

MO 6: Theory of Molecular Dynamics

Time: Tuesday 11:00–12:45

Location: N 25

Invited Talk

MO 6.1 Tue 11:00 N 25

Illuminating Molecular Symmetries with Bicircular High-Order-Harmonic Generation — ●DANIEL M. REICH^{1,2} and LARS BOJER MADSEN¹ — ¹Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark — ²Theoretische Physik, Universität Kassel, Heinrich-Plett-Straße 40, 34132 Kassel, Germany

High-order-harmonic generation (HHG) represents one of the primary gateways towards obtaining novel tabletop light sources with unique properties for a wide range of applications. In this work we present a general theory of bicircular HHG from N-fold rotationally symmetric molecules.

Using a rotating frame of reference we predict the complete structure of the high-order-harmonic spectra for arbitrary driving frequency ratios and show how molecular symmetries can be directly identified from the harmonic signal. Our findings reveal that a characteristic fingerprint of rotational molecular symmetries can be universally observed in the ultrafast response of molecules to strong bicircular fields pointing towards the possibility of ultrafast readout of molecular symmetries in, e.g., chemical reactions.

MO 6.2 Tue 11:30 N 25

Interference stabilization for discrete states coupled to a number of continua — ●NICOLA MAYER, OLEG KORNILOV, and MISHA IVANOV — Max Born Institute, Max-Born-Straße 2A, 12489 Berlin, Germany

When two discrete states coupled to a common continuum overlap in energy, a counterintuitive quantum mechanical effect, commonly known as interference stabilization [1] or interference narrowing, manifests itself by stabilizing one of the two states as the coupling strength to the continuum increases. The effect was first proposed and studied for laser-dressed Rydberg states. In our recent work we demonstrated that interference stabilization also takes place in auto-ionizing states of N₂ molecule using a time- and angular-resolved photoelectron spectroscopy experiment [2] [3]. Here we generalize the theory of Ref. [3] for an arbitrary number of continua coupled to two states and tackle the problem of three or more states coupled to two or more continua, drawing analogies with the Stimulated Raman Adiabatic Passage (STIRAP) effect, in search for possible geometric-phase-induced effects on the populations of the states.

Reference:

[1] M.V. Fedorov, Atomic and free electrons in a strong light field. World Scientific, 1998.

[2] M. Eckstein, et al., Phys. Rev. Lett., 116, 153003, 2016.

[3] M. Eckstein, N. Mayer et al., Faraday Discuss., DOI: 10.1039/C6FD00093B, 2016.

MO 6.3 Tue 11:45 N 25

Non-Hermitian Surface Hopping — ●XING GAO¹ and WALTER THIEL² — ¹Max-Planck-Institut für Physik komplexer Systeme — ²Max-Planck-Institut für Kohlenforschung

It is quite a challenge to balance coherence and decoherence effects in non-adiabatic mixed quantum-classical dynamics such as Ehrenfest and surface hopping dynamics. Here we address this challenge by presenting a generalized non-Hermitian equation of motion (nH-EOM) which is derived using the Born-Huang expansion of the total wavefunction and the polar representation of the nuclear factor. Compared to standard trajectory surface hopping, the nH-EOM contains two additional terms, a skew symmetry term $i\Gamma$ with dissipation operator Γ to account for decoherence and a renormalized kinetic-energy term to take care of phase shifts, without destroying the invariance to the choice of representation. Numerically, the nH-EOM can still be solved efficiently using a semiclassical approximation in the framework of Tully's fewest-switches surface hopping (FSSH) algorithm. Applications to molecular collision model Hamiltonians demonstrate improved performance over the standard FSSH approach, through comparison to exact quantum results.

MO 6.4 Tue 12:00 N 25

Current density calculation using quantum hydrodynamics

approach — ●TAMADUR ALBARAGHTEH, KLAUS RENZIEHAUSEN, and INGO BARTH — Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle (Saale), Germany

The inability of the Born-Oppenheimer approximation (BO) to predict accurately electron current densities for dynamics of molecular vibronic wave packets in a single electronic state is a well-known problem [1]. These electron current densities vanish incorrectly within the BO approximation. However, the electron current density is one of the important quantities that characterize the electron motion. Quantum hydrodynamics (QHD) approach has turned out to be the most convenient approach to overcome the BO failure. This approach provides a way to calculate non-zero electron current densities. In this work, one free particle described by a Gaussian wavepacket is used as a test system for the calculation of the current density and other quantities. Our QHD approach to calculate these quantities is to solve the Ehrenfest equation of motion numerically using modern numerical methods, based on computational fluid dynamics (CFD) [2]. The numerical results of different quantities of the system show good agreement with corresponding analytic results. Moreover, we plan to calculate the electron current density of the vibrating H₂⁺ molecule in a single electronic BO state.

[1] I. Barth et al., Chem. Phys. Lett. 481, 118 (2009)

[2] R. J. Leveque, Finite Volume Methods for Hyperbolic Problems, Cambridge University Press, Cambridge (2004)

MO 6.5 Tue 12:15 N 25

Electron-nuclear wave-packet dynamics through a conical intersection: does the electron care? — ●JULIAN ALBERT¹, KILIAN HADER¹, E. K. U. GROSS², and VOLKER ENGEL¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

We investigate the coupled electron-nuclear dynamics in a model system showing a conical intersection (CoIn) between two excited state potential energy surfaces. Within the model, a single electron and nucleus move in two dimensions in an external static field. It is demonstrated that the nuclear density conserves its initial Gaussian shape when passing the CoIn whereas the electronic density remains approximately constant. This is in sharp contrast to the picture which evolves from an analysis within the basis of adiabatic electronic states. There, dramatic changes are seen in the dynamics of the different nuclear components of the total wave function. It is thus documented that neither the nuclear nor the electronic density obtained directly from the wave packet motion in the complete configuration space spanned by electronic and nuclear degrees of freedom, are influenced by the existence of a CoIn.

MO 6.6 Tue 12:30 N 25

Coupled electron-nuclear dynamics: A comparison of methods and dimensionality — ●THOMAS SCHNAPPINGER, JULIUS ZAULECK, ROBERT SIEMERING, and REGINA DE VIVIE-RIEDLE — Department Chemie, LMU München

The purpose of this work is a first comparison of two methods describing a coupled electron-nuclear dynamics: the purely quantum mechanical ansatz NEMol and the TD-DFT based Ehrenfest dynamics. For this purpose the dynamics of (Z)-3-aminoacrolein in the electronic ground state was analyzed. Using different quantum chemical methods the potential profile of tautomerism was calculated and the critical points of the reaction were identified to set up one-dimensional potential energy surfaces along the reaction.

We introduce a novel form of the NEMol ansatz which is formulated for a single electronic state. Using the one-dimensional potential energy surfaces of the tautomerism we are able to calculate the coupled electron-nuclear dynamic.

The comparison between the NEMol ansatz and the TD-DFT Ehrenfest dynamics is so far limited due to the difference in dimensionality. Therefore an approach for one-dimensional TD-DFT Ehrenfest dynamics is presented. In addition a short outlook is provided how to select and evaluate the chosen dimensions for a dynamic simulation.