time-dependent Schroedinger equation. Such separation of electronic and nuclear motion is the natural starting point for systematic approximations, mainly devoted to a classical (or semiclassical) treatment of nuclear degrees of freedom. The procedure for the derivation of such approximation will be described, along with the mixed quantum-classical scheme based on this exact factorization of the time-dependent molecular wave-function. The application to a model system and the comparison with exact results will also be shown.
[1] A. Abedi, N.T. Maitra, E.K.U. Gross, Phys. Rev. Lett. 105, 123002 (2010).

MO 4.4　Mon 15:00　F 102
Following the non-Born-Oppenheimer electron dynamics after photoionization in the Zundel cation — •Zheng Li[1,2],

Mohamed El-Amine Madjet[1], Oriol Vendrell[1], and Robin Santra[1,2] — [1]CFEL, DESY, Notkestr. 85, D-22607 Hamburg, Germany — [2]Department of Physics, University of Hamburg, D-20355 Hamburg, Germany

To investigate the molecular non-Born-Oppenheimer effects, the Coulomb explosion after valence photoionization provides an excellent test-ground, since it is associated with ultrafast non-adiabatic electronic decay, and is experimentally practical with well developed techniques. We have employed full quantum (MCTDH) and quantum-classical approaches to study the Coulomb explosion of the Zundel dication $H_5O_2^{2+}$.

In the present study, we have calculated time-resolved observables that are able to provide a clear picture of the specific electronic and nuclear motions arising exclusively from the non-Born-Oppenheimer effects.

The Coulomb explosion experiments of molecular ions are suitable to be carried out with the XUV free electron laser FLASH, which can address the valence electrons for chemical reactions, meanwhile the high brightness of FEL offers sufficient signal strength, as illustrated experimentally [1].
[1] L. Lammich et al., Phys. Rev. Lett. 105, 253003 (2010).

MO 4.5　Mon 15:15　F 102
Quantumchemical studies and non-adiabatic on-the-fly dynamics on furan, furfural and β-furfural — •Sven Oesterling, Daniel Keefer, Florian Rott, Artur Nenov, and Regina de Vivie-Riedle — Ludwig-Maximilians-Universität, München

Photoexcited furan shows ultrafast relaxation into the groundstate, possible photophysical and photochemical pathways have been discussed, based on TDDFT and DFT/MRCI results.[1,2] We performed quantumchemical studies and non-adiabatic on-the-fly dynamics simulations on CASSCF/PT2 level of theory, on furan, and two of its derivates, furfural and β-furfural.

In furan, we find both pathways to be competing on a sub-100 fs timescale, furfural and β-furfural exhibit a significantly slower decay. The effect of the carbonyl group on the reaction dynamics will be presented. Key factors are the excited state properties, and the conical intersection, whose energetics and structure will be rationalized using the extended two-electron two-orbital theory [3,4].
[1] Fuji et al., J. Chem. Phys. 133, 234303 (2010)
[2] Gavrilov et al., Chem. Phys. 349, (2008) 269-277
[3] Nenov et al., J. Chem. Phys. 135, 034304 (2011)
[4] Nenov et al., J. Chem. Phys. 137, 074101 (2012)

MO 4.6　Mon 15:30　F 102
Exact Potential Energy Surfaces in the Presence of Cornical Intersections — •Seung Kyu Min[1,2], Ali Abedi[1,3], Kwang Soo Kim[2], and Eberhard Gross[1,3] — [1]Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany — [2]Center for Superfunctional Materials, Department of Chemistry, POSTECH, San 31, Hyojadong, Namgu, Pohang 790-784, Korea — [3]European Theoretical Spectroscopy Facility (ETSF)

We study exact potential energy surfaces (EXPESs) that emerge from the exact factorization of the electron-nuclear wavefunction for the static case [1,2]. Employing model systems, we show that where two Born-Oppenheimer surfaces become degenerate at points of conical intersections, exact potential energy surfaces intersect along lines and behave similar to diabatic surfaces. Whereas, when a Born-Oppenheimer (BO) surface is far from other BO surfaces (adiabatic regime), the corresponding exact potential energy surfaces are on top of the BO one except for the region they display spikes at positions of nodes of BO vibrational states [3,4]. In addition, we show how the discontinuity of adiabatic electronic wavefunctions around conical intersections disappears in the exact treatment. We further discuss how this may shed light on our perception of the concept of the Berry phase in molecular systems. We furthermore present EXPESs for various nonadiabatic situations. [1] G. Hunter, Int. J. Quant. Chem. 9, 237 (1975). [2] N. I. Gidopoulos and E. K. U. Gross, arXiv:cond-mat/0502433 (2005). [3] G. Hunter, Int. J. Quant. Chem. 19, 755 (1981). [4] J. Czub and L. Wolniewicz, Mol. Phys. 36, 1301 (1978).

MO 4.7　Mon 15:45　F 102

Quantum dynamics on flexible space grids — •Julius Za-uleck and Regina de Vivie-Riedle — Department Chemie, Ludwig-Maximilians-Universität München

An increasing number of successful ultrafast experiments are reported in the field of complex chemical reactions. For their interpretation quantum dynamical simulations are helpful. Most of them use constant equidistant space or momentum grids. This works well because many efficient algorithms – like the fast Fourier transform – have been developed for such conditions. However, as a result the whole grid that is used during the propagation is needed at each time step. This means that most of the time large parts of the grid carry very little information while they still require the full computing time.

Alternatives are given by flexible grids. One of several approaches uses the de-Broglie-Bohm formulation of quantum mechanics in a quantum trajectory method. This leads to a split of the Schrödinger equation into an imaginary and a real part. The resulting quantum hydrodynamical equations of motion can now be handled in analogy to classical fluid dynamics. A useful tool is the Lagrangian frame of reference. It describes the movement of the space grid along with the fluid elements that represent the wave packet. As a result the space grid is moving with it and can be chosen much smaller than constant grids.

In addition to the general structure of the methods, problems with the maintenance of the grid will be discussed and different procedures will be shown by means of examples.