

## MO 8: Theory: Quantum Chemistry

Time: Tuesday 11:00–13:00

Location: PH/HS1

**Invited Talk**

MO 8.1 Tue 11:00 PH/HS1  
**Novel computational approaches to molecular electronic-structure theory** — ●WIM KLOPPER — Karlsruhe Institute of Technology (KIT), Institute of Physical Chemistry, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany — Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

The talk will give an overview of some recent progress made (in the Karlsruhe research group) in the development of computational approaches to molecular electronic-structure theory. These approaches comprise methods that employ explicitly correlated wave functions on the one hand and methods based on a quasirelativistic two-component framework on the other. Concerning explicitly correlated wave functions, we have recently implemented a direct ring-coupled-cluster-doubles (drCCD) method that employs such functions and which yields density-functional electron-correlation energies in the random-phase approximation in the limit of a complete one-electron basis set. Concerning quasirelativistic two-component methods, we have recently implemented a corresponding linear-response, approximate coupled-cluster method (in the CC2 approximation) for the treatment of electronically excited states. These methods have been implemented in the TURBOMOLE program package and examples of their application will be given. The talk will also provide examples of recent applications of other computational methods available in this program package.

MO 8.2 Tue 11:30 PH/HS1

**MC-Potfit: Transforming high-dimensional potential energy surfaces into a sum-of-products form using Monte-Carlo methods** — ●MARKUS SCHRÖDER and HANS-DIETER MEYER — Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg

We present a Monte-Carlo variant of the well known Potfit algorithm [Jäckle *et al.*, J. Chem. Phys. 104, 7974 (1996)] to transform potential energy surfaces into a sum-of-products form. This transformation leads to an enormous reduction of data and in particular to a representation of the potential which is suitable for calculations with the Heidelberg multi-configuration time-dependent Hartree method. The modified Potfit variant uses Monte-Carlo integration techniques and can therefore be used to tackle larger problems than the original Potfit. Furthermore, inclusion of weight functions to emphasize important regions of the potential is straight forward. We present example calculations and discuss benefits and limitations of the algorithm.

MO 8.3 Tue 11:45 PH/HS1

**A relativistic time-dependent density functional study of the excited states of the group 12 dimers (Zn2-Cn2).** — ●OSSAMA KULLIE — Institut für Physik, Universität Kassel

We use the (relativistic) time-dependent density functional (TDDFT) to study the ground-state as well as the excited states corresponding to the atomic asymptotes ( $ns^2 + nsnp$ ), ( $ns^2 + ns(n+1)s$ ) and ( $ns^2 + ns(n+1)p$ ),  $n=4-7$ , for these dimers (Zn2-Cn2) [1]. We analyze the spectrum obtained from all-electron calculations performed with the relativistic Dirac-Coulomb and relativistic spinfree Hamiltonian as implemented in Dirac-Package. A comparison with the literature is given as far as available. A detailed analysis of the spectrum of the dimers is given, including a comparative analysis especially for the relativistic effects, the spin-orbit interaction, and the performance of some well-known density functionals. [1] O. Kullie. J. Chem. Phys. **140**, 024304 (2014). O. Kullie Chem. Phys. **415**, 112 (2013). O. Kullie. (open access) J. At. Mol. Opt. Phys. **2012**, 361947 (2012).

MO 8.4 Tue 12:00 PH/HS1

**Multi-Reference Theoretical Approach to Photoelectron Spectroscopy** — ●GILBERT GRELL, SERGEY I. BOKAREV, and OLIVER KÜHN — Institut für Physik, Universität Rostock, Universitätsplatz 3, D-18055 Rostock, Germany

The L-edge X-ray photoelectron and Auger spectroscopy is a powerful tool for investigating the local electronic structure of transition metal compounds in condensed and gaseous phases. The assignment and analysis of the results obtained for transition metal ions in solution [1] requires high-quality theoretical methods.

Here, we utilize the multi-reference Restricted Active Space SCF

(RASSCF) method together with state interaction (RASSI) for spin-orbit coupling [2], implemented in the MOLCAS program package to obtain high quality wave functions. On this basis, XPS matrix elements are calculated using a Dyson orbital approach [3]. Applications will be presented for aqueous transition metal ions surrounded by the first solvation shell.

1. R. Seidel *et al.* J. Am. Chem. Soc. **134**, 1600 (2012), S. Thürmer *et al.* J. Am. Chem. Soc. **133**, 12528 (2011)
2. P. A. Malmquist *et al.* Chem. Phys. Lett. **357**, 230 (2002)
3. C. Melania Oana *et al.* J. Chem. Phys. **127**, 234106 (2007)

MO 8.5 Tue 12:15 PH/HS1

**Electronic structure calculations of multiple core hole states in molecules** — YAJIANG HAO<sup>1,2</sup>, ●LUDGER INHETER<sup>2</sup>, SANG-KIL SON<sup>2</sup>, and ROBIN SANTRA<sup>2,3</sup> — <sup>1</sup>CFEL, Desy, Hamburg — <sup>2</sup>USTB, Beijing, China — <sup>3</sup>Fachbereich Physik, Universität Hamburg

Newly available x-ray light sources such as X-ray Free Electron Lasers allow one to study highly excited electronic states with one or several core vacancies. These states may appear with significant probability if a sample is exposed to highly intense x-ray radiation and, they may, thus, crucially determine the evolution of radiation damage[1]. Further, spectroscopy of multiple core hole states is of great relevance, because the associated strong chemical shifts reveal detailed information on the surrounding chemical environment[2,3].

For the theoretical modelling of these states a relative large basis set is required to capture the strong electronic relaxation effects upon core ionization. We present a new scheme for the electronic structure calculation of these states based on basis functions obtained by previous atomic Hartree-Fock-Slater calculations[3]. Results are shown for all combinations of core vacancies in the carbon monoxide molecule. By using basis functions adapted to the respective core vacancy states, we show that the number of the basis functions can be reduced while achieving results of similar quality. This reduction makes calculations of multiple core hole states also in larger molecules feasible.

- [1] Young *et al.* Nature **466**, 56 (2010) [2] Cederbaum *et al.* JCP **85**, 6513 (1986) [3] Berrah *et al.* PNAS **108**, 16912 (2011) [4] Son *et al.* PRA **83**, 033402 (2011)

MO 8.6 Tue 12:30 PH/HS1

**Population dynamics, decoherence and wave packet splitting: The essential features of non-adiabatic process from a novel trajectory-based quantum-classical method** — ●SEUNG KYU MIN, FEDERICA AGOSTINI, and E. K. U. GROSS — Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

We present a novel quantum-classical algorithm to non-adiabatic dynamics that is deduced from the coupled electronic and nuclear equations in turn derived in the framework of the exact factorization[1] of the electron-nuclear wave function. The aim is to devise a trajectory-based procedure which is free of the shortcomings from the conventional approaches and therefore able to capture the basic physics of non-adiabatic process. The theoretical derivation will be supported by numerical results that are compared to quantum mechanical calculations[2].

- [1] A. Abedi, N.T. Maitra, and E.K.U.Gross, Phys. Rev. Lett. **105**, 123002 (2010); J. Chem. Phys. **137**, 22A530 (2012). [2] S.K. Min, F. Agostini, and E.K.U. Gross, in preparation.

MO 8.7 Tue 12:45 PH/HS1

**Using ICD for structural analysis of clusters: A case study on NeAr clusters** — ●ELKE FASSHAUER<sup>1</sup>, MARKO FÖRSTEL<sup>2</sup>, SEBASTIAN PALLMANN<sup>3</sup>, MARKUS PERNPOINTNER<sup>3</sup>, and UWE HERGENHAHN<sup>4</sup> — <sup>1</sup>CTCC, Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway — <sup>2</sup>University of Hawai'i at Manoa, 96816 HI Honolulu, USA — <sup>3</sup>Theoretische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany — <sup>4</sup>Max Planck Institute for Plasma Physics, 17491 Greifswald, Germany

We present a method to utilize Interatomic Coulombic Decay (ICD) to retrieve information about mean geometric structures of heteronuclear clusters. It is based on observation and modelling of competing ICD channels, which involve the same initial vacancy, but energetically dif-

ferent final states with vacancies in different components of the cluster. Using binary rare gas clusters of Ne and Ar as an example, we measure the relative intensity of ICD into  $(\text{Ne}^+)_2$  and  $\text{Ne}^+\text{Ar}^+$  final states with spectroscopically well separated ICD peaks. We compare in detail the experimental ratios of the Ne-Ne and Ne-Ar ICD contributions and their positions and widths to values calculated for a diverse set of possible structures. We conclude that NeAr clusters exhibit a core-shell

structure with an argon core surrounded by complete neon shells and, possibly, further incomplete shell of neon atoms for the experimental conditions investigated. Our analysis allows to differentiate between clusters of similar size and stoichiometric Ar content, but different internal structure. We find evidence for ICD of  $\text{Ne } 2s^{-1}$ , producing  $\text{Ar}^+$  vacancies in the second coordination shell of the initial site.