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1-3 September 2016
Hotel Helikon
Keszthely, Hungary
1st of September, Thursday

14:10 – 14:25 Opening

Chair: Péter Surján

14:25 – 15:00 István Mayer
Local spins

15:00 – 15:30 Denisa Suchá
Relativistic effects on halogen bonding

15:30 – 16:00 János Sarka
Interpretation of the rotational-vibrational energy level structure of astructural molecules

coffee break

Chair: Attila Tajti

16:30 – 17:00 Mihály Purgel
A DFT Investigation on Hydrogenation and Redox Isomerization of Allylic Alcohols Catalyzed by Pd-Sulfosalan Complex

17:00 – 17:30 Mateusz Witkowski
Investigation of SCS-MP2 method and proposition of slightly modified parametrization of scaled-opposite-spin (SOS) MP2 variant

dinner from 18:00
2nd of September, Friday

Chair: Ágnes Szabados

9:30 – 10:00 Péter Szalay
Characterization of the excited states of DNA building blocks: a coupled cluster computational study

10:00 – 10:30 Michał Chojecki
On the Interaction of Boron-Nitrogen Doped Benzene Isomers with Water

10:30 – 11:00 Gyula Samu
Efficient implementation of three-center Coulomb-integrals and their first derivatives

coffee break

Chair: Mihály Purgel

11:30 – 12:00 Tibor Nagy
Sampling initial states for quasiclassical trajectory calculations using adiabatic switching

12:00 – 12:30 Péter Pál Fehér
Quantum chemical modeling of an acrylated isocyanonaphthalene based solvatochromic click reagent

lunch from 13:00
Chair: **István Mayer**

14:30 – 15:00  *Martin Blaško*
Interaction of small Au\textsubscript{n} clusters (n = 1 - 4) with SCH\textsubscript{3} and CH\textsubscript{2} radicals

15:00 – 15:30  *Éva Zsuzsanna Mihálka*
Convergence Enhancement in Rayleigh-Schrödinger Perturbation Theory

15:30 – 16:00  *Ádám Ganyecz*
High-Accuracy Thermochemistry of Fluoroethane Radicals

**coffee break**

Chair: **Tibor Nagy**

16:30 – 17:00  *Ádám Margócsy*
Geminal-based ring-CCD

17:00 – 17:30  *Daniel Hollas*
On the importance and modelling of quantum nuclear effects

**dinner from 18:00**
3rd of September, Saturday

Chair: Péter Szalay

9:30 – 10:00 Martin Michalík
Theoretical Study of Metal-Quercetin Complexes

10:00 – 10:30 Dóra Papp
Computation of unbound states of van der Waals complexes

10:30 – 11:00 Maciej Kosicki
Ab initio study of the electronic structure of trimers containing SrF and selected alkali-metal atoms

coffee break

Chair: Péter Surján

11:30 – 12:00 Peter Poliak
Theoretical Study of Protolytic Reactions and Tautomerization of Alizarin and Purpurin in Aprotic Solvent

12:00 – 12:30 Zsuzsanna Tóth
Revisiting Hartree-Fock instability

12:30 – 12:35 Closing

lunch from 13:00
Local Spins

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It is known that for singlet systems the spin density vanishes everywhere. Nonetheless, there are systems (e.g., antiferromagnets, singlet diradicals) for which the physics indicates that the overall singlet state is resulting from singlet coupling of non-vanishing local spins. In order to study these local spins on the wave function level, one has to decompose the expectation value $\langle \hat{S}^2 \rangle$ of the total spin-square operator $\hat{S}^2$. But $\langle \hat{S}^2 \rangle$ is a single number, for its meaningful decomposition additional conditions should be considered.

A long quest resulted in a set of requirements that permit to decompose $\langle \hat{S}^2 \rangle$ in a unique and physically relevant manner. In the lecture these requirements will be described and the derivation of the resulting formulas for single determinant and correlated wave functions will be discussed, along with some numerical examples and some further aspects of the formalism.
The present study deals with complexes which contain halogen bond. In our case, halogen bond occurs between positively charged σ-hole on atoms I or Br and negatively charged O or S atoms and π-electrons. Our trial set contains trifluoroiodomethane (or trifluorobromomethane) ...formaldehyde, iodobenzene (or bromobenzene) ... methanethiol and trifluoroiodomethane (or trifluorobromomethane) ... benzene. The structures was taken from work of Řezáč et al. We have focused our attention on impact of scalar relativistic effects on interactions energies of complexes under investigation, because it has not yet been systematically and adequately investigated yet. Bromine, and especially Iodine are heavy atoms, thus (scalar) relativistic effects could have non-negligible impact on molecular properties and interactions of such molecules.

Calculations were performed using MOLCAS and Gaussian09 program packages. Interaction energies were corrected for basis set superposition error using counterpoise correction, highest quality results were obtained using CCSD(T) method with Cholesky decomposed two-electron integrals. Relativistic effects were treated at DKH2 level, or alternatively (for Iodine) using the effective core potential.

Figure 1 Electrostatic potentials showing positively charged σ-hole on Iodine in complex F3CI...OCH2.

REFERENCES
Interpretation of the rotational-vibrational energy level structure of astructural molecules

Graduate Conference on Theoretical Chemistry 2016

János Sarka\textsuperscript{1,2}, Edit Mátyus\textsuperscript{2} and Attila G. Császár\textsuperscript{1,2}

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The molecular ion $\text{H}_5^+$ and its deuterated isotopomers have considerable relevance in interstellar processes. Complexes of methane and water are important for natural gas storage, including the naturally captured methane in marine and arctic reservoirs, and transportation. These systems are also extremely interesting molecular systems on their own right since they fall into the category of astructural molecules, where the rotational and vibrational degrees of freedom cannot be separated. For astructural molecules the standard tools of quantum chemistry, the harmonic oscillator (HO) and the rigid rotor (RR) models, fail to provide a proper zeroth-order description. The unusual structural and dynamical behavior of $\text{H}_5^+$ and the deuterated $\text{H}_5^+\text{D}_n^+$, $n = 1$–5 systems is due to the symmetry of the system, the absence of a “heavy” central atom, the light mass of the whole system, and the existence of several strongly coupled large-amplitude motions hindered by small barriers, which together cause the loss of a well-defined equilibrium structure.\textsuperscript{1–3}

The quantum dynamical description of the $\text{CH}_4\cdot\text{H}_2\text{O}$ complex\textsuperscript{4} is challenging because all intermolecular degrees of freedom correspond to highly delocalized motions, resulting from the fluxional and loosely bound character of this complex. These ‘difficult’ fluxional degrees of freedom play a central role in binding the water and the methane moieties.

The fourth-age quantum chemical code GENIUSH,\textsuperscript{5,6} employing an exact kinetic energy operator and two different potential energy surfaces (PES) for both species were used for the variational determination of rotational-vibrational energy levels corresponding to full-dimensional models of $\text{H}_5^+$ and an intermolecular model with rigid monomers for $\text{CH}_4\cdot\text{H}_2\text{O}$. Detailed investigation of the (ro)vibrational wavefunctions\textsuperscript{1,3,4} results in physically intuitive labels for several states computed. The rovibrational energy level structure of the astructural $\text{H}_5^+$ molecular ion\textsuperscript{1,2} and the $\text{CH}_4\cdot\text{H}_2\text{O}$ complex\textsuperscript{4} deviates significantly from that characterizing semirigid molecules or even those showing one or two large-amplitude motions, as observed by negative rotational excitation energies. The variational computations were supplemented with one- and two-dimensional analytic models for $\text{H}_5^+$ and detailed energy decomposition analysis for $\text{CH}_4\cdot\text{H}_2\text{O}$, which help to understand the peculiar rovibrational energy-level structure computed correctly for the first time for both molecules.
A DFT Investigation on Hydrogenation and Redox Isomerization of Allylic Alcohols Catalyzed by Pd–Sulfosalan Complex

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[Pd(HSS)] complex shows an activity in hydrogenation and redox isomerization of allylic alcohols in homogeneous aqueous solutions where HSS is the sulfosalan ligand which is the tetrahydrogenated form of sulfosalen \cite{1}. DFT calculations were carried out to investigate the hydrogenation process and the formation of the catalytically active species. The latter one is a [Pd(H)(HSS-Hphen)] complex where an incoming hydrogen molecule protonates the dissociating phenolate arm and the remaining hydrogen gives a mono hydride complex. The formation of this species can occur in two pathways due to role of the solvent molecule. This active species can hydrogenate C=O and C=C bonds in a concerted process where the proton and hydride are added to the substrate at the same step.

\cite{1} Voronova K.; Purgel M.; Udvardy A.; Bényei A. C.; Kathó A.; Joó F. Hydrogenation and Redox Isomerization of Allylic Alcohols Catalyzed by a New Water-Soluble Pd–tetrahydrosalen Complex, \textit{Organometallics} \textbf{2013}, \textit{32}, 4391–4401
Recently, there was a large interest in spin-component scaled second-order Møller-Plesset (SCS-MP2) methods, which are based on the spin resolved MP2 formula for the correlation energy. It was found that, with a proper choice of the scaling parameters, a significant improvement over standard MP2 is possible. Following the "standard" Grimme parametrization, several sets of scaling parameters were proposed [1]. Unfortunately it seems to, then there is not possible to choose one set of parameters for all applications.

Here we investigate the parametrization of the SCS-MP2, based on the correlation energy and electron density analysis. We show that the same-spin- and opposite-spin-correlated electronic densities are almost proportional to each other at each point in the real space. We also propose a slightly modified parametrization of scaled-opposite-spin (SOS) MP2 variant, which allow to obtain results with almost CCSD(T) accuracy and computational cost O(N^4).

Characterization of the excited states of DNA building blocks: a coupled cluster computational study

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DNA building blocks consisting of up to four nucleobases are investigated using the EOM-CCSD and CC2-LR methods in two B-DNA-like arrangements of a poly-adenine:poly-thymine (poly-A:poly-T) system. Excitation energies and oscillator strengths are presented and the characteristics of the excited states are discussed. Excited states of single-stranded poly-A systems are highly delocalized, especially the spectroscopically bright states, where delocalization over up to four fragments can be observed. In the case of poly-T systems, the states are somewhat less delocalized, extending to maximally about three fragments. A single A:T Watson–Crick pair has highly localized states, while delocalization over base pairs can be observed for some excited states of the (A)2:(T)2 system, but intrastrand delocalization is more pronounced in this case, as well. As for the characteristics of the simulated UV absorption spectra, a significant decrease of intensity can be observed in the case of single strands with increasing chain length; this is due to the stacking interactions and is in accordance with previous results. On the other hand, the breaking of H-bonds between the two strands does not alter the spectral intensity considerably, it only causes a redshift of the absorption band, thus it is unable to explain the experimentally observed DNA hyperchromism on its own, and stacking interactions need to be considered for the description of this effect as well.
Owing to being isoelectronic with the carbon-carbon bond, the boron-nitrogen bond has recently attracted attention of many researchers. On the one hand, an equal number of valence electrons in both cases leads to similar properties and reactivity, but on the other hand the polar character of the boron-nitrogen bond affects characteristics of a system through shifts in the electronic distribution. These shifts may lead to qualitative changes in physicochemical properties, e.g. a formation of a band gap in graphene doped with the boron-nitrogen moieties which results in a semiconductor character of these materials.

The interaction of 1,2-dihydro-1,2-, 1,3-dihydro-1,3- and 1,4-dihydro-1,4-azaborine isomers with one and two water molecules has been studied using a variety of supermolecular (Møller-Plesset – MP, and coupled cluster – CC) as well as perturbational (symmetry-adapted perturbation theory – SAPT) electron-correlation methods. It has been found that the water molecule binds to azaborine isomers through $O \cdot \cdot \cdot \pi$, $\pi \cdot \cdot \cdot H \cdot \cdot \cdot O$, and dihydrogen bonding linkages. The SAPT interaction energy decomposition shows that these complexes are mostly stabilized by dispersion followed closely by induction contributions.

The complexes of azaborines with two water molecules tend to arrange in a circular fashion with a recognizable water dimer attached to the azaborine molecule. A comparison with the CCSD(T) benchmarks shows that the non-additive contribution to the interaction energy of the trimers is negative and with a good accuracy can be accounted for by the MP2 method. A good agreement between Hartree-Fock (HF) and MP2 nonadditive energy, as well as the decomposition of HF nonadditive interaction energies divulge the importance of nonadditive induction energy in the trimers.
Efficient implementation of three-center Coulomb-integrals and their first derivatives

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Electron repulsion integral (ERI) evaluation is a key step in electronic structure calculations, and the first geometrical derivatives of such integrals are needed for geometry optimization. Even with the density fitting approximation, these tasks remain computationally demanding.

An efficient scheme for the evaluation of three-center two-electron ERIs over solid-harmonic Gaussian functions and their first geometrical derivatives based on the Obara-Saika recursion is presented. The approach uses automatically generated, optimized subroutines for shell tripets of arbitrary angular momentum quantum numbers. Integral and integral-derivative calculations are based on integrals over Cartesian Gaussian [1] and Hermite Gaussian [2] basis functions, respectively. The codes are largely vectorized, contain only the necessary operations for a given shell triplet, and calculate a reduced number of intermediate integrals during the recursion. The memory layout is designed to maximize the usage of the CPU cache, from which data arrive to the CPU about two magnitudes faster than from main memory.

Compared to our approach using a single general routine, the speedup with the optimized codes is 4 for the integral, and more than a magnitude for the integral-derivative evaluation. The scheme, after minor modifications, will be used for higher order derivative evaluation as well.

Sampling initial states for quasiclassical trajectory calculations using adiabatic switching

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The quasi-classical trajectory (QCT) method is widely used in the state-resolved theoretical investigations of elementary reactions in gas phase. In the QCT method, the motion of the atoms is simulated classically, and the only quantum effect considered is that the initial rovibrational states of reactant molecules are semiclassically quantized. Initial states are usually prepared using normal mode sampling, a method based on the harmonic approximation to the Hamiltonian, which reduces the problem of quantization to that of independent normal modes.

A sensible expectation is that the initial ensemble of classical molecular states generated this way should be stationary, similarly to the quantum state it is supposed to represent. We demonstrate that normal mode sampling provides a nonstationary ensemble even for a simple rigid molecule like methane (CH₄). Because of the nonstationarity, QCT cross sections for reaction R1: CH₄+H→CH₃+H₂ oscillate periodically as a function of the initial distance of the colliding partners. We proposed an ad hoc correction, in which reactivity parameters are calculated by averaging over a period of the oscillation [1].

Primitive semiclassical theory and Ehrenfest’s adiabaticity theorem provides a physically more established means, called adiabatic switching (AS), to prepare initial states with semiclassical quantization of the uncoupled anharmonic full Hamiltonian [2,3]. However, the applicability of Ehrenfest’s theorem is not guaranteed for molecules with chaotic and/or resonant motion [4]. A previous application of AS to CH₄ was unsuccessful [5]. We revisited the problem [6] and here we report on successful convergence of semiclassical energies. By running QCT simulations of reaction R1 we also demonstrate that the CH₄ ensembles obtained by AS are stationary.

Recently, we evaluated the Palma-Clary (PC) reduced-dimensional (RD) model in QCT simulations of reaction R1 using normal-mode sampling of initial states [7]. Here, we report on applying AS to quantize vibrational states of CH₄ for a hierarchy of RD models to investigate their reactivity in RD models of reaction R1 [8]. We also present the methods we develop for the normal mode analysis of RD models [9] and for adiabatic switching to quantize molecular vibrational states.

References
Quantum chemical modeling of an acrylated isocyanonaphthalene based solvatochromic click reagent

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The optical and biolabeling properties of a novel molecule 1-(2-acryloyloxy-3-chloro-prop-1-yl)-amino-5-isocyanonaphthalene (ACAIN) was reported in our recent publication.[1] In addition to being a real solvatochromic fluorophore it reacts quantitatively and rapidly with simple thiols in a thiol-ene click reaction. This hydrothiolation reaction is accompanied by a 1.5–19 fold increase in fluorescence intensity depending on the solvent. The theoretical investigation of this phenomenon revealed a dark state associated with the excited state relaxation of ACAIN. This process involves a “LUMO switch” between the naphthalene π* and the acryl π* orbitals. Also this S_1 state lies very close to a triplet minimum on the potential energy hypersurface giving rise to the possibility of an additional non radiative transition. Furthermore, based on these results ACAIN derivatives with modified acryl groups were synthetized and their measured optical properties agreed with the theoretical predictions.

Interaction of small Au\textsubscript{n} clusters (n = 1 - 4) with SCH\textsubscript{3} and CH\textsubscript{2} radicals

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The SCH\textsubscript{3}S radical is the smallest representative species for understanding the binding characteristics in the important class of species, Self-Assembled Monolayers (SAMs)\textsuperscript{1}, created most frequently on the gold or silver surfaces. Most important SAMs, based on the family of thiolate containing ligands\textsuperscript{2} are considered in material science, catalysis and nanotechnologies. In some applications of SAMs it may be desirable avoiding sulphur participating in a ligand. Therefore we will consider an alternative open-shell ligand, namely CH\textsubscript{2}, a diradical.

Calculations were performed using Gaussian 09 program packages. We compare DFT binding energies (BE), vibrational frequencies and thermodynamical properties of small gold clusters Au\textsubscript{n} (n=1–4) interacting with SCH\textsubscript{3} and CH\textsubscript{2} ligands (M–L complexes). The spin state and the binding mechanism in M–L varies with the participation of singly or doubly occupied lone-pair orbitals of a ligand and on the number of atoms (even or odd) of the cluster, similarly as it was observed with closed shell ligands\textsuperscript{3}. The highest BE, 338 kJ/mol, is calculated for the Au\textsubscript{4}– CH\textsubscript{2} complex with the covalent bond created by two singly occupied lone–pair orbitals of CH\textsubscript{2}. The highest binding energy in complexes with SCH\textsubscript{3} is observed for the Au\textsubscript{3}–SCH\textsubscript{3} complex with BE of 276 kJ/mol.

Figure 1 Au\textsubscript{4}CH\textsubscript{2} and Au\textsubscript{3}SCH\textsubscript{3} complex with the highest BE

REFERENCES
In Rayleigh-Schrödinger perturbation theory the energy expressions contain the product of two operators, \( \hat{Q} \) and \( \hat{W} \), where \( \hat{W} \) is the perturbation operator while \( \hat{Q} \) denotes the reduced resolvent of the zero order Hamiltonian. Although the necessary and sufficient condition for the convergence of the PT series is unknown, the appearance of the powers of \( \hat{Q}\hat{W} \) suggests that by making the norm of this operator smaller, better convergence can be achieved.

By adding a diagonal operator to the zero order Hamiltonian, we introduce level shift parameters. If we minimize the Frobenius norm of the operator \( \hat{Q}\hat{W} \) with respect to these level shift parameters, we get the so-called \( QW \)-optimized partitioning. This technique has been applied to study the convergence behaviour of the quartic anharmonic oscillator and it can also be used to calculate electron correlation in chemical systems.

We apply this method to quantum chemical problems where the usual PT does not work (e.g. it is divergent) to achieve nice numerical convergence. We calculate the correlation energy for small chemical systems such as molecules with prolonged bond length or noble gas atoms using diffuse basis set.

Convergence radii of the Møller-Plesset and \( QW \) partitionings are analysed by Goodson’s method, i.e., by finding singular branchpoints of the energy function \( E(z) \) on the complex plane via quadratic Padé approximants. Preliminary results show a significant enlargement of the convergence radii in the \( QW \) partitioning.
Since the 1990s chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) have been replaced with ozone friendly alternatives, such as hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) to use them as refrigerants, foam blowing agents or propellant gases. Although HFCs have low ozone depleting potential, because of their long atmospheric lifetime and strong infrared absorption capability their global warming potential is notable. It is important to know as accurately as possible the kinetic and thermodynamic parameters of atmospheric reactions and corresponding species for the so-called chemistry-climate models, to provide more accurate forecast on climate change. In our work we studied the following fluoroethane radicals: CH$_3$-CHF, CH$_3$-CF$_2$, CH$_2$F-CH$_3$, CH$_2$F-CHF, CHF$_2$-CH$_3$, CF$_3$-CH$_2$, CF$_3$-CHF, and CF$_3$-CF$_2$.

The geometries were optimized using the coupled-cluster singles, doubles and perturbative triples [CCSD(T)] method and the cc-pVQZ basis set. In the energy calculations, additivity of the various contributions was assumed according to the following scheme:

$$E_{TOT} = E_{HF}^\infty + \Delta E_{CCSD(T)}^\infty + \Delta E_{CCSDT} + \Delta E_{CCSDT(Q)} + \Delta E_{core} + \Delta E_{ZPE} + \Delta E_{DBOC} + \Delta E_{Rel}$$

where $E_{HF}^\infty$ is the basis set limit Hartree-Fock (HF) energy extrapolated from aug-cc-pVXZ (X=T, Q, 5) energies. $\Delta E_{CCSD(T)}^\infty$ is the correlation energy evaluated by the CCSD(T) method and extrapolated to the basis set limit using aug-cc-pVXZ (X=Q,5) results. $\Delta E_{CCSDT}$ and $\Delta E_{CCSDT(Q)}$ are the CCSDT and CCSDT(Q) contributions obtained with cc-pVTZ and cc-pVDZ basis sets, respectively. $\Delta E_{core}$ is the core correlation contribution defined as the difference between all-electron and frozen-core CCSD(T) energies. The contribution was extrapolated to the basis set limit using results from cc-pCVTZ and cc-pCVQZ basis sets. The zero-point vibrational energy (ZPE), $\Delta E_{ZPE}$, was calculated with CCSD(T)/cc-pVQZ level of theory using harmonic oscillator approximation. The anharmonic contribution were also investigated with MP2/cc-pVTZ method. The deficiencies of the Born-Oppenheimer (BO) approximation were corrected by adjusting the energy with the diagonal BO correction (DBOC) calculated at the CCSD/cc-pCVTZ level ($\Delta E_{DBOC}$). The scalar relativistic contributions ($\Delta E_{REL}$) were taken into account by determining the expectation value of the mass-velocity and one- and two-electron Darwin operators at the CCSD(T)/cc-pCVTZ level.

To correct the errors of rigid-rotor harmonic oscillator model, the torsional and inversion potential energy surfaces (PESs) were also investigated at MP2/cc-pVTZ level. Using these PESs and the hindered rotor model the ZPE, the entropy and the thermal corrections were modified accordingly.

To obtain more accurate heat of formation values, using our previous data for fluoromethane and fluoroethane derivatives, thermochemical network approach was utilized using several experimental and calculated heat of reactions ($\Delta_r H$). The heat of reactions can be written in the following form: $\Delta_r H = \Sigma \nu_j \Delta_f H (j) + \epsilon$, where $\epsilon$ is the uncertainty of $\Delta_r H$, $\Delta_f H (j)$ is the heat of formation of species $j$ and $\nu_j$ is its corresponding stoichiometric coefficient in the reaction. The set of reactions give an overdetermined system of linear equations, which was solved using iteratively reweighted least-squares (IRLS) method.
Quantum chemical correlation methods based on a single Slater determinant (so-called single-reference methods) usually describe ground state molecular systems near the equilibrium geometry well, but tend to fail at stretched geometries or excited states. These problems might be bypassed using multi-determinantal wave functions as reference (so-called multi-reference methods).

Geminal theories construct the total wave function of two-electron building blocks, providing a multi-determinantal description. One of the simplest geminal wave functions, the Antisymmetrized Product of Strongly Orthogonal Geminals (APSG) has been investigated as starting point for multi-reference correlation treatment for some time.

Corrections to the APSG wave function are mostly obtained by perturbation theory (PT). Recently, the Random Phase Approximation (RPA) based correction scheme has got extended for the APSG reference. Here, we explore a third method for correcting the APSG wave function: Coupled Cluster Doubles (CCD) within the ring approximation. We present the formulation of the problem and derivation of the working equations.

The ring-CCD energy formula is known to be equivalent to the RPA expression within the single-reference framework. It is our goal is to explore this relation at the multi-reference level of theory.
On the Importance and Modeling of Quantum Nuclear Effects

Daniel Hollas, Petr Slavíček

While the quantum nature of the electrons is unquestionable to any physicist or chemist, nuclei are often imagined and being modeled as classical particles. In my talk I would like to point to the general importance of quantum nuclear effects (NQE) in different areas of computational chemistry and how they can be effectively modeled in molecular dynamics (MD) simulations.

First, I will show how NQE typically change the structure and electronic spectra of molecules using several example systems studied in our laboratory. In some cases, the inclusion of NQE qualitatively changes the outcome of the simulations. For example, in the case of HCl(H$_2$O)$_x$ clusters, it was found that the very notion of proton dissociation becomes ill-defined due to quantum delocalization of the proton.[3]

A traditional way how to model (static) NQE is via Path Integral MD (PIMD). Using this approach, one can get the exact result, but the computational cost can be quite high, particularly in the \emph{ab initio} context. However, several methods have been recently suggested that lower the cost significantly.[4] I will focus on the so called quantum thermostat technique that relies on the Generalized Langevin Equation.[2] With this approach, NQE can be modeled at the cost of classical simulations. I have implemented these techniques into the ABIN program that is being developed in our laboratory.[1] The strength of this program is its flexibility. While it handles the propagation of the system in time, energies and forces are taken from an external \emph{ab initio} program via simple file-based interface. Utilizing these algorithmic advances and software availability, NQE can nowadays be routinely modeled within MD simulations.

References


THEORETICAL STUDY OF METAL-QUERCETIN COMPLEXES

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Since the late ’60s number of papers studying common flavonoid quercetin grows exponentially. Recently, biological and antioxidant activity of metal complexes of flavonoids have attracted interest. In terms of chelating abilities, quercetin possesses three possible metal binding sites. Despite numerous indirect evidence of preferred complexation site reported, coordination mechanism is still not completely understood. Contradictory results are often obtained probably due to the variation in experimental conditions [1]. X-ray diffraction may shed light on preferred chelating site, but there seems to be a problem with growing single crystal large enough for x-ray diffraction [2].

This study explores the affinity of quercetin to form the metal complexes with Al³⁺, Cr³⁺, Cu⁺, Cu²⁺, Fe²⁺, Fe³⁺, Mg²⁺, Ni²⁺ and Zn²⁺ ions by means of quantum chemical calculations. Employing widely used B3LYP functional complexation energy for every metal and binding site combination was evaluated. Additionally, theoretical electron transitions were calculated and compared with experimental UV-VIS spectra.

For most structures, theoretical calculations point to the 5-hydroxy-4-keto site as energetically preferred. On the other hand, 3-hydroxy-4-keto site was favored in the case of deprotonated quercetin chelating Cr³⁺ or Cu²⁺ ions. According to the complexation energy, Fe³⁺ complexes with deprotonated quercetin were most stable and Cu⁺ complexes less stable.

The results of this study could contribute to the understanding of Alzheimer disease initiation and the chemical mechanism of the potential cure by minimization the metal-induced oxidation stress in brain tissue.

Acknowledgement

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Computation of unbound states of van der Waals complexes

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Unbound states of weekly bound flexible molecules are of great interest in the field of high-resolution spectroscopy. Quasi-bound or resonance states are either associated with metastable states of a system that has sufficient energy to break up into subsystems, or, with states of a target-particle system having longer lifetimes than the collision time in a direct collision process [1]. These two different definitions give rise to two ways of determining resonance states: the first correspond to a spectroscopic approach, while the second rather indicates a dynamic point of view. Our work is based on the first definition, in as much as we are computing unbound states using a variational non-Hermitian technique, the corresponding code is called GENIUSH-CAP [2]. Determination of resonance states with this method involves the perturbation of the original rovibrational Hamiltonian with a complex absorbing potential (CAP) [3,4], thereby making the eigenfunctions of the complex Hamiltonian square integrable so that they can be expanded in the $L^2$ basis of the bound states and states above dissociation, computed with the fourth-age quantum chemical program package GENIUSH [5]. Using GENIUSH facilitates the study of reduced-dimensional models, which, besides reducing computational cost, can yield interesting information about the dynamics of the studied system. The following systems have been investigated via the GENIUSH-CAP protocol: ArNO$^+$ [6], H$_2$He$^+$[2], and the H$_2$CO [7] benchmark neutral van der Waals complex. Weekly bound van der Waals complexes are good test systems to obtain accurate resonance energies by bridging variational nuclear motion computations and scattering theory; thus, our results are compared to those obtained from scattering computations when they are accessible. In the case of H$_2$CO, experimental results are also available [2].

Ab initio study of the electronic structure of trimers containing SrF and selected alkali-metal atoms

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Slowly-moving polar molecules in the gas phase at the ultralow temperature have been extensively studied in recent years because of their potential applications in quantum information theory, simulations of quantum gases or high-precision spectroscopy. Recently, gas of SrF molecules has been directly laser-cooled to ultracold regime using a magneto-optical-trap (MOT) by DeMille and collaborators. The fact that SrF molecule is an open shell system in $^{2}\Sigma^{+}$ opens possibilities to control it with both, electric and magnetic field at the same time. There are also promising initial conditions to study the collisions with cotrapped atom to predict possibilities for cooling them by collisions with ultracold atomic gas, which can result in achievement of yet lower temperature.

The purpose of our investigations is to understand the nature of interactions in trimers including SrF molecule and alkali-metal-atoms for future studies of cold collisions. To this end, first, we study SrF molecule employing high-level quantum chemistry calculations in the frame Born-Oppenheimer approximation in their electronic ground state: equilibrium distance, dissociation and bond-dissociation energy, harmonic frequency, rotational constant, dipole moment, the average polarizability and the polarizability anisotropy were estimated. Next, we examine potential energy surfaces in trimers formed from fluoride, strontium and selected alkali-metal-atoms. Short- and long-range interactions, as well as corresponding reaction pathways are done. The calculated potentials exhibit extremely strong anisotropy which possibly contribute to large fraction of inelastic cross sections. Results are promising to perform the scattering calculations which can suggest a possibility to sympathetic cool SrF molecules using ultracold alkali-metal atom.

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References
THEORETICAL STUDY OF PROTOLYTIC REACTIONS AND TAUTOMERIZATION OF ALIZARIN AND PURPURIN IN APROTIC SOLVENT

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The density functional theory (DFT) was applied in the study of alizarin (1,2-dihydroxyanthraquinone) and purpurine (1,2,4-trihydroxyanthraquinone), the main components of a natural red dye. The energetics of the protolytic and tautomeric equilibria were calculated using the B3LYP/6-311++G** approach. Using the time-dependent DFT, the UV-VIS absorption bands of all species were predicted. Solvent effect was taken into account in all calculations by the means of solvation model based on the quantum mechanical charge density of a solute molecule interacting with a continuum (SMD model). Obtained results enabled the identification of the individual protonated/deprotonated tautomeric forms present in the experimental systems.

Fig. 1: B3LYP/6-311++G** electrostatic potential of alizarin anion radical

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Revisiting Hartree-Fock instability

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In even-electron systems with sufficiently strong electron correlation, the lowest energy Hartree-Fock solution breaks spin symmetry, resulting in an unrestricted (UHF) wavefunction, a phenomenon called triplet instability. Symmetry breaking solutions of the Hartree-Fock equations have been used to generate active spaces automatically for strongly correlated systems since the late 1980’s. Finding the lowest energy UHF solution is not simple, however. The usual procedure of starting SCF with a symmetry-broken wavefunction obtained by pairwise mixing of occupied and virtual orbitals often fails for systems with multiple instabilities which are common in organometallics. SCF convergence is also very slow near the triplet instability point, due to large quartic terms in the UHF energy as a function of orbital rotations. The directions of the triplet instabilities can be determined from the eigenvectors of the orbital Hessian with negative eigenvalues.

We have developed a method for locating the minimum on the spin symmetry breaking UHF energy surface analytically through fifth order in the orbital rotation angles. This allows the selection of the absolute minimum, and gives a wavefunction which is close to the final solution. An analytical solution for the minimum of a quartic function in several unknowns (quantic terms are zero) is made possible by the observation that mixed terms which contain an odd power of any of the rotation parameters, vanish in the basis of the eigenvectors of the orbital Hessian. The system of equations for the minimum becomes thus linear in terms of the squared orbital rotation angles in this basis. The method will be illustrated with strongly correlated systems containing several instabilities.