26th Winter School in Theoretical Chemistry

Accurate Molecular Structure by Experiment and Theory

Department of Chemistry
University of Helsinki
Finland

December 13-16 2010

Programme

Monday 13.12 **Morning: B123** **Afternoon: A129**		**Tuesday 14.12** **Whole Day: A129**		**Wednesday 15.12** **Whole Day: B123**		**Thursday 16.12** **Whole Day: CK112**	
09:15	Welcome	09:00	Gauss 1	08:15	Stanton 2	08:15	Allen 2
09:30	Stanton 1	09:45	Gauss 2	09:00	Girichev 2	09:00	Grabow 2
10:15	Oberhammer 1	10:30	Break	09:45	Break	09:45	Break
11:00	Break	11:00	Helgaker 3	10:00	Grabow 1	10:00	Fromager 1
11:30	Mitzel 1	11:45	Lunch	10:45	Allen 1	10:45	Fromager 2
12:15	Lunch	13:00	Puzzarini 1	11:15	Break	11:30	Break
13:15	Helgaker 1	13:45	Puzzarini 2	11:30	Lignell 1	11:45	Oberhammer 3
14:00	Helgaker 2	14:30	Break	12:15	Lunch	12:30	Discussion
14:45	Break	15:00	Helgaker 4	Free Afternoon		13:00	Lunch/ Departure
15:15	Oberhammer 2	15:45	Girichev 1				
16:00	Break	16:30	Break				
17:00	Posters	16:45	Mitzel 2				
		18:00	Div. of Comp. Chem (meeting in finnish)				

Lecture Halls

Due to final exams taking place at our Department, we are forced to move around a bit. We hope you will not be confused by this. The local participants will help you to find the lecture halls. Please follow them.

B123 is in Exactum, there will be signs guiding you to the lecture hall. A129 is in Chemicum, this is also were the poster session will be held. Please put up your poster before 6 pm on Monday and remove it before departure. CK112 is also in Exactum. Please also note, that we are forced to start 08:15 on Wednesday and Thursday. We hope you will be awake!

To help you find you way arund the campus, we include a map of the campus area. From it you will find the way to Exactum (Mathematics and Computer Science Building) and Chemicum (Chemistry Building).

We will inform the janitors of the school. If you get lost, please also ask them for advice. They can be found in a booth in the entrance hall of Exactum and Chemicum. Keep this schedule with you, so you remember the room numbers!

Lectures

Wesley Allen, University of Georgia

- Interplay of derivatives of the eletronic and nuclear repulsion energy
  The nonzero force dilemma (1h)
- Fulminic acid, a quasilinear spectacle & Semiexperimental structures of amino acids (1h)

Emmanuel Fromager, Université de Strasbourg

- Investigating rigourous combinations of wave function and density-functional theories (1h)
- Combining wave function and density-functional theories
  by means of range separation: progress report" (1h)

Jürgen Gauss, Johannes Gutenberg-Universität Mainz

- Coupled-Cluster Theory as a Tool for High-Accuracy Quantum-Chemical Calculations (1h)
- Accuracy of Computed Equilibrium Geometries (1h)

Georgiy V. Girichev, Ivanovo State University of Chemistry and Technology

- High Temperature Gas-Phase Electron Diffraction (1h)
- Molecular Structure of Lanthanide Trihalides (1h)

Jens-Uwe Grabow, Leibniz Universität Hannover

- Accurate Molecular Structure, Dynamics and Precise Physics
  from Molecular Rotation Spectra (1h)
- Microwave Coherence Spectroscopy (1h)

Trygve Helgaker, University of Oslo

- Geometry optimization (2h)
- The exhaustion of the Schrödinger equation (1h)
- Molecules in strong magnetic fields (1h)

Hanna Lignell, University of California, Irvine

- Structure, isomerization, and ionization of dinitrogen tetroxide
  on water (ice) and silica surfaces (1h)

Norbert Mitzel, Universität Bielefeld

- The symbiosis between theory and experiment in gas phase structure determination:
  Methods for combination to combine the best from both worlds (1h)
- Solid and gas-phase structures: the whole is more than the sum of its parts (1h)

Heinz Oberhammer, Universität Tübingen

- Gas Electron Difraction: Theory (1h)
- Gas Electron Diffraction: Experiment (1h)
- Gas Electron Diffraction and Quantum Chemical Calculations (1h)

Cristina Puzzarini, Università di Bologna

- Introductory lesson on rotational spectroscopy (1h)
- Rotational spectroscopy at work (1h)

John Stanton, The University of Texas at Austin

- The meaning(s) of molecular structure (1h)
- “Semi-experimental” structures (1h)

Posters

Molecular Dipole Effects on Tuning Electron Transfer in a Porphine-Quinone Complex: A DFT and TDDFT Study

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Presenting author: Pekka Aittala

We have computationally investigated how the electric fields induced by molecular dipoles of one (PQ±1P) or two (PQ±2P) short ambient helical Aib8 homopeptide chains influence the ground state electronic structure and the excited states of a porphine 2,5-dimethyl-1,4-benzoquinone (PQ) complex by using density functional theory (DFT) and time-dependent DFT (TDDFT) with the BH&HLYP and the CAM-B3LYP functionals. Two different relative orientations of the ambient Aib8 chains with respect to the PQ complex have been studied: one in which the C-terminus is on quinone side of the PQ complex and the field induced by the peptides is directed from porphine to quinone and one in which the orientation is the opposite corresponding to two opposite field directions.

The electric field induced by the molecular dipoles of the ambient peptides from their N-terminus to the C-terminus is of the order of magnitude of 10^9 V/m and is practically parallel to the helical axis. The overall effect of the peptide-induced electric field on the energies of the MOs of the PQ complex is very similar to that of the external electrostatic field [1]. However, depending on the relative orientation with respect to the PQ complex the molecular dipoles of the ambient peptides affect the MOs localized either on porphine or quinone, whereas the external electrostatic field affects the energies of the MOs localized on quinone only. Additionally, the molecular dipoles of the peptides affect the HOMO-LUMO gaps of the PQ-1P and PQ-2P systems more strongly than those of the PQ+1P and PQ+2P systems. The influences of the strengths of the electric fields induced by the molecular dipoles of the ambient helical peptides are stronger than expected on the basis of the previous electrostatic field calculations [1,2].

The perturbation generated by the ambient Aib8 peptides affects the energies of the locally excited porphine Q and B states of the PQ complex clearly less than that of the lowest CT state. One Aib8 chain with the N-terminus oriented to the quinone side of the PQ complex affects the energy of the CT state by roughly the same amount as the external electrostatic field of $0.8 \cdot 10^9$ V/m whereas one Aib8 chain with the C-terminus oriented to the quinone side has roughly the same effect as the external electrostatic field of +0.4×10^9 V/m. Because the induced electric field has a similar effect on the energies of the excited states of the PQ complex as the external electrostatic field, it would be possible to control the crossings of the PECs of the locally excited porphine states (Q and B) and the lowest CT state by using the perturbation created by ambient Aib8 peptide chains. Hence, the ambient Aib8 homopeptides can be used to control the ET in the PQ complex.

[1] P.J. Aittala, O. Cramariuc, T.I. Hukka, J. Chem. Theory Comput. 2010, 6, 805.
[2] P.J. Aittala, O. Cramariuc, T.I. Hukka, Chem. Phys. Lett. In Press.

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A robust genetic algorithm for the structure optimization of metal clusters: structure search aided by electron diffraction data

ABSTRACT

Elucidation of the physical and chemical properties of gold clusters paves the way for their application in novel nanotechnological devices. A prerequisite for this understanding, however, is the efficient determination of cluster structures. Some challenges faced by global minimum structure searches – such as the well-utilized genetic algorithm (GA) optimization scheme – include flat potential energy surfaces and the existence of multiple local minima, the number of which increases with increasing number of atoms in the cluster. In this study, the convergence of the GA search strategy is accelerated as follows: the experimental electron scattering data is incorporated into the fitness function that selects which candidate structures are "fit" enough to serve as parents for the succeeding generations. The fitness criterion is based upon the agreement of the theoretical scattering intensities with its experimental counterpart. The combined theoretical and experimental approach, consisting of a density functional theory (DFT) GA-based optimization and trapped ion electron diffraction (TIED) data, is used to assign gold cluster anion (Au_{21}^- and Au_{22}^-) structures.

Growth of polycyclic aromatic hydrocarbons: Reactions under different temperature regimes

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Presenting author: Robert Barthel

Hydrocarbons, in particular polycyclic aromatic hydrocarbons (PAHs), have been long discussed to be carriers of many interstellar infrared (IR) emission bands and ultraviolet (UV) absorption features. Although the formation of PAHs in circumstellar envelopes (CSEs) is supposed to be similar to pyrolysis and combustion processes, the origin of PAHs in dense phases of the interstellar medium (such as molecular clouds), i.e., formation/growth versus migration from CSEs, remains unclear.

We present reaction pathways for the growth of cationic and neutral PAHs and hydrocarbons under ultracold, interstellar conditions and hot, circumstellar conditions, respectively.
All equilibrium and transition state (TS) structures are computed at DFT-B3LYP and MP2 level of theory using the def2-TZVP basis set. Due to complexity of the PES, TS search is based on the nudged elastic band method. Energies and enthalpies relate to single point calculations using explicitly correlated CCSD(T) and the cc-pV{D,T}Z-F12 basis.

For the ultracold conditions we show energetics and kinetics of post processes from ion-molecule collisions between hydrocarbon precursors, e.g. CH, and larger hydrocarbon ions such as cyclization which is crucial to the PAH growth. In the second part we focus on the formation of benzyne (C_6H_4) and its contribution to the aryl-aryl combination mechanisms of the PAH growth.

Gas-Phase Electron Diffraction in Bielefeld

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Bielefeld, Germany

Presenting author: Raphael J. F. Berger

The gas-phase electron-diffractometer and the high-temperature evaporation nozzle of the Bielefeld group is presented. Along with the instrument also some recent exemplary results of structural investigations on $P(C2F5)3$, $P4$, $P3As$, $Ir(NC5H4-C6H5)3$ and $H3Si(CH2)3N(CH3)2$ are given. The results show, that on the basis of experimental gas-phase structures in combination with high-level ab-initio calculations, the origins and extents of subtle effects like van-der-Waals interactions, relativity or multiconfiguration character of wave functions can be assigned and quantified.

New Use of Pseudopotential : Application to π System

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Pseudopotentials are used since many year in order to reduce the number of electrons of a system, to take into account only valence electron. They allow to decrease the size of a system and calculation time. Many approaches were developed (frozen core approximation, *ab initio* model potentials [1] and effective core potentials) to replace the effect of core electrons in a molecular framework. To reduce the number of electrons, the effective group potential method [2] was developed. This method allows to replace a part of the molecule by a potential. Only electron which are usefull for the chemical reaction are treated explicitely.

We try to replace some atoms by one proton and one electron plus a potential. We decide to work on carbon π systems and on cyclic molecules. The aim of this work is to use pseudopotential to create a pseudocarbon made of one electron in one p orbital with an effective charge of 1 and a carbon basis set. We apply one s projector along the z axis of carbon atom to modify the energy of pz orbital only.

Initially we use the pseudocarbon on π planar cyclic systems (C_6H_6, $C_5H_5^-$, $C_8H_8^{2-}$). We tried different approaches similar to energy consistent methods [3], and shape consistent methods [4] to extract parameters. In a second time we use this system to study the electronic spectroscopy of sandwich complexes. We present in the last part, our project of molecular orbital projection, that we want to implement in the molcas [5] program package.

References

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COMPUTATIONAL STUDIES OF MAGNETICALLY INDUCED CURRENTS IN AROMATIC AND HYDROGEN BONDED SYSTEMS

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The aromatic pathway and the degree of aromaticity of Möbius twisted expanded hexaphyrins have been determined by explicit calculations of the routes and strengths of the magnetically induced currents using the gauge-including magnetically induced current (GIMIC) approach [1]. The degree of aromaticity can be assessed by calculating the strength of the magnetically induced ring current flowing around the molecular ring [2]. Density functional theory calculations show that the doubly-twisted hexaphyrins fulfilling Hückel's $(4n+2)$ π-electron rule for aromaticity and those obeying the $4n$ π-electron rule for antiaromaticity are aromatic and antiaromatic, respectively [3].

A linear relation between current strengths and interaction energies is obtained from calculations on typical H-bonded systems. The current strengths for Watson-Crick base-paired nucleotides, adenine-thymine (A-T) and cytosine-guanine (C-G), with two and three intermolecular H-bonds are investigated and analyzed. An estimation of individual H-bonding strengths via magnetically induced current strengths is proposed [4].

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[3] H. Fliegl, D. Sundholm, S. Taubert and F. Pichierri, *J. Phys. Chem. A* 114 (2010) 7153.
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Highly accurate geometry optimizations at MP2 level of theory

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Recently, two of us have reported the derivation and implementation of analytical nuclear gradients for explicitly correlated MP2 using density fitting (RI-MP2-F12) in Turbomole [1-2], using Ansatz 2^* without coupling terms, standard approximation A and a Slater-type geminal (STG-6G). Additionaly, a second-order perturbation theory correction for single excitations into a complementary auxiliary basis set (CABS singles) is included to reduce the Hartree-Fock error [3].

Here we present an application of the new method by investigating different local minima of $(H_2O)_2$, $(HF)_2$, and $(NH3_3)_2$, and we compare these to conventional results [4]. Since conventional dimer calculations suffer significantly from basis-set incompleteness leading to basis-set superposition errors (BSSE) and converge very slowly to the basis set limit, extrapolation techniques and counterpoise correction are needed already during the geometry optimization to obtain reliable geometries close to the basis set limit.

Our explicitly correlated results for quadruple-zeta basis sets are in very good agreement with the best, *i.e.*, counterpoise corrected and extrapolated conventional results. We are able to demonstrate, that—especially for dimers to be computed with small basis sets—RI-MP2-F12 yields reliable structures for the right reason, since basis-set incompleteness errors (BSIE) and, hence, basis set superposition errors are largely avoided.

Literature:

1. S. Höfener, C. Hättig, W. Klopper, *Z. Phys. Chem.* **224**, 695 (2010).
2. S. Höfener, W. Klopper, *Mol. Phys.* **108**, 1783 (2010).
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   Phys. Chem. Chem. Phys. (in press)

The effect of water in the oxidation process of methane sulfenic acid and its oxidation products.

Camilla Jensen, Henrik G. Kjærgaard, Solvejg Jørgensen

The global sulfur cycle is unique in that anthropogenic emissions are larger than natural emissions. The ocean is the largest natural source of atmospheric sulfur. The sulfur is emitted in a reduced form, which is subsequently oxidised in the atmosphere. The reaction mechanisms for the oxidation are far from understood, limiting our ability to model the sulfur cycle. The initial sulfur oxidation reactions take place close to the ocean surface, where the concentration of hydrated complexes is at its highest. The role of hydrated complexes in the atmospheric oxidation reactions has so far been ignored. We will investigate the oxidation process from methane sulfenic acid (MSEA) through methane sulfinic acid (MSIA) to methane sulfonic acid (MSA). We will investigate the effect of water on the oxidation process.

We have calculated the energetics of the hydrogen abstraction channel for the reaction between the OH radical and MSEA, MSIA and MSA in the absence and presence of a single water molecule. The reaction mechanism involves hydrated complexes and we have identified two possible initial reactions that involve a hydrated complex. The hydrated complex of MSIA (H_2O-MSIA) can react with OH or MSIA can react with the hydrated complex of HO (H_2O-HO). We compare our calculated energetics of the H_2O-MSIA + OH and MSIA + H_2O-HO reactions with those of the MSIA + OH reaction to illustrate the importance of these hydrated complexes. We have also calculated analogous reactions for the first MSIA oxidation product MSEA and MSA. The calculations are carried out with DFT calculations.

The hydrogen abstraction channel for the reaction between the OH radical and MSEA, MSIA and MSA has been investigated in the absence and presence of a single water molecule. The water molecule plays a role in all the reaction. The presence of the water molecule reduces the barrier height of the reaction and stabilizes the transition state compared to the separated reactants, hence may accelerate the H-abstraction reaction.

Calculation of the vibronic spectrum in the $X\,^2\Pi_u$ electronic state of $\mathrm{NC_4N^+}$

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In order to calculate the vibronic spectrum in the $X\,^2\Pi_u$ state of the dicyanoacetylene cation, NC_4N^+, we apply previously developed model Hamiltonian [1,2] for handling the combined effect of the vibronic and spin-orbit coupling in degenerate Π electronic states of symmetric six-atomic molecules with linear equilibrium geometry. This model has already been successfully applied for calculation of vibronic spectrum in the ground states of C_6^- and C_6^+ ions [1,3].

Equilibrium bond lengths (1.1746Å, 1.3342Å and 1.2359Å - outermost, middle and innermost) and potential energy surfaces computed at the UB3LYP/aug-cc-pVTZ level [4], were used to obtain bending vibrational frequencies of $\mathrm{NC_4N^+}$. Calculated values are $\omega_{\mathrm{T1}} = 550\,\mathrm{cm^{-1}}$, $\omega_{\mathrm{T2}} = 260\,\mathrm{cm^{-1}}$, $\omega_{\mathrm{C1}} = 464\,\mathrm{cm^{-1}}$ and $\omega_{\mathrm{C2}} = 107\,\mathrm{cm^{-1}}$. Spin-orbit coupling constant was calculated employing the state-average CASSCF(11,10) wavefunctions in the framework of the MRCI method [5,6] and value $A_{\mathrm{SO}} = 44.29\,\mathrm{cm^{-1}}$ was obtained. These data enabled us to calculate vibronic energy levels and their spin-orbit splitting by means of the second-order perturbation theory.

Comparison of bending frequencies that we calculated and available experimental [7] and theoretical data shows a very good agreement.

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Structural Principles of Semiconducting Group 14 Clathrate Frameworks

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Presenting author: Antti J. Karttunen

Semiconducting clathrates are inorganic inclusion compounds structurally related to the clathrate hydrates. The semiconducting clathrates are currently investigated intensively due to their high application potential as thermoelectric materials for converting temperature differences to electric energy (Seebeck effect) or vice versa (Peltier effect). Empty ("guest-free") clathrate frameworks are also of particular interest, as they could turn out to be very useful materials for optoelectronics or photovoltaics

We have carried out a comprehensive theoretical investigation of the structural principles of semiconducting clathrate frameworks composed of group 14 elements carbon, silicon, germanium, and tin. We have investigated the basic clathrate frameworks together with their polytypes, intergrowth clathrate frameworks, and extended frameworks based on larger icosahedral building blocks. Quantum chemical calculations with the PBE0 hybrid density functional method provided a clear overview of the structural trends and electronic properties among the various clathrate frameworks. In agreement with previous experimental and theoretical studies, the clathrate II framework proved to be the energetically most favorable, but novel hexagonal polytypes of clathrate II proved to be energetically very favorable, as well. Several of the studied clathrate frameworks possess direct and wide band gaps in the case of silicon, which is interesting from the point of view of optoelectronic applications.

Theoretical Studies on the Photoinduced Biomimetic Synthesis of (+)-Intricarene

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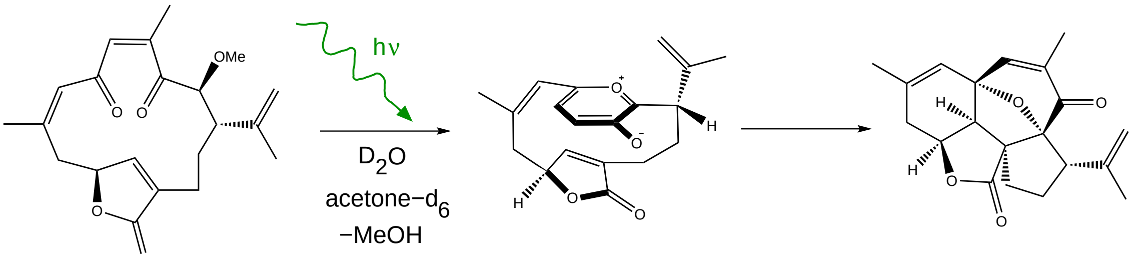
(+)-intricarene, a novel furanocembranoid isolated from the Caribbean gorgonian coral *Pseudopterogorgia kallos* [1], has gained the interest of natural product chemists due to its unique structure and potential biological activity [2,3]. In 2006, Roethle *et al.* [2] and Tang *et al.* [3] each described a thermal conversion from the natural product (-)-bipinnatin J to (+)-intricarene. However, the used reaction conditions (particularly temperatures of 150°C) can not be regarded as "biomimetic“. Recently, Trauner *et al.* [4] discovered a new photoinduced biomimetic synthesis of (+)-intricarene from the methoxy derivative of the natural product isoepilophodione B. The key step is believed to be the formation of the intermediate oxdiopyrylium, followed by an intramolecular 1,3-dipolar cycloaddition leading to (+)-intricarene [5].



methoxy derivative of isoepilophodione B

oxidopyrylium

(+)−intricarene

Based on ab initio ground state quantum chemical calculations on the methoxy derivative, we constructed a reduced model system in order to examine the excited states and to elucidate the mechanism of the photochemical reaction. The solvent water was explicitly incorporated by an microsolvation model showing significant effect on the ground state as well as on the excited state reaction. Our results demonstrate that a cascade of conical intersections mediates the formation of a protonated oxdiopyrylium, a possible precursor for (+)-intricarene. Furthermore, the interplay of the dynamic response of the solvent and the fast intramolecular reaction determines the mechanism of the excited state reaction.

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Calculation of isotropic Compton profiles with Gaussian basis sets

Jussi Lehtola, Mikko Hakala, Juha Vaara and Keijo Hämäläinen

Compton scattering experiments can be used to obtain information about the ground state electron density in momentum space. This information can be used in structure studies, by comparing spectra of materials in different conditions. However, to do this, one must be able to model the Compton profile to see how changes in the atomic and molecular structure are reflected on the Compton profile.

In general, the Compton profile J(q) measures the one-dimensional projection of the momentum density N(p) and is thus orientation dependent. In isotropic systems one measures the spherical average instead.

We have developed an algorithm for calculating the isotropic Compton profile in arbitrary precision, for any type of Gaussian basis set. We have performed accurate calculations of isotropic Compton profiles and moments of the electron density in momentum space for water and helium using density functional theory (DFT), Hartree-Fock and post Hartree-Fock methods such as Møller-Plesset and Coupled Cluster theory, using Dunning-type ((d-)aug-)cc-pVXZ basis sets.

We examine the convergence of the Compton profile as the function of the basis set size and the method used in calculating the wave function. We find that diffuse basis functions are of utmost importance to the calculation of Compton profiles, and that at least aug-cc-pVTZ basis sets should be used in Compton profile calculations.

Optical Properties of Oxygen Containing Silicon Nanoclusters

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Light emitting silicon nanoclusters have been studied extensively during recent years [1]. However, the actual mechanism responsible for the strong optical activity of the nanoclusters has remained unsolved. We have studied small oxygen containing silicon nanoclusters in order to investigate the role of oxygen in the luminescence process using time-dependent density functional theory. Benchmark computations with approximate second-order coupled cluster theory (CC2) have also been carried out. The results are also compared to previously reported many-body perturbation theory based studies [2].

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The Direct Approach to Gravitation and Electrostatics Method for Periodic Systems

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The Direct Approach to Gravitation and Electrostatics (DAGE) algorithm [1,2] is an accurate, efficient, and flexible method for calculating electrostatic potentials. We have shown that the algorithm can be easily extended to consider systems with many different kinds of periodicities[3], such as crystal lattices, surfaces, or wires. The accuracy and performance are in practice the same for periodic and aperiodic systems. The electrostatic potential for semi-periodic systems, namely defects in crystal lattices, can be obtained by combining periodic and aperiodic calculations. The method has been applied to an ionic model system mimicking NaCl, and to a corresponding covalent model system.

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Theoretical Study of Pyrolysis of Hexafluoropropylene Oxide (HFPO)

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Abstarct

Hexafluoropropylene oxide (HFPO) is a common precursor used in chemical vapour deposition (CVD) for manufacturing fluorocarbon thin films. A fluorocarbon thin film consisting of mainly linear polymers with little branching is preferred as that resembles the structure of polytetrafluoroethylene (PTFE) which has a low dielectric constant and is biocompatible. The concentration of CF_2 above the substrate in a CVD process, depending on the pyrolytic temperature, is a critical factor in determining the branching fraction in the thin film. Therefore, understanding the reaction mechanism of HFPO decomposition in CVD would help to optimize the decomposition process. Although there have been numerous experimental investigations on the pyrolysis of HFPO, its decomposition mechanism is still not well understood. In this connection, two primary reaction channels in the decomposition of HFPO have been chosen as the subject in this study. Above 150℃, HFPO starts to decompose thermally. The dominant pathway (1a) gives CF_2 which contributes to film deposition via polymerization and CF_3COF as the products, while the alternative reaction channel (1b) produces CF_2O and CF_3CF. *Ab initio* and density functional theory (DFT) calculations were performed to study the two channels of pyrolysis at the B3LYP, BH&HLYP, B3PW91, MPW1PW91, M05, M06, M06-2X and MP2 levels with 6-311++G** basis set. Higher level single-point energy calculations were performed at the RCCSD(T)/aug-cc-pVDZ, RCCSD(T)/aug-cc-pVTZ and RCCSD(T)/CBS levels with geometries optimized at MP2/6-311++G**. The computed minimum energy paths (MEPs) as well as the associated gradients and Hessians were then employed in the subsequent Transition State Theory (TST) calculations to determine the rate coefficients. The rate coefficients were computed at the TST, CVT and ICVT levels with ZCT and SCT in a temperature range of 300K to 1500K. Both the two channels are found to be endothermic. Channel (1a) is more preferred than channel (1b) both thermodynamically and kinetically as the computed reaction and activation energies for channel (1a) are about 20-25 kcal/mol and 10-15 kcal/mol lower than those in channel (1b). Most of the computed activation energies for channel (1a) are in good agreement with the experimental values except that of B3LYP/6-311++G** which underestimated the barrier height. In addition, CCSD(T)/CBS//MP2/6-311++G** is found to give the best agreement with the experimentally determined rate coefficients.

Paramagnetic nuclear magnetic resonance, solvation structure and dynamics of Ni(II) (*aq*) from first principles

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Presenting author: Jirí Mares

Aqueous solution of Ni(II) was investigated using first principles molecular dynamics (FPMD) simulation. The experimental structural parameters of the Ni(*aq*) complex are reproduced well by the simulation. An exchange event of the water molecule in the first solvation shell is observed, supporting the proposed dissociative mechanism of exchange.

The calculated dynamic characteristics of the surrounding water molecules, indicate too slow translational diffusion, in agreement with other FPMD studies employing similar level of theory. We also find that the reorientational dynamics of water is an order of magnitude slower as compared to the experimental results.

On the other hand, the angular momentum dynamics is in better agreement with the experimental data than the reported results from MD simulations employing emprical forcefields. The obtained MD trajectory supplies accurate structures for the calculation of the average hyperfine properties and paramagnetic nuclear magnetic resonance (pNMR) shieldings.

Statistical averages of the hyperfine coupling, g, and zero-field splitting tensors as well as the resulting pNMR terms were calculated using density functional theory (DFT) from instantaneous simulation snapshots extracted from the (FPMD) trajectory. We report tests of the reliability of systematically selected DFT functionals with respect to the calculated properties.

The isotropic nuclear shieldings of the ^{17}O nuclei can be obtained with good predictive power. The accuracy of the calculated ^{1}H shieldings is hindered by the fact that the proton spin-density at the is not reproduced reliably with the tested functionals, rendering the dominant Fermi contact isotropic shielding term obscure. On the other hand, the dominant spin-dipole term of the shielding anisotropy, which gives a practically vanishing isotropic contribution, can be obtained with a good reliability for both ^{1}H and ^{17}O nuclei. The anisotropic shielding tensor can be thus utilized reliably in the calculation of Curie-type paramagnetic relaxation.

MODELING 5f ELEMENTS: A CASE STUDY OF TH(IV) - FROM QUANTUM MECHANICS TO MOLECULAR MECHANICS

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A whole theoretical study on the Th(IV)-OH_2 dimer system is presented here; from the first diabatized interaction energy curves at multi-reference level to a fully transferable potential. As more and more force fields are being developed for lanthanides and actinides, it is necessary to propose one that can take into account the various and complex physical effects that occur in those very heavy elements. Through quantum Energy Decomposition Analyses (EDA) of the interaction energy of our dimer, we have pointed out the need for a polarizable force field including charge transfer. The SIBFA (Sum of Interactions Between Fragments Ab-initio computed) force field, also based on EDA has given a close reproduction of the global quantum interaction energy as well as for the different contributions to that energy. SIBFA has also been proven fully transferable up to the more realistic $[Th\text{-}(OH_2)_9]^{4+}$ clusters. Moreover, as a complementary method to SIBFA, the AMOEBA (Atomic Multipoles Optimized Energetics for Biomolecular Applications) potential has also been derived for the Th(IV) cation with good correspondence to experimentation.

Interaction of formic acid with nitrogen

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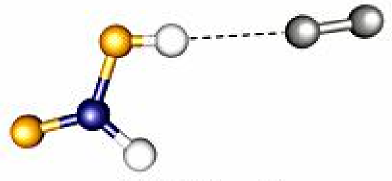
In chemistry, conformational isomerism is a form of stereoisomerism in which the isomers can be interconverted by rotations about formally single bonds. The simplest organic acid, formic acid (HCOOH, FA) can exist in two planar forms differing by the O–H bond orientation in respect to C–O bond with 0° (*cis*-FA) and 180° (*trans*-FA) H–C–O–H dihedral angles. By vibrational excitation of the lower-energy *trans*-FA monomer, the higher-energy *cis* form can be prepared in low-temperature matrices. *cis*-FA converts to *trans*-FA by proton tunneling, which limits its lifetime [1].

In order to prepare the *cis*-FA$\cdots N_2$ complex, we combine annealing in an argon matrix with vibrational excitation of the *trans*-FA monomer as it has previously been used by us for the preparation of the *cis*-FA$\cdots H_2O$ complex [2]. This new *cis*-FA$\cdots N_2$ complex has been characterized spectroscopically and the experimental complexation-induced shifts are in a good agreement with the computational results.



cis-FA$\cdots N_2$

The *cis*-FA$\cdots N_2$ complex decays in the dark by quantum tunneling of hydrogen atom. It was found that the *cis*-FA$\cdots N_2$ complex lifetime is ca. 6.5 times longer than that of the *cis*-FA monomer at 9 K in an argon matrix. A number of solvation effects in an argon matrix are computationally estimated and discussed.In agreement with the experimental observations, the *ab initio* calculations predict a substantial increase of the *cis*-to-*trans* barrier for the *cis*-FA$\cdots N_2$ complex compared to the *cis*-FA monomer.

The present results on the *cis*-FA$\cdots N_2$ complex show that hydrogen bonding can lead to the stabilization of intrinsically unstable conformers [3]. The significant stabilization effect was previously found for *trans-cis* FA dimers, complexes of *cis*-FA with water and with atomic oxygen [2, 4-5].

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Two–electron Darwin contribution in RI–MP2 and RI–MP2–F12 theory

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Nowadays, there is a consensus to include scalar-relativistic effects when, *e.g.*, highly accurate reaction energies are to be calculated. In contrast to one-electron contributions such as the (one-electron) Darwin and mass-velocity term, however, relativistic two-electron contributions are mostly neglected. In case of the two-electron Darwin (D2) correction, the two major drawbacks are the calculation of expensive two-electron integrals and the slow convergence to the basis set limit with X^{-1}, where X is the cardinal number of the orbital basis set [1].

We show that robust density fitting as used in modern F12 methods is a valuable tool to compute efficiently also integrals needed for the D2 correction without loss of accuracy. The problem of the slow convergence can be overcome by using modern explicitly correlated F12 methods providing a dramatically improved description of the Coulomb hole and, hence, leading to a much faster convergence to the basis set limit.

Since even extrapolated MP2 results exhibit non-negligible error-bars for the slow converging D2 correction, the RI-MP2-F12 ansatz proofs to be a valuable tool to obtain converged results at the MP2 basis set limit—only using quadruple-zeta basis sets.

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Modelling oxidation stage in the GFP chromophore biosynthesis

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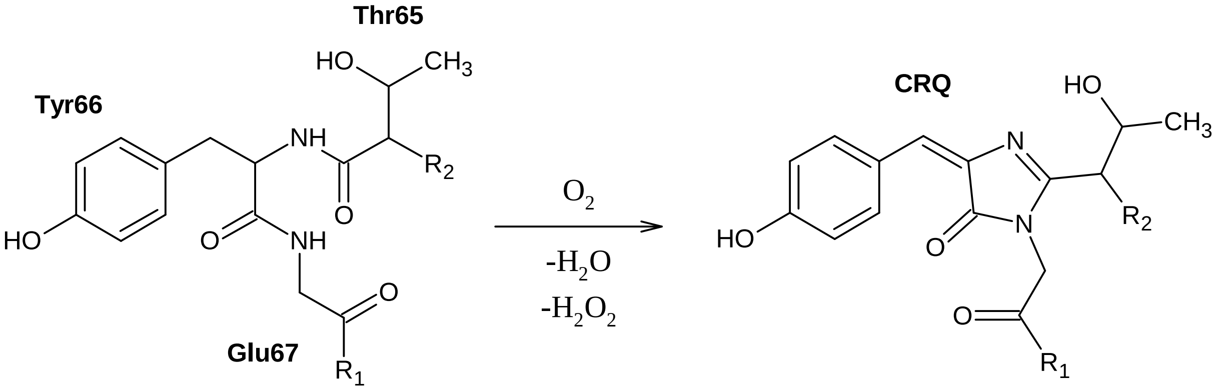
The green fluorescent protein (GFP) and its homologues have become a very popular instrument in biology as a fluorescent tag. The fluorescent properties of these proteins are provided by the chromophore, which is formed upon an autocatalytic cyclization and subsequent oxidation of three amino acid residues. Understanding of this process should make us able to construct proteins with desired photophysical properties. However, details of the chromophore biosynthesis are still veiled.



Reaction of the chromophore biosynthesis in GFP (S65T)

Current work is devoted to modelling the oxidation step of this reaction. We have calculated gas-phase energy profiles of this reaction at the CASSCF(20,14)/cc-pVDZ level. The oxidation mechanism has been shown to include four main steps: the chromophore deprotonation, the electron transfer from the chromophore anion to the oxygen in the triplet state, the triplet-singlet intersystem crossing and formation of the product.

This work is supported by the RFBR (projects № 08-03-00914-a) and the grant from the President of Russian Federation for young scientists (MK-64815.2010.4). We also thank the SKIF-GRID program, the Research Computing Center of the M.V. Lomonosov Moscow State University for providing resources at the computational facilities.

Molecular mechanism of green fluorescent protein decarboxylation process.

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Wild type green fluorescent protein (GFP) from *Aequorea victoria* absorbs predominantly at 398 nm. Illumination with UV (254 nm) or visible (390 nm) transforms this state into one absobing at 483 nm. However, experimental data shows that this photoconversion is a one-photon process which is paralleled by decarboxilation of Glu222. Long irradiation of GFP results in decomposition of chromophore. Reported, that the rate of the light-driven decarboxylation reaction strongly depends on the excitation wavelength, decreasing in the order 254 nm > 404 nm > 476 nm.

The relative efficiencies of decarboxylation are explained in terms of the Kolbe-type mechanism in which the excited state of the chromophore acts as an oxidant by accepting an electron from Glu222. It is proposed that 254 nm excitation populates the S2 (or higher) excited state of the chromophore, whereas 404 and 476 nm excitation populate the S1 excited state of neutral and anionic forms, respectively, and that the relative oxidizing power of the three excited states controls the rate of the decarboxylation reaction.

This work is devoted to *ab initio* study of GFP decarboxylation process. The electron affinity of GFP chromophore in the ground (S0) and the first excited (S1) stated and the electron detachment energy of glutamate anion are calculated. It is shown that GFP chromophore can't oxidize Glu222 anion even in the first excited state. Absorption spectra of GFP chromophore and glutamate anion are calculated at MCQDPT2/CASSCF level of theory. Absorption spectra shows that 254 nm can't be an excitation of glutamate anion, however there is a high excited state of chromophore with the similar energy. Also, energies of excited states with direct electron transfer from glutamate anion to GFP chromophore is calculated. It is proposed that 254 nm can be attributed to an excited state with electron transfer.

We thanks the SKIF-GRID program and the Research Computing Center of the M.V. Lomonosov Moscow State University for providing resources at the computational facilities.

Phosphorus Chemical Shifts in a Nucleic Acid Backbone from Combined Molecular Dynamics and Density Functional Calculations

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Presenting author: Marketa Munzarova

A comprehensive quantum chemical analysis of the influence of backbone torsion angles on 31P chemical shifts in DNAs has been carried out. An extensive DFT study employed snapshots obtained from the molecular dynamics simulation of [d(CGCGAATTCGCG)]2 to construct geometries of hydrated dimethyl phosphate, which was used as a model for the phosphodiester linkage. Our calculations provided differences of 2.1±0.3 and 1.6±0.3 ppm between the BI and BII chemical shifts in two B-DNA residues of interest, which is in a very good agreement with the difference of 1.6 ppm inferred from experimental data. A more negative 31P chemical shift for a residue in pure BI conformation compared to residues in mixed BI/BII conformation states is provided by DFT, in agreement with the NMR experiment. Statistical analysis of the MD/DFT data revealed a large dispersion of chemical shifts in both BI and BII regions of DNA structures. dP ranges within 3.5±0.8 ppm in the BI region and within 4.5±1.5 pp
m in the BII region. While the 31P chemical shift becomes more negative with increasing alpha in BI-DNA, it has the opposite trend in BII-DNA when both alpha and zeta increase simultaneously. The 31P chemical shift is dominated by the torsion angles alpha and zeta, while an implicit treatment of beta and epsilon is sufficient. The presence of an explicit solvent leads to a damping and a 2?3 ppm upfield shift of the torsion angle dependences.

Internally Contracted for Inactive Excitations in State Specific MRCC

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One generic difficulty of most state-specific many-body formalisms using the Jeziorski-Monkhorst Ansatz is the large number of redundant cluster amplitudes. The number of cluster amplitudes up to a given rank are many more in number compared to the dimension of the Hilbert Space spanned by the virtual functions of upto the same rank of excitations. At the same time, all inactive excitations - though linearly independant are far too numerous. It can be argued that the model space dependence, especially for the inactive doubles, is weak. Considerable simplification, can thus be obtained, by using a partial internally contracted description, which uses physically appealing approximation. We propose and implement such a formalism with internal contractions for inactive excitations (ICI) within the State Specific MRCC framework of Mukherjee, et al (a.k.a. Mk-MRCC). One of the major advantages of the ICI-SS-MRCC, unlike other analogous internally contracted theories, is that it can use relaxed coefficients for the model functions and at the same time employ projection manifolds for the virtuals obtained from inactive n hole-n particle (nh-np) excitations on the entire reference functions containing relaxed model space coefficients. To the extent the μ independence of T_i is valid, we expect the ICI-SS-MRCC to retain the conceptual advantages of size-extensivity yet using a drastically reduced number of cluster amplitudes without sacrificing accuracy.

The efficacy of the method will be proved by applying it to compute the potential energy surfaces, tortional potential enery barriers and single point calculations on prototypical systems of pronounced multi reference character.

Quantum-chemical study of the amidyl radicals conjugated with phenyl ring

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Presenting author: Fabijan Pavosevic

The results of quantum chemical calculations of N-phenylacetamidyl radical and several of its derivatives will be discussed. Distribution of the relative energies and electronic structure of the PI and SIGMA states of the N-centered radicals as a function of (i) the angle at the nitrogen atom ; (ii) the dihedrel angle between the benzene ring and the amidyl group ; (iii) electronic and steric effects of the substituents on the phenyl ring will be discussed in detail. In most of the studied radicals the PI-N state was found to be preferred over the SIGMA-N configuration in accordance with available computational and EPR studies. An exception is provided by sterically hindered N-(2, 6-di-tert-butylphenyl)acetamidyl radical for which SIGMA?N state was found to be of lower energy than the PI-N state.

Calculation of the Histidine pKa Values in Water Using COSMO, COSMO-RS and Modified Cluster Continuum Models

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Presenting author: Nena Peran

Histidine is part of the set of 22 proteinogenic amino acids. It is one of the most abundant amino acids in biological systems. A side chain of histidine has imidazole as functional group, which can be protonated in slightly acidic conditions. This makes him an important part of the catalytic sites in enzymes.
In water solution, at neutral pH, histidine adopts a cationic form possessing the NH_3^+ and COO^- groups, and protonated imidazole ring, which are stabilized by solvation with water molecules [1]. The standard thermodynamic cycle for calculating pKa values includes energies of the equilibrium gas phase geometries, which are corrected by solvation Gibbs free energy. Since water molecules are needed to stabilize cationic and zwitterionic form of histidine in gas phase, its clusters with one and two water molecules were investigated.
The geometries of histidine in water solution and corresponding energies were estimated by using COSMO-RS and COSMO solvation models. Calculated pKa values are in good accordance with experiment.

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An efficient sparse matrix algorithm to speed up the calculation of the ladder term in Coupled Cluster programs

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Presenting author: Zoltan Pillio

The CCSD (Coupled Cluster Singles and Doubles) method is an important tool of quantum chemistry, providing a large portion of correlation energy. Traditional algorithms are formulated in terms of MO (Molecular Orbital) integrals, where efficient matrix multiplications can be used in the calculations. However, computation of some of the terms, in particular the most expensive ladder contribution, is more efficient in terms of AO base two-electron integrals [1]. In the latter case, sparse matrix-matrix multiplication need to be performed. In the CFOUR program package, for example, the sparse matrix-matrix multiplication is based on the selection of the non-zero elements of the AO based two-electron integrals, which are used in scalar multiplication with vectors of the (half-transformed) amplitudes. This is preferable since it keeps the multiplication count to minimum by avoiding multiplication by zero, but disadvantageous because the scalar-vector multiplications are not efficient enough especially on massively parallel device such as GPU (Graphics Processing Unit), FPGA (Field-Programmable Gate Array), or many core CPUs with vector instruction as SSE or AVX.

The efficiency of the computation can be enhanced by sparse matrix partitioning techniques. In the continuous (well occupied) parts of the sparse matrix can be handled with general matrix-matrix multiplication (GEMM), and only the loosely occupied parts need to be processed by scalar/matrix multiplications.

The sparse matrix partitioning is well known in the field of the high-performance computing (MeTiS[2]). The available algorithms, however, require that the non-zero matrix elements are kept in memory, thus rendering application in practical quantum chemical calculations impossible. Therefore, we have developed a new partitioning technique for the two-electron integrals, which is based on the spatial spread of the orbitals (basis functions or localized molecule orbitals). We also modified the original AO-based algorithm in CFOUR program package to use this partitioned data.

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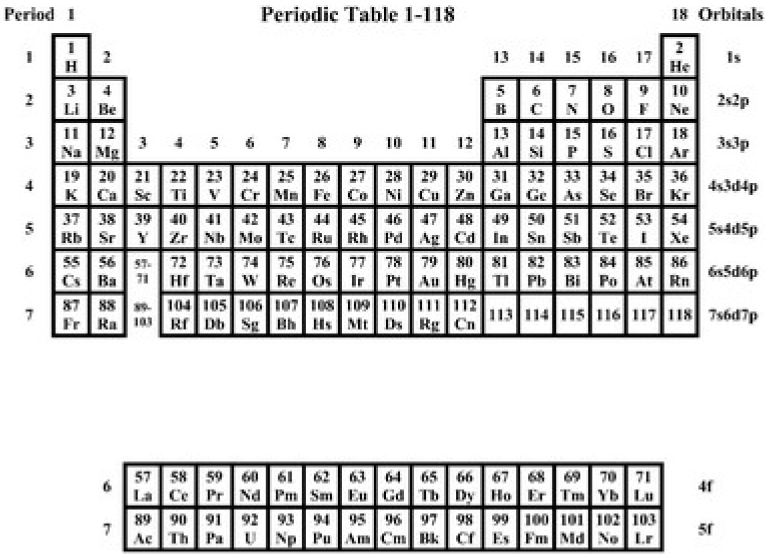
A suggested periodic table up to $Z \leq 172$, based on Dirac–Fock calculations on atoms and ions

Pekka Pyykkö

Extended Average Level (EAL) Dirac–Fock calculations on atoms and ions agree with earlier work in that a rough shell-filling order for the elements 119–172 is $8s < 5g \leq 8p_{1/2} < 6f < 7d < 9s < 9p_{1/2} < 8p_{3/2}$.

The present Periodic Table develops further that of Fricke, Greiner and Waber [*Theor. Chim. Acta* 1971, **21**, 235] by formally assigning the elements 121–164 to (*nlj*) slots on the basis of the electron configurations of their ions. Simple estimates are made for likely maximum oxidation states, *i*, of these elements M in their MX_i compounds, such as $i = 6$ for UF_6. Particularly high *i* are predicted for the 6*f* elements.



Periodic Table 1-118

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Orbitals
1	1 H																	2 He	1s
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2s2p
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3s3p
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4s3d4p
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5s4d5p
6	55 Cs	56 Ba	57- 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6s5d6p
7	87 Fr	88 Ra	89- 103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118	7s6d7p

6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	4f
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	5f

Pekka Pyykkö ***Phys. Chem. Chem. Phys.***, 2011, **13**, 161-168 **DOI:** 10.1039/C0CP01575J, Paper

Ab-initio studies of Cu electronic structure in sufficiently high electric fields

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Presenting author: Ruzibaev A.

In the present work we perform ab initio density-functional calculations to investigate the properties of copper surface under sufficiently high external electric fields. Lattice constants, cohesive energies, surface energies and work functions are strongly affected by the applied field. In the same time, this effect depends on the crystallographic orientation of Cu surfaces. In order to find the differences we calculate the above-mentioned quantities for the most common crystal surfaces. After implementation of external electric field with the strength from 0.1 V/Å up to 1 V/Å the charge transfer on surface atoms is analysed by Mulliken and Bader charge analysis technique [1,2]. We investigate the structure relaxation of a surface with a single adatom in different lattice sites compared to the same flat surface. Band structure analysis is provided to study high electric field effects on Cu surface properties. Shifts in Fermi level and surface energies are calculated in order to estimate the modification of the work function in the presence of external electric field exerted on the surface with a single adatom.

For our calculations we use Spanish initiative for electronic structure with thousands of atoms (SIESTA) [3,4] ab initio simulation package, which uses linear combination of atomic orbitals (LCAO) type basis functions and norm conserving pseudopotentials. Perdew, Burke & Ernzerhof (PBE) scheme of Generalized gradient approximation (GGA) was used for the exchange and correlation functionals. The Cu surface has been modelled by using a super-cell with 256 atoms. The bulk lattice constant and some properties of the surface, such as the cohesive energy, surface relaxation, and surface energy were calculated prior to the application of an external electric field. The convergence tests of the total energy and lattice constant with respect to the mesh cutoff and k-point sampling have been carefully examined. As a basis set we have chosen the split type basis set with multiple ξ size, which includes polarization and diffuse orbitals.
The 290 eV cutoff value for the realspace integration mesh was used for computing the final set of energies.

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High-valent Iron Fluorides

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High-valent iron fluorides up to and including FeF_6 have been investigated by quantum chemical calculation son DFT and coupled-cluster level. Iron di- and trifluoride are well known molecules that have been extensively investigated both experimentally[1, 2] and theoretically[3, 4]. The highest known fluoride of iron, FeF_4, has been characterized by mass spectroscopy and IR spectroscopy using the matrix isolation technique[5]. Here we show the structures and stabilities of high-valent iron fluorides.

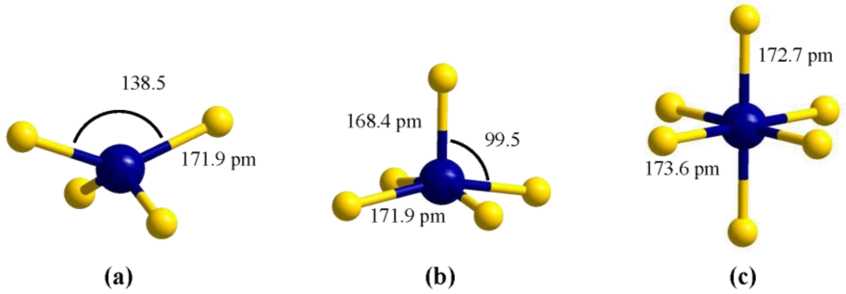

Figure 1 Optimised structures of (a) FeF_4 (D_{2d}, quintet), (b) FeF_5 (C_{4v}, quartet) and (c) FeF_6 (D_{4h}, triplet).

Based on our calculations, iron pentafluoride might be stable at very low temperatures or at least, once formed, kinetically stabilized by a high activation barrier. By contrast iron hexafluoride showed only exothermic decomposition channels. Interestingly, calculated electron affinities (EA) and fluoride ion affinities (FIA) are very similar to those of the predicted AuF_6 species[6, 7].

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Stabilization of the peroxy intermediate in the oxygen splitting reaction of cytochrome *cbb*$_3$

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The proton-pumping *cbb*$_3$-type cytochrome *c* oxidases catalyze cell respiration in many pathogenic bacteria. For reasons not yet understood, the apparent dioxygen (O2) affinity in these enzymes is very high relative to other members of the heme-copper oxidase (HCO) superfamily. Based on density functional theory (DFT) calculations on intermediates of the oxygen scission reaction in active-site models of *cbb*$_3$- and *aa*$_3$-type oxidases, we find that a transient peroxy intermediate (**IP**, Fe[III]-OOH^-) is ~6 kcal/mol more stable in the former case, resulting in more efficient kinetic trapping of dioxygen and hence in a higher apparent oxygen affinity. The major molecular basis for this stabilization is a glutamate residue, polarizing the proximal histidine ligand of heme b_3 in the active site.

Molecules on the Borderline of Bonding - the case of Nitrososilanes, R_3Si-NO.

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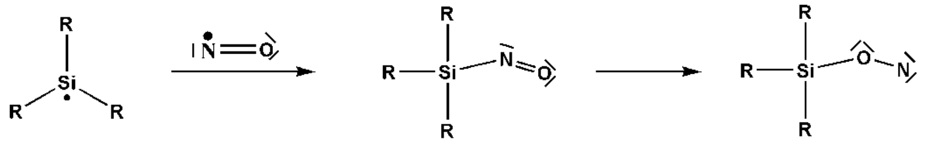
NO and its related chemistry have been fascinating chemists all over the world for decades. While it plays an important role in industry for the production of HNO_3, it is also a major player in biological processes involving radical reactions. Nitric oxide is the smallest known stable radical and it is readily oxidized to NO_2 even in ambient atmosphere. Organic NO compounds, in the simplest case nitroso alkanes, have also been known for a long time. They possess properties of general interest, e.g. as spin trapping agents or in high energy materials.

In recent years, in organometallic main group chemistry attention was focused on the synthesis of carbon analogues using heavier group IV elements. In the meantime, a lot of carbon congeners have been synthesized, e.g. disilenes, disilynes, iminosilanes, to mention only a few. However, although a substantial number of compounds with silicon linked to N-O units do exist, reports on nitroso compounds of heavier group IV elements are very rare.

In this contribution, we describe investigations on nitrososilanes, R_3SiNO (R=H, Me, NH_2, OH, F, Cl), using different theoretical approaches (HF, DFT) and basis sets. The computed reaction of NO with silylradicals to nitrososilanes proceeds spontaneous with reaction enthalpies of -26 to -35 kcal/mol. As expected, no barrier is found for this radical reaction. Si-N bond lengths exhibit large values in a range between 1.80 and 1.93 Å which is much more than the average value of a silicon nitrogen bond of about 1.70 Å. TD-DFT calculations on the nitrososilanes indentify low lying excited triplet states, the singlet-triplet excitation energy is calculated 8-10 kcal/mol. In comparison to the singlet state geometries, those of the triplet state exhibit smaller Si-N bond lengths and wider Si-N-O angles.



R=H, Me, NH_2, OH, F, Cl

Possible rearrangements to the corresponding nitrenes, RSiON, are disfavored energetically by 20-30 kcal/mol. Transition states for this rearrangement reaction could be located and barriers of about 40 kcal/mol have been determined.

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Simulations of ^{129}Xe chemical shift of atomic xenon dissolved in liquid benzene

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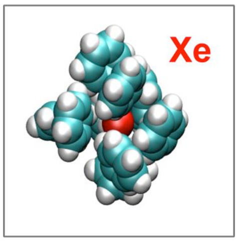
Inert Xe atom is an excellent NMR probe. The sensitivity of the ^{129}Xe NMR chemical shift to the environment of the Xe atom provides an excellent non-invasive tool for studying different materials, electronic and solvent effects, microscopic biological processes, etc. Computational studies help to predict the ^{129}Xe NMR parameters and are very useful in interpretations of the experimental data.[1]



In this pilot study, our goal was to demonstrate how the dynamic effects arising from intermolecular interactions of xenon atom with surrounding solvent (here benzene) influence the ^{129}Xe NMR chemical shift. We have performed 1000 ps run of NPT molecular dynamics (MD) simulation of a Xe atom dissolved in a box of benzene molecules using the Amber software. Subsequently, we used snapshots from the resulting trajectory for calculations of the ^{129}Xe NMR shift at the DFT level of theory keeping only the first solvation shell.

Averaging results for 512 snapshots of the 512 ps trajectory using quantum-chemical calculations (BHandHLYP/MHA/SVP) of the snapshots cropped to the first solvation shell (typically 8-12 benzene molecules) gives theoretical value of Xe shift in benzene of 175±4 ppm. This value is further improved by the relativistic contribution to 189 ppm. This compares to the previous experimental results[2] of 188.14 ppm.

The relativistic corrections are calculated employing the leading-order Breit-Pauli perturbation theory (BPPT)[3] at the same level of theory (BHandHLYP/FIVu61/SVP) and are currently in progress.

We find out that the ^{129}Xe NMR shifts are strongly influenced by the benzene solvent molecules. MD simulation in combination with the BHandHLYP calculations of the snapshots provides affordable results that can be used for supporting the experiment or serve as a model in more complicated computational studies.

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On the Role of Mercury in the Non-Covalent Stabilisation of Consecutive U-Hg^{II}-U Metal-Mediated Nucleic Acid Base Pairs: Metallophilic Attraction Enters the World of Nucleic Acids

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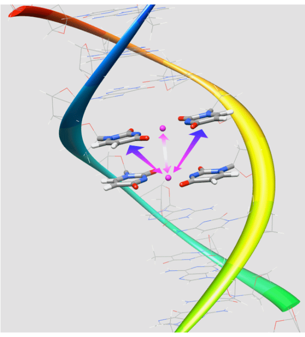
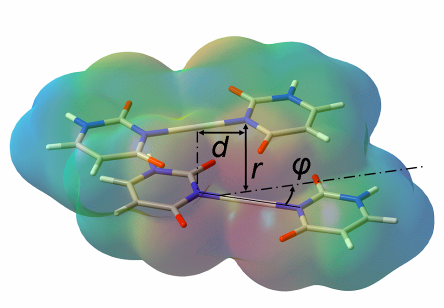
Metal atoms with a closed-shell electronic structure and positive charge as for example the Au^{I}, Pt^{II}, Ag^{I}, Tl^{I} or Hg^{II} atoms do not in some compounds repel each other due to the so-called metalophillic attraction (P. Pyykkö, *Chemical Reviews* 1997, *97*, 597-636). Here we highlight role of the Hg^{II}…Hg^{II} metalophillic attraction acting between the consecutive metal-mediated mismatched base pairs of nucleic acids. Usually, the base stacking dominates the non-covalent interactions between steps of native nucleic acids. In the presence of metal-mediated base pairs are these non-covalent interactions enriched by the metal-base interactions and the metalophillic attraction. The two interactions arising due to the metal linkage of the mismatches in this study were found to have a stabilizing effect on nucleic acid structure. (PCCP 2010, accepted manuscript). The calculated data are consistent with recent experimental observations. The stabilization due to the metalophillic attraction seems to be generally important concept for the nucleic acids containing heavy metals with short contacts.





Acknowledgements: This project was supported by European Reintegration Grant No. 230955 (M.S.) and by Human Frontiers Science Organization's Young Investigator Grant (V.S. and Y.T).

Magnetically induced currents in [n]cycloparaphenylenes

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We present a computational study of the current pathways and ring current strengths in [n]cycloparaphenylenes, n=6…11 [1]. The dianion of [6]CP is also investigated along with the corresponding complexes with divalent metal cations. The [n]cycloparaphenylenes are hoop-shaped molecules made of 1,4-connected phenylene rings where the carbon p orbitals lie in the plane of the ring and are thus oriented towards the ring center.

The Gauge-including magnetically induced currents (GIMIC) method [2] is used to determine the current strengths and current pathways of the molecules. GIMIC has proven to be a useful tool for determining the degree of aromaticity of multiring molecules because it explicitly provides the strength of the magnetically induced current passing through selected chemical bonds and the strength of the currents circling around molecular rings [3,4]. The current strengths are obtained through numerical integration of the current density. The current density can be calculated at the DFT or at the *ab initio* (SCF, MP2, Coupled-Cluster) levels of theory.

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Ultrafast photochemical bond cleavage of diphenylmethylphosphonium cations

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Diphenylmethylphosphonium cations (DPM–PR$_3^+$) are known as one of the most effective precursors for photo-produced benzhydryl cations [1], which are carbocationic key intermediates in S$_\mathrm{N}$1 reactions. With a combined theoretical and experimental investigation we elucidate the mechanism of the initial ultrafast bond cleavage process of DPM–PPh$_3^+$. The calculations are performed for a model system with only two phenyl rings shown in figure 1 (left). It is designed to preserve the main properties of the large system, still allowing the use of highly correlated quantum chemical methods.

Contrary to other diphenylmethane derivatives [2] excitation to the first excited state S$_1$ (π-π^*-transition) occurs in the phenyl ring of the phosphonium group (fig. 1), which is the leaving group. The second excited state S$_2$ mainly corresponds to a π-π^*-transition localized on the benzyl group. Only the third excited state S$_3$ induces the charge exchange between the π^*-orbitals of the phenyl rings and the σ^*-orbital of the C-P bond which finally leads to bond cleavage of the C-P bond.

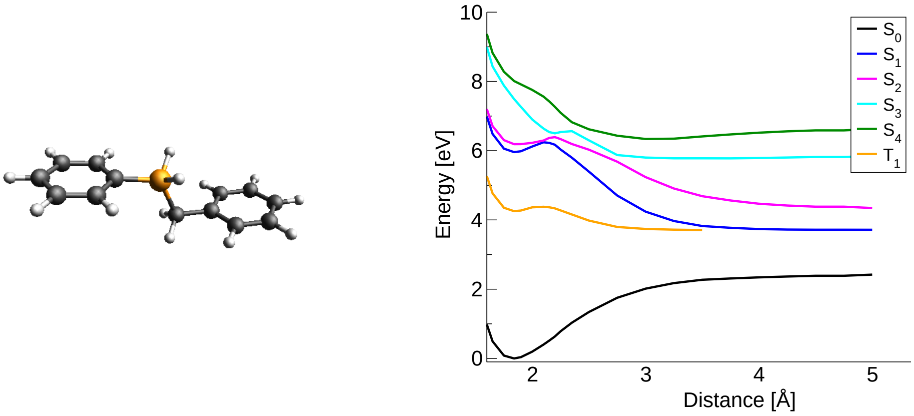

FIG. 1: Ground state equilibrium geometry of the theoretical model system phenylmethylphenylphosphonium cation (left). Potential energy curves for the C-P bond cleavage in the phenylmethylphenylphosphonium cation (right).

Ultrafast broadband transient absorption measurements [3] of DPM–PPh$_3^+$ and DPM–PMePh$_2^+$ show similar dynamics, supporting an identical mechanism for both, the complete and the reduced system. Therefore it is legitimate to transfer the theoretical results of the reduced model system to DPM–PPh$_3^+$. The rise of the cation signal after 10 – 20 ps indicates the expected bond cleavage. The theoretically predicted initial radical formation on the sub-picosecond timescale is not confirmed yet due to the overlay of several transient signals.

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Quantum defect theory of cold and ultracold collisions between molecules and atoms

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Presenting author: Michal Tomza

State-of-the-art quantum chemical methods give a full picture of collisional processes but the analysis of molecular collisions is computationally very demanding. Simple quantum defect model within the multichannel description gives physically reasonable results and (semi)quantitively explains the orders of magnitude of the measured rate constants for ultracold atomic collisions. Here a simple dynamical model based on the multichannel quantum defect theory within the complex potential formalism was constructed for the collisions of cold polar molecules with ultracold atoms. Collisions of cold LiH molecules with Li/Rb atoms were studied in details and the applicability of the proposed model in the case of strongly anisotropic interaction potential was analyzed. The proposed approach allows to reproduce the results of exact quantum dynamical calculations by adjusting a few parameters. It can be shown that these parameters are related to the complex s and d wave scattering lengths.

NMR, X-ray and DFT investigations of Pt(IV) complexes with aromatic cytokinins

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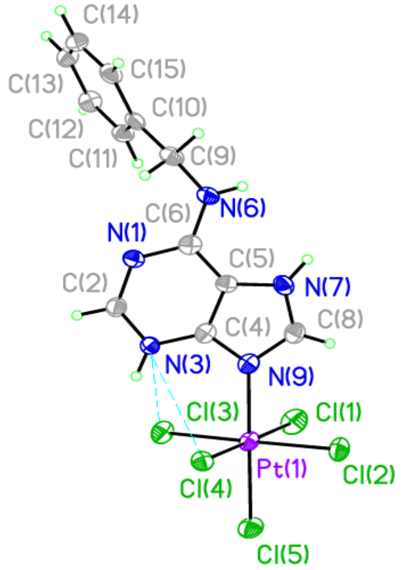
Two novel Pt(IV) complexes of aromatic cytokinins with possible antitumor properties were prepared by the reaction of selected aminopurines with K_2PtCl_6. Structures of both complexes, 9-[6-(benzylamino)purine] pentachloroplatinate (IV) (**1**) and 9-[6-(furfurylamino)purine] pentachloroplatinate (IV), have been characterized by using single crystal X-ray diffraction and CP/MAS NMR techniques in the solid state, followed by an investigation of the structure and protonation patterns in the solution (DMF) using ^{1}H, ^{13}C, ^{15}N, and ^{195}Pt NMR spectroscopy.



Molecular topology determined by single-crystal X-ray diffraction has been compared with DFT optimized geometry (B3LYP with 6-31G* for light atoms and ECP60MDF and ECP60MDF_wcVTZ for platinum) *in vacuo*. Nuclear magnetic shielding calculations (GIAO, B3LYP with HIII for light atoms and ECP60MDF with cc-pVTZ-PP for platinum with PCM solvent model) as implemented in Gaussian 03 and spin-orbit zeroth-order relativistic approximation (SO-ZORA, PBE0 with TZP and COSMO solvent model) calculations as implemented in ADF-2009 have been tested and compared.

*Figure 1: Molecular structure of **1** determined by X-ray diffraction with N3-H...Cl stabilizing interactions*

The platinum has been determined to be coordinated at N9 with N3 and N7 bearing hydrogen atoms (see Figure 1). Intramolecular interactions N3-H...Cl(3) and N3-H...Cl(4) partially stabilize the structures of **1** and **2** and suppress the chemical-exchange processes involving the N3-H hydrogen atom in solution. In contrast, the N7-H is exposed to the solvent and undergoes the fast chemical exchange in solution (broadened lines, significant pH dependence for N7 chemical shift). DFT calculated ^{15}N NMR chemical shift for N7 atom has been used to estimate a degree of protonation at this nitrogen atom in solution.

Accurate Molecular Structure of the Strained 3-Methyl-1-boraadamantane as Determined by Gas-Phase Electron Diffraction

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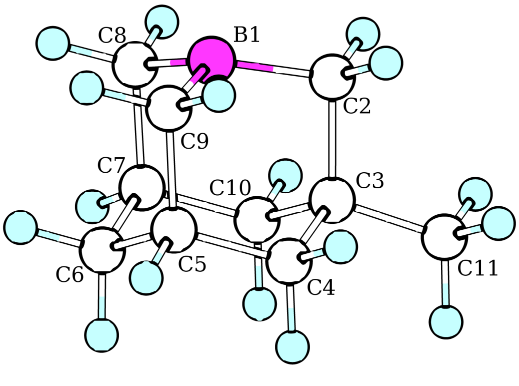
The method of predicate observations [1] has played important role in gas-phase electron diffraction (GED) [2]. On the basis of this method we have developed an improved approach for refining molecular geometries from GED data in terms of cartesian coordinates with regularization constraints to the full set of internal geometrical parameters. In the least squares procedure the following functional is refined:

$$Q = \sum [sM(s)^{exp} - sM(s)^{model}]^2 + \alpha \sum w_i (p_i^0 - p_i)^2 \rightarrow min$$

$sM(s)^{exp}$ and $sM(s)^{model}$ are the experimental and model molecular electron diffraction intensity curves, α is the regularization constant, p_i^0 and p_i are the regularization and model values of the i-th structural parameter of the molecule, w_i is the weight of the i-th parameter.

The structure of free 3-methyl-1-boraadamantane molecules has been determined at $100\,^{\circ}\mathrm{C}$ using both new and conventional refinement procedures by GED. The detailed analysis of parameter errors shows that the new approach allows obtaining much more accurate results for this molecule. The most important obtained semi-experimental equilibrium parameters and their total errors are: r(B-C)$_{av}$ = 1.556(5) Å, $\angle$(C-B-C)$_{av}$ = 116.5(2)°. The configuration of the boron atom is pyramidal with $\sum \angle$(C-B-C) = 349.4(4)°.



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Molecular dynamics simulations of a “blistering”-like effect in tungsten carbide

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Tungsten carbide (WC) is a very hard material with a high melting point, and it is commonly used as a substitute for diamond in drilling tools. Due to these features, it is also of interest for applications in fusion reactors.
Knowledge of the D and noble gas interaction with WC is also of importance in the manufacturing process of WC films.

Generally, solid materials degrade due to hydrogen accumulation, where the trapped hydrogen can form voids, bubbles, and blisters. Energetic D implantation into tungsten leads to the formation of blisters on its surface. This effect is also seen if carbon is present in the tungsten matrix. A “blister” is a void or bubble close to the sample surface. As blistering, we refer in this work to a rupture in the sample leading to an expanding void. This process is also sometimes called flaking or exfoliation. The mechanism of blister formation in tungsten is not yet fully understood, although both experiments and FEM simulations have been performed to tackle this problem. Recent experiments indicate that diffusion processes of D in tungsten are responsible for forming blisters.

Results of molecular dynamics simulations of cumulative deuterium cobombardment with C, W, He, Ne, or Ar impurities on crystalline tungsten carbide are presented. The simulations were performed using a reactive bond-order potential for the W-C-H system, that can both describe pure materials and compounds reasonably compared to experimental and ab initio data [1]. The studied bombardment energy range was 100 to 300 eV. During the bombardment, the sample surface changed from crystalline to amorphous. Deuterium was trapped in the sample, followed by D_2 accumulation into bubbles, which lead in some cases to a “blistering”-like effect [2].

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The structures of yttrium, lanthanum and lutetium complexes of an ABABAB-type macroheterocycle: a theoretical study

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Metallocomplexes of an ABABAB-type macroheterocyclic compound (trithiadiazoletri (4-*tert*-butylisoindole)macrocycle) with trivalent metals (La, Tm, and Lu) were synthesized for the first time in 2008 [1, 2]. The obtained substances were characterized by infrared and UV-vis spectroscopy, but their structure remains unknown.

We studied the molecular structures of the macroheterocycle complexes with yttrium, lanthanum and lutetium by the density functional theory computations using the B3LYP hybrid functional, correltaion-consistent cc-pVTZ basis sets for C, N, S and H atoms, and ECPs and triple-ζ valence basis sets for Y, La and Lu atoms. Since the previous structural studies [3, 4] have shown that the external substituents have negligible influence on the structure of the inner macrocycle, the calculations were carried out for the unsubstituted complexes (trithiadiazoletriisoindolemacrocycles).

According to the results of our investigation the $YC_{30}N_{15}H_{12}S_3$, $LaC_{30}N_{15}H_{12}S_3$ and $LuC_{30}N_{15}H_{12}S_3$ molecules have equilibrium structures of the C_S symmetry with non-planar macrocycles (see Fig. 1 for the structure of the lanthanum complex). The metal-nitrogen bond lengths are 2.370–2.409 Å, 2.559–2.578 Å, and 2.334–2.380 Å (yttrium, lanthanum and lutetium complexes, correspondingly).

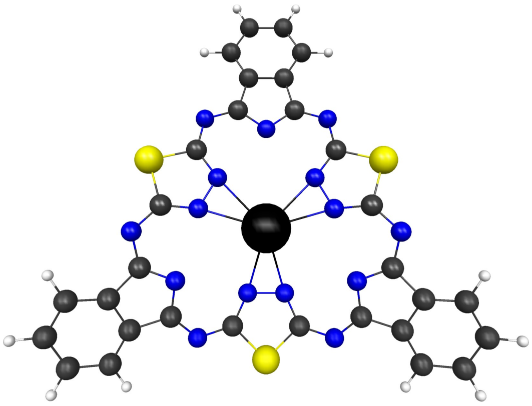

Fig. 1. Molecular structure of the $LaC_{30}N_{15}H_{12}S_3$ complex

Planar structures of the D_{3h} symmetry with the metal atom located in the center of the macrocycle correspond to transition states. The barriers to the macrocycle inversion are 40 kJ/mol (Y), 5 kJ/mol (La), and 52 kJ/mol (Lu).

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A stationary property of the APSG wavefunction

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In the standard theory of geminals[1] one constructs the wavefunction as the antisymmetrized product of two-electron functions:

$$\Psi(1,2,...,N) = \hat{A}[\varphi_1(1,2)\varphi_2(3,4)...\varphi_{\frac{N}{2}}(N-1,N)].$$

In this form, the two electronic orbitals (the *geminals*) are also antisymmetrized products of one-electron functions:

$$\varphi_i(1,2) = \sum_{\mu<\nu} C^i_{\mu\nu}\hat{A}[\chi_\mu(1)\chi_\nu(2)].$$

To obtain the final APSG wavefunction (Antisymmetric Product of Strongly Orthogonal Geminals), we have to optimize the coefficients of the geminals which can be done by solving local Schrödinger equations. However the effective Hamiltonian for one geminal depends on the coefficients of the other geminals, so we have to do this process in an iterative manner. With this method we can obtain some part of the correlation energy and if we use perturbative treatment, we can get a greater fraction of the correlation energy as well.

In our studies we considered the unitary transformation of geminals, that means an extra degree of freedom in the energy expression. In our first model calculations we considered only two geminals (four electron systems). We got that the APSG energy is stationary according to this transformation, this was a previously unknown property of the APSG wave function. This result can be verified as well by taking a closer look at the form of the matrix elements of the Hamiltonian.

[1] P. R. Surján: An Introduction to the Theory of Geminals (in Topics in Current Chemistry: Correlation and Localization, 1999, Springer-Verlag)

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Raitiovaunupysäkit:

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Ⓑ	8

Bussipysäkit:

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Ⓙ	52, 55, 55A, 506
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Kävely- ja pyöräilytiet ··········