MO 2: Theory: Quantum Chemistry and Molecular Dynamics

Time: Monday 10:30–13:00 Location: MER 02

MO 2.1 Mon 10:30 MER 02

Time-dependent density functional and excited states calculations for the group 12 dimers (Zn2,Cd2,Hg2) — •Ossama Kullie[1] and Trond Saue[2] — [1]Institute de Quantique Chimie, Uni Strasbourg, 4, rue de Blais Pascal, 67000 Strasbourg, France. — [2]Laboratoire de Chimie et Physique Quantiques, Université de Toulouse 3 (Paul Sabatier). Toulouse, France.

In this talk I will present a time-dependent density functional (TDDFT) calculations for the lower excited states of the group 12 dimers (Zn2,Cd2,Hg2) based on a response formalism, we employ the adiabatic approximation with approximate functionals and the 4-component relativistic Hamiltonian, with and without spin-orbit coupling included. These dimers have been considered candidates for excimer lasers since the ground-states are van der Waals dimers and the excited states are covalently bound. The calculations are preformed using the DIRAC-package [1]. I will discuss the performance of TDDFT using different density functional approximations like GGA's. [1] A relativistic ab initio electronic structure program. Release DIRAC10 (2010), http://dirac.chem.vu.nl.

MO 2.2 Mon 10:45 MER 02

Screening of possible reactants to isolate a stable titantiumimidospecies — •Christian Lasar, Ruediger Beckhaus, and Thorsten Klüner — Carl von Ossietzky Universität, Oldenburg, Deutschland

Titaniumimidocomplexes play an important role in many chemical reactions. To isolate a stable imido species the reaction of bis(η^5 : η^1-pentafulven)titaniumcomplexes with amines was analysed.[1] In this study free gibbs energies were calculated with the B3LYP-functional and a 6-31G* basis set for different amines. There are several possible reaction products which have to be taken into consideration. The protonation of the exocyclic carbon atoms of the two coordinated fulven ligands by the amine can take place on only one or on both ligands. This leads to the monoamide or the imidospecies. Due to the high reactivity of the titanium complexes against amines, the reaction can not be controlled by the given äquivalents. Due to this fact the diamide can also be formed. To stabilise the imido species it is necessary to saturate the fourth coordination center of the titanium atom. This can be done by substituting the amines with pyridine. Through the variation of the properties of the amine, different amines were found which stabilise the imidospecies with respect to all other reaction products. Those amines were finally used for synthesis.

1 T.Janssen, R.Severin, M.Diekmann, M.Friedemann, D.Haase, W.Saak, S.Doye, R.Beckhaus, Organometallics, 2010, 29, 1806-1817.

MO 2.3 Mon 11:00 MER 02

Pt_2^{6+} dumbbells: Calculated Structure and properties of $Gd_2[Pt_2(SO_4)_4(HSO_4)_2](HSO_4)_2$ — •Wilke Dononelli, Thorsten Klüner, and Mathias S. Wickleder — Institut für Reine und Angewandte Chemie, Carl von Ossietzky Universität Oldenburg, Ammerländer Heerstraße 114-118, 26129 Oldenburg, Germany

Red single crystals of $Gd_2[Pt_2(SO_4)_4(HSO_4)_2](HSO_4)_2$ were obtained by reaction of $[Gd(NO_3)(H_2O)_7][PtCl_6]\cdot 4H_2O$ with sulfuric acid at 320 °C in a sealed glass ampoule by Arndt and Wickleder.[1] In the crystal structure Pt_2^{6+} dumbbells are coordinated by four chelating sulfate groups and two monodentate hydrogen sulfate ions. [1] At first geometry optimizations of the $[Pt_2(SO_4)_4(HSO_4)_2]^{4-}$ moiety on the Hatree-Fock (HF), MP2 and DFT level of theory, using the B3LYP and PBE0-functional, respectively, were performed. Then, the IR- and Raman-spectra were calculated. Since the complete $Gd_2[Pt_2(SO_4)_4(HSO_4)_2](HSO_4)_2$ system is quite large (more than 4000 basis functions using a 6-31G* basis set), semi-empirical methods (PM6) were used as well. In order to investigate the influence of the ligands surrounding the Pt_2^{6+} dumbbells the compounds $[Pt_2(SO_4)_4(HSO_4)_2]^{4-}$, $[Pt_2(SO_4)_4(H_2O)_2]^{2-}$, $[Pt_2(SO_4)_4(C_6H_4(SO_3)_2)_2]^{4-}$ and $Pt_2(C_2H_3O_2)_6$ were calculated on the Hatree-Fock (HF), MP2 and DFT level of theory.

[1] A. Arndt, M. S. Wickleder, *Z. Anorg. Allg. Chem.* 2008, 369–372

MO 2.4 Mon 11:15 MER 02

Ab initio and DFT Calculations of the structure, properties and aromaticity of HATN derivates — •Florian Habecker and Thorsten Klüner — Carl von Ossietzky Universität Oldenburg, Ammerländer Heerstr. 114-118, 26129 Oldenburg, Germany

In this study the aromatic heterocyclic compounds hexaazatrinaphtylene (dihydrodiquinoxalio[2,3-a:2',3'- c]phenazine, HATN) and its sixfold methylatet derivate (2,3,8,9,14,15-hexamethyldiquinoxalio[2,3-a:2',3'-c]phenazine, $HATNMe_6$) together with their anti-aromatic derivates 5,18-dihydrodiquinoxalio[2,3-a:2',3'-c]phenazine (H_2HATN) and 2,3,8,9,14,15-hexamethyl-5,18-dihydrodiquinoxalio[2,3-a:2',3'- c]-phenazine ($H_2HATNMe_6$) have been investigated by ab initio and density functional theory (DFT) calculations. Different methods, such as HF, MP2 and various functionals (B3LYP, PBE and PBE0) were applied with various basis sets, e.g. 6-31G*, 6-311G**, cc-pVDZ and cc-pVTZ, respectively. The aim was to determine the structure and properties of all four heterocyclic compounds and to gain insight into the selective, reductive N-hydrogenation of one bisazine moiety of the hexaazatrinaphtylene derivates, especially concerning the formation of an antiaromatic system. Hence, calculations of the ultraviolet-visible and the infrared spectrum on PBE0/cc-pVDZ level were carried out, too. Additional calculations of the structural phenazine unit of the HATN derivates were performed revealing similar results concerning the structural and electronic alterations. Therefore, our theoretical findings are valid for a large group of derivates of the phenazine structure.

MO 2.5 Mon 11:30 MER 02

First-principles GW calculations for the DNA/RNA nucleobases and for molecules of interest for organic photovoltaics — •Carina Faber[1,2], Claudio Attaccalite[2], Valerio Olevano[2], Erich Runge[1], and Xavier Blase[2] — [1]Institut für Physik, Technische Universität Ilmenau, 98693 Ilmenau, Germany, — [2]Institut Néel, CNRS and Université Joseph Fourier, BP 166, 38042 Grenoble Cedex 9, France

We evaluate the performance of ab-initio GW calculations for the ionization energies (IEs) and HOMO-LUMO gaps of thirteen molecules of interest for organic photovoltaics. Standard G0W0 calculations significantly improve the IE and the bandgap as compared to DFT Kohn-Sham results, but the calculated quasiparticle values remain too small as a result of overscreening. Starting from HF-like eigenvalues yields much better results with only 2-4% deviation from experiment and is equivalent to performing self-consistency on the eigenvalues. As further test, we study the quasiparticle properties of the DNA/RNA nucleobases. Starting from KS-eigenstates obtained with (semi)local functionals, self-consistency on the eigenvalues allows to obtain IEs and electron affinities within an average 0.1 eV and 0.2 eV error, respectively, with respect to coupled-cluster and multi-configurational perturbative quantum chemistry approaches. GW calculations predict the correct pi-character of the HOMO as result of several level crossings between DFT and GW calculations. Our calculations are based on an efficient Gaussian-basis implementation of GW with explicit treatment of the dynamical screening through contour deformation techniques.

MO 2.6 Mon 11:45 MER 02

Theoretical investigation of the X-ray adsorption spectra (XAS) of the charged chromium dimer using DFT. — •Rolf Würdemann and Michael Walter — Freiburger Materialforschungszentrum, Freiburg, Germany

Current research using X-ray adsorption spectroscopy (XAS) exhibits a interesting behaviour of the Cr_2^+ dimer. While one would expect, that the XAS-spectrum of the charged Cr_2^+ dimer differs from the XAS-spectrum of the neutral atom, the spectra are nearly identical.

Keeping this in mind, we discuss the magnetic ordering, potential energy surface (PES), binding energies and -distances of the charged chromium dimer using DFT with the use of different functionals and compare this to other published work. We also discuss the situation in charged small gold-chromium clusters (Au_nCr^+, $n \leq 7$).

MO 2.7 Mon 12:00 MER 02

Kinetic-energy density dependent functionals within the relativistic DFT — •Josef Anton and Timo Jacob — Institut für Elektrochemie, Universität Ulm, 89069 Ulm

Density functional theory is the workhorse in many studies related to modern computational quantum chemistry. It allows calculating many ground state and excited state properties of molecules, clusters, and surfaces with reasonable accuracy, though the quality of such calculations very much depends on the choice of the exchange-correlation functional. For instance the spectroscopic properties of almost all closed-shell molecules or clusters could be very well described by functionals, which only depend on the density and its gradient. These functionals, however, are often not capable to describe properties of open-shell systems where the coupling of the electrons' spins is not negligible anymore. In non-relativistic DFT this finally led to the development of spin-density functionals. However, some years ago Perdew [1] introduced the idea of using the kinetic-energy density as third independent variable in the xc-functionals in order to improve the description of dispersion interactions. In this presentation we will discuss a relativistic generalization of this idea and the implementation in our fully relativistic DFT-code [2]. The approach is then applied to noble gas dimers and other vdW systems, followed by a comparison of our results to other calculations and experiments.

[1] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, *Phys. Rev. Lett.*, **91**, 146401 (2003).

[2] J. Anton, B. Fricke, E. Engel, *Phys. Rev. A*, **69**, 012505 (2004).

MO 2.8 Mon 12:15 MER 02

Theory corroborates experiment: a relativistic study of the isotopic field shift in rotational spectra — •Stefan Knecht[1] and Trond Saue[2] — [1]Institut for Fysik og Kemi, Syddansk Universitet, Odense, Danmark — [2]Laboratoire de Physique Quantique, CNRS/Université Paul Sabatier, Toulouse, France

A number of distinctive molecular properties such as the nuclear magnetic resonance shielding parameters, Mössbauer isomer shifts and isotopic field shift probe the electronic density near the nuclei. Their appealing feature is that they provide local information at a nuclear center with great sensitivity to the chemical environment.

Here, we present accurate theoretical estimates of the isotopic field shift in rotational spectra of lead chalcogenides PbX (X=S,Se,Te) and thallium halides TlY (Y=F,Cl,Br,I) derived from 4-component relativistic Coupled-Cluster and Density Functional Theory calculations. We compare our findings [1] with the early experimental work [2,3] on this correction term to the Dunham coefficient Y_{01}, which is due to a finite nuclear charge distribution, as well as with other theoretical predictions [4]. It is highlighted that a sophisticated relativistic approach is required to achieve an excellent agreement with the experiment.

[1] S. Knecht and T. Saue, *in preparation* (2010).

[2] J. Schlembach and E. Tiemann, *Chem. Phys.* 68 (1982) 21.

[3] H. Knöckel, T. Kröckertskothen, and E. Tiemann, *Chem. Phys.* 93 (1985) 349.

[4] K. C. Etchison, C. T. Dewberry, and S. A. Cooke, *Chem. Phys.* 342 (2007) 71.

MO 2.9 Mon 12:30 MER 02

Multilayer multi-configuration time-dependent Hartree method: implementation and applications to a Henon-Heiles Hamiltonian and to pyrazine. — •Oriol Vendrell[1] and Hans-Dieter Meyer[2] — [1]Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany — [2]Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

The multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) method is discussed and a fully general implementation for any number of layers based on the recursive ML-MCTDH algorithm given by Manthe [J. Chem. Phys. **128**, 164116 (2008)] is presented. The method is applied first to a generalized Henon-Heiles (HH) Hamiltonian. For 6D HH the overhead of ML-MCTDH makes the method slower than MCTDH, but for 18D HH ML-MCTDH starts to be competitive. We report as well 1458D time propagations based on the HH Hamiltonian using a seven layer scheme. The photoabsorption spectrum of pyrazine computed with the 24D Hamiltonian of Raab *et. al.* [J. Chem. Phys. **110**, 936 (1999)] provides a realistic molecular test case for the method. Quick and small ML-MCTDH calculations needing a fraction of the time and resources of reference MCTDH calculations provide already spectra with all the correct features. Accepting slightly larger deviations, the calculation can be accelerated to take only 7 minutes. When pushing the method towards convergence, results of similar quality than the best available MCTDH benchmark are obtained faster and with a much more compact wavefunction.

MO 2.10 Mon 12:45 MER 02

An accurate representation of the *ab initio* potential-energy surface of the water dimer by neural networks — •Tobias Morawietz, Vikas Sharma, and Jörg Behler — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Understanding the properties of water still represents a significant challenge for theory and experiment. Investigations using computer simulations, e.g. by molecular dynamics, require a reliable description of the atomic interactions. A large number of efficient potentials for water has been published in past decades. A promising way for the construction of potential-energy surfaces (PESs) is based on artificial neural networks (NNs). These flexible functions allow to interpolate a set of energies and forces obtained from electronic structure calculations very accurately. We present results for the water dimer as a first step towards the construction of a NN potential for liquid water. The properties of the potential are analyzed and the obtained results are compared to electronic structure calculations.