

MO 18: Theory 3: Quantum Chemistry

Time: Thursday 14:00–15:45

Location: BEBEL SR144

MO 18.1 Thu 14:00 BEBEL SR144

Auger decay of double core holes in small linear molecules — ●LUDGER INHESTER¹, GERRIT GROENHOF², and HELMUT GRUBMÜLLER¹ — ¹Max Planck Institut für biophysikalische Chemie, Göttingen — ²Universität Jyväskylä

Because of its high intensity X-FEL light is able to sequentially photo-ionize multiple core electrons and thus enables one to probe molecules with multiple core holes. Using quantum mechanical ab-initio methods we have investigated the Auger decay of single and double core hole states in small linear molecules, such as acetylene, nitrogen and carbon-monoxide. In our approach we use multi-reference configuration interaction calculation for the bound electrons while the electronic continuum is represented via the single center method, in which the continuum electron is expanded on a radial grid with spherical harmonics[1,2]. We find that the decay rate depends on where the core vacancies are located and that the highest decay rate is obtained if two vacancies are located on the same nucleus. This result is explained by the core hole induced rearrangements of the valence electronic structure. The implications of our findings for single molecule diffractive imaging application with X-FEL's will be discussed.

[1] Inhester et al., JCP 136, 144304 (2012) [2] Inhester et al., JCP 138, 164304 (2013)

MO 18.2 Thu 14:15 BEBEL SR144

Exact Factorization of the Electron-Nuclear Wavefunction: Exact Electronic Potentials in Coupled Electron-Ion Dynamics — ●YASUMITSU SUZUKI¹, ALI ABEDI¹, NEENA MAITRA², KOICHI YAMASHITA³, and E. K. U. GROSS¹ — ¹Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany — ²Department of Physics and Astronomy, Hunter College and the City University of New York, 695 Park Avenue, New York, New York 10065, USA — ³Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

We develop a novel approach to the coupled motion of electrons and ions that focuses on the dynamics of the electronic subsystem. Usually the description of electron dynamics involves an electronic Schrödinger equation where the nuclear degrees of freedom appear as parameters or as classical trajectories. Here we derive the exact Schrödinger equation for the subsystem of electrons, staying within a full quantum treatment of the nuclei. This exact Schrödinger equation features a time-dependent potential energy surface for electrons (e-TDPES). We demonstrate that this exact e-TDPES differs significantly from the electrostatic potential produced by classical or quantum nuclei.

[1] Y. Suzuki, A. Abedi, N. T. Maitra, K. Yamashita and E. K. U. Gross, e-print arXiv:1311.3218v1

MO 18.3 Thu 14:30 BEBEL SR144

Exact factorization of the electron-nuclear wave function: Applications — ●FEDERICA AGOSTINI — Max Planck Institute of Microstructure Physics, Halle, Germany

The exact factorization [1] of the molecular wave function offers a new perspective on the correlated dynamics of electrons and nuclei. In particular, the Hamiltonian generating the nuclear evolution contains time dependent vector and scalar potentials. These potentials are uniquely defined, up to within a gauge transformation, and govern nuclear dynamics, yielding the nuclear wave function. They represent the exact electronic effect on the nuclei.

This reformulation of the time dependent Schroedinger equation is the starting point for the development of approximations, consisting in the classical treatment of only the nuclear degrees of freedom. With this objective in mind, we investigate the properties of the potentials in a model for proton coupled electron transfer. The exact solution of the full quantum mechanical problem gives access to the scalar potential [2,3], in a gauge where the vector potential is zero. We study the features of the potential and we test the performance of the classical approximation, given that the exact effect of the electrons on the nuclei is known.

[1] A. Abedi, N.T. Maitra and E.K.U. Gross, Phys. Rev. Lett. 105 (2010); J. Chem. Phys. 137 (2012) [2] A. Abedi, F. Agostini, Y. Suzuki and E.K.U. Gross, Phys. Rev. Lett. 110 (2013) [3] F. Agostini, A. Abedi, Y. Suzuki and E.K.U. Gross, Mol. Phys. 111 (2013)

MO 18.4 Thu 14:45 BEBEL SR144

The exact time-dependent potential energy surface for the strong field dynamics of H_2^+ — ●ELHAM KHOSRAVI¹, ALI ABEDI², ALEJANDRO SAENZ¹, and E. K. U. GROSS² — ¹Institut für Physik, Humboldt-Universität zu Berlin, Newtonstraße 15, 12489 Berlin, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

It was recently shown [1,2] that the complete wave-function for a system of electrons and nuclei evolving in a time-dependent external potential can be exactly factorized into an electronic wave-function and a nuclear wave-function. The concepts of an exact time-dependent potential energy surface (TDPES) and exact time-dependent vector potential emerge naturally from the formalism. These potentials mediate the couplings between the nuclear and the electronic degrees of freedom in a formally exact way. In this framework, the nuclear dynamics is governed by a Schrödinger equation that contains a TDPES and a time-dependent vector potential. Here we study the concept of the exact TDPES for the H_2^+ molecular ion exposed to a laser field and demonstrate the significance of this concept as a powerful tool in analyzing multiphoton processes.

[1] Ali Abedi, Neepa T. Maitra, and E. K. U. Gross, Phys. Rev. Lett. 105, 123002 (2010)

[2] Ali Abedi, Neepa T. Maitra, and E. K. U. Gross, J. Chem. Phys. 137, 22A530 (2012)

MO 18.5 Thu 15:00 BEBEL SR144

Exact factorization of the time-dependent electron-nuclear wavefunction — ●ALI ABEDI¹, FEDERICA AGOSTINI¹, NEENA MAITRA², and E. K. U. GROSS¹ — ¹Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany — ²Department of Physics and Astronomy, Hunter College and the City University of New York, New York, New York 10065, USA

We present an exact factorization of the complete wavefunction into a purely nuclear part and an electronic wavefunction which parametrically depends on the nuclear configuration. We derive equations of motion for the nuclear and electronic wavefunctions. The nuclear dynamics is governed by a time-dependent Schrödinger equation featuring a vector potential and a potential energy surface. These potentials are unique and give a purely nuclear wave-function yielding the true nuclear N-body density and the true nuclear N-body current density of the full electron-nuclear system. Hence, in the classical limit, the gradient of this exact potential energy surface yields the "correct" classical force on the nuclei [3,4]. Therefore, the exact splitting of electronic and nuclear degrees of freedom lends itself as a rigorous starting point for the systematic development of (semi)classical approximations. Here, we present a novel mixed-quantum-classical algorithm to treat the coupled electron-nuclear motion. [1] A. Abedi, N.T. Maitra, E.K.U. Gross, PRL 105, 123002 (2010). [2] A. Abedi, N.T. Maitra, E.K.U. Gross, JCP 137, 22A530 (2012). [3] A. Abedi, F. Agostini, Y. Suzuki, E.K.U. Gross, PRL 110, 263001 (2013). [4] F. Agostini, A. Abedi, Y. Suzuki and E.K.U. Gross, Mol. Phys. 111, 3625 (2013)

MO 18.6 Thu 15:15 BEBEL SR144

Fixing long range behaviour: range separated functionals — ●ROLF WÜRDEMANN¹ and MICHAEL WALTER^{1,2} — ¹FMF, Uni-Freiburg, Freiburg, Germany — ²IWM, Freiburg, Germany

The description of exchange and correlation energies in density functional theory (DFT) in the local- or semi-local approximation is quite successful. But it also leads to an improper description of the effective potential in the $r \rightarrow \infty$ asymptote. This leads to an improper description of the interactions between s and d electrons in transition metals and problems including charge transfer.

Hartree-Fock theory (HFT) evaluates also non-local contributions to the exchange energy and is also referred as "exact exchange". By its definition HFT is free of delocalisation errors but suffers from the lack of the inclusion of (dynamic) correlation.

Range separating functionals (RSF) use a distance dependent function to switch between HFT and DFT dependent on the spatial distance between the two points under consideration. Thus it is possible to use DFT on short-range and HFT on long-range interaction, correcting the long-range behaviour of DFT. Functionals of this type are also called long-range corrected (LC) functionals. We discuss our im-

plementation of LC using a multi grid technique and show first results.

MO 18.7 Thu 15:30 BEBEL SR144

Reflectance Anisotropy spectrum of water covered Cu(110) surface studied from first principles. — ●AMIRREZA

BAGHBANPOURASL¹, KURT HINGERL¹, and WOLF GERO SCHMIDT² —
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In this contribution we study Reflectance Anisotropy Spectroscopy (RAS) of Cu(110) surface covered with different water structures. Re-

flectance Anisotropy Spectroscopy is a simple and useful optical surface sensitive probe which can be used to study water covered surfaces. Theoretical calculations that are necessary to aid preparing experimental setup and to interpret the results are not present in literature for water covered copper surface. For this purpose we used Density Functional Theory to calculate dielectric constant and then RAS of Cu(110) surface with the latest studied water adsorbed structures. At the end the effect of different adsorption structures on RAS and surface states is studied.