

MO 3: Quantum Chemistry

Time: Monday 14:00–16:00

Location: V38.02

Invited Talk

MO 3.1 Mon 14:00 V38.02

Quantum chemical description of photo-induced molecular processes — ●ANDREAS DREUW — Interdisziplinäres Zentrum für wissenschaftliches Rechnen, Universität Heidelberg, Deutschland

The development of quantum chemical methods and their application to photo-induced processes in chemistry, biology and physics is one of the most active research fields of contemporary theoretical chemistry. Here, we review briefly existing theoretical approaches and own developments in this field focussing on time-dependent density functional theory and the algebraic diagrammatic construction (ADC) of the polarisation propagator. It will be shown how quantum chemical calculation can lead to an in depth understanding of electronic spectra. Results for photo-electron spectra of small molecules will be shown and the two-photon absorption spectrum of octatetraene will be analyzed.

MO 3.2 Mon 14:30 V38.02

Static and Frequency Dependent Dipole Polarizabilities from the Ground-State Electron Density — ●VIVEKANAND GOBRE¹, ROBERT DiSTASIO JR.², MATTHIAS SCHEFFLER¹, and ALEXANDRE TKATCHENKO¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Princeton University, Princeton, NJ, USA

Molecular polarizability is an essential observable, and its accurate determination is important, e.g., for calculation of van der Waals interactions. Accurate polarizability calculations in principle require computationally expensive electronic structure methods with an explicit treatment of many-electron excitations. These methods can only be applied to systems with less than about 100 atoms. However, one is often faced with the problem of computing polarizabilities for large systems with thousands of atoms. We present a parameter-free computationally efficient approach to calculate accurate static and frequency dependent polarizabilities for molecules and non-metallic solids. Specifically, we link the TS-vdW [1] method, which accurately treats hybridization effects, with the self-consistent screening equation from classical electrodynamics [2]. Using only the electron density and reference data for the free atoms, we obtain an accuracy of about 7% for both static polarizabilities and van der Waals coefficients for a wide variety of systems. We illustrate the interplay of hybridization and long-range electrostatic screening effects for the polarizability of large proteins and condensed-matter systems. [1] A. Tkatchenko and M. Scheffler, PRL **102**, 073005 (2009); [2] B. U. Felderhof, Physica **76**, 486 (1974).

MO 3.3 Mon 14:45 V38.02

Relativistic time-dependent density functional theory and excited states calculations for the Zn₂ and Cd₂ dimers. — ●OSSAMA KULLIE — CNRS et Université de Strasbourg, Institut de Chimie, Laboratoire de Chimie Quantique, 1 Rue Blaise Pascal, F-67008 STRASBOURG cedex, France. ossama.kullie@unistra.fr

In this work I present a (time-dependent) density functional study of the low-lying excited states as well the ground states of the zinc and cadmium dimers Zn₂ and Cd₂. I analyze the spectrum of the dimers obtained from all electrons calculations which are performed using time-dependent density functional with a relativistic 4-components-, and spin-free-Hamiltonian [1]. I will show results for different well-known density functional approximations, in comparing with literature and experimental values, the results are very encouraging, especially for the lowest excited states of these dimers. However, the results show that only the long-range corrected functionals such CAMB3LYP gives the correct asymptotic behavior for the higher states, for which the best result is obtained, and a comparable result is obtained from PBE0 functional. An outlook for Hg₂ and possibly Cn₂ dimers will be given. [1] O. Kullie, to be published in JPB (2012).

MO 3.4 Mon 15:00 V38.02

Auger spectrum of a water molecule after single and double core ionization — ●LUDGER INHESTER, CARL F. BURMEISTER, GERIT GROENHOF, and HELMUT GRUBMÜLLER — Max Planck Institut für biophysikalische Chemie, Göttingen

The high intensity of Free Electron Lasers (FEL) opens up the possibility to do single-shot molecule scattering experiments. However, even for small molecules radiation damage induced by absorption of high intense x-ray sources is not yet fully understood. To provide insight

into this process, we have studied the dynamics of a water molecule in single and double core ionized states by means of electronic transition rate calculations and ab initio molecular dynamics (MD) simulations. From MD trajectories photoionization and Auger transition rates were computed based on electronic continuum wavefunctions obtained by explicit integration of the coupled radial Schrödinger equations. To account for the nuclear dynamics during the core hole lifetime the calculated electron emission spectra for different molecular geometries were accumulated according to time-dependent populations.

We find that, in contrast to the single core ionized water molecule, the nuclear dynamics for the double core ionized water molecule during the core hole lifetime strongly affects the resulting electron emission spectra. In addition, the lifetime of the double core ionized water was found to be significantly shorter than half of the single core hole lifetime.

MO 3.5 Mon 15:15 V38.02

Theoretical investigation of the X-ray adsorption spectra (XAS) of charged chromium-gold clusters using DFT. — ●ROLF WÜRDEMANN, KLAUS ZIMMERMANN, and MICHAEL WALTER — Freiburger Materialforschungszentrum, Freiburg, Germany

Current research using X-ray adsorption spectroscopy (XAS) exhibits a interesting behaviour of the Au₂Cr⁺ molecule. While one would expect, that the XAS-spectrum of the charged Au₂Cr⁺ dimer differs from the XAS-spectrum of the neutral chromium atom, the spectra are nearly identical. This effect is also known from the charged chromium dimer, where the spectra of the charged dimer and the neutral atom where nearly identical.

Keeping this in mind, we discuss the magnetic ordering, potential energy surface (PES), binding energies and -distances of the charged Au₂Cr⁺ molecule using DFT and compare this with other small Au_nCr⁺ molecules (n<=5) and the charged chromium dimer.

MO 3.6 Mon 15:30 V38.02

Theoretical study of Ir(III) based systems for photocatalytic water splitting — ●SERGEY BOKAREV, OLGA BOKAREVA, and OLIVER KÜHN — Institut für Physik, Universität Rostock, Rostock, Deutschland

Photocatalytic water splitting into hydrogen and oxygen is a very attractive direction in the search for new energy sources. One of the schemes for a homogeneous water splitting solar cell involves an Ir(III) containing photo-sensitizer, a Fe(II) catalyst, and the sacrificial reductant [1]. In the present work, we focused on the first stage of the process involving the structure of the ground and lowest excited electronic states of [Ir(ppy)₂(bpy)]⁺ and a number of derivatives in oxidized and reduced forms and their interaction with a sacrificial reductant. Based on the results of TDDFT (LC-BLYP) and CASSCF calculations we assigned the bands in the UV-Vis absorption spectrum and proposed a scheme for the photophysical and photochemical processes involving the lowest excited states of Ir(III) photosensitizers. 1. F. Gärtner et al. Angew. Chem. Int. Ed. 2009, V. 48, P. 9962.

MO 3.7 Mon 15:45 V38.02

DFT Study of Charged Gold Clusters in Different Environments — ●ALEXANDER HELD and MICHAEL WALTER — FMF Uni Freiburg, Germany

The charge dependent cluster capacitance $C(z)$ of gold nanoparticles is investigated in different environments using density functional theory (DFT) calculations.

In the gas phase, $C(z)$ is influenced primarily by electronic shell closing effects and the spatial extent of the excess charge. For gold nanoparticles prepared in a wet chemical process, the ligands may affect the cluster capacitance in different ways. Recent experimental results show evidence for quantized charging effects of quasi-unprotected gold nanoparticles in the ionic liquid [C₄mim][BF₄] for the first time. A peak like shape of $C(z)$ has been observed. This feature is reproduced by our DFT model calculations and is found to originate from a polarity inversion of the ionic liquid surrounding the nanoparticles [1].

Furthermore, the DFT results are interpreted with an electrostatic model. Within the parameters of this model, different shapes of $C(z)$ occur, suggesting further experimental investigations and comparison to other theoretical approaches.

[1] S. F. L. Mertens, C. Vollmer, A. Held, M. H. Aguirre, M. Walter, C. Janiak and T. Wandlowski, *Angew. Chem. Int. Ed.* 2011, 41, 9735 | – 9738