



Norwegian Chemical Society
Annual Meeting in Computational Chemistry
June 12 -13, 2012
Hamn in Senja





Norwegian Chemical Society Annual meeting in Computational Chemistry

The meeting will take place June 12-13 in Hamn in Senja, a Lofoten in miniature (<http://www.hamnisenja.no>), and is organized by the Computational Chemistry group in the Norwegian Chemical Society.

NB! If you have special dietary request, please send an email to the contact person.

Program

The meeting starts at 9 am on Tuesday June 12 and ends at 2 pm on Wednesday June 13. Please make your travels plans accordingly. The meeting schedule is planned so that participants can attend the Schrödinger workshop in Tromsø on June 11 (from 10 am to 5 pm), as well as the Notur workshop June 14 and 15. Please see travel details for more information on flights.

We expect that all suggested contribution will be accepted for a short presentation (20 min including questions and discussion). Please submit a title for your presentation to the contact person.

Abstracts

Contributors are requested to submit a one-page abstract as a **pdf-file**. As last year, we adopt the layout and templates of [13th ICQC – International congress of quantum chemistry](#). A book of abstracts will be provided on-line three days before the workshop (a printed version will not be available).

Accommodation

We have reserved single and double rooms at Hamn. Due to limited number of single rooms we strongly encourage participants to share room. Please indicate in your registration if you need a single room.

Registration and fees

The participation fee is 2,000 NOK with double room and 2,400 NOK for single room, and for non-members 400 NOK is added. The participation fee covers transport from Tromsø (or Bardufoss Airport) to Hamn and return to Tromsø (or Bardufoss Airport), housing and food. Payment is done at Hamn.

Not a member in the Computational Chemistry branch of the Norwegian Chemical Society (NKS)? You can register [here](#) for an annual fee of 300 NOK.

Registration is done by sending an email to the Contact person (see below) stating Name, Affiliation and NKS membership number (to get the reduced fee), room preference (single or double) and whether you will travel via Tromsø or Bardufoss.

Travel details

Bus transportation will be arranged from the University of Tromsø on June 11 at 5:30 pm and we will shortly after the meeting ends on June 13.

Bardufoss Airport is located about 45 mins from Hamn, and Norwegian has flights from Oslo to Bardufoss. You should book the flight that leaves Oslo at 8:30 pm on June 11 and return at 5:05 pm on Wednesday June 13. Bus transport from Bardufoss to Hamn is arranged for the flight that arrives 10:15 pm, as well transport from Hamn to Bardufoss for the return flight at 5:05 pm.

Sponsor

The Centre for Theoretical and Computational Chemistry (<http://www.ctcc.no/>)

Contact

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Norwegian Chemical Society
Annual Meeting in Computational Chemistry
Program

Tuesday 12.06.2012

| | | |
|-----------|-------------------------|---|
| 09:00 | Bjørn Olav Brandsdal | Welcome |
| Chairman: | Per-Olof Åstrand | |
| 09:15 | Vidar Jensen | DFT-D Studies of Transition Metal-Catalyzed Reactions: Accuracy and Insight |
| 10:00 | Ulf Ekström | Wild and tame density functional theories |
| 10:20 | Ole Swang | Computational chemistry for a better society: Atom-scale modeling at SINTEF Materials and Chemistry. |
| 10:40 | Coffee break | |
| Chairman: | Trygve Helgaker | |
| 11:00 | Clemens Woywod | Theoretical investigation of a model system for molecular photoswitch functionality |
| 11:20 | Alexey Zatula | Proton hopping through water wires in clusters $MH+(H_2O)_n$ ($M = 2,2'-BiPy, 4,4'-BiPy, 2,2'-EtBiPy, 4,4'-EtBiPy$) |
| 11:40 | Anna Pikulska | Optical rotatory dispersion (ORD) and circular dichroism (CD) of lactamide and 2-amino-1-propanol |
| 12:00 | Karina Kovalchuk | Molecular dynamic study of carboxylic acids at the water/oil interface |
| 12:20 | Maarten Beerepoot | Linear and non-linear absorption in fluorescent proteins |
| 12:40 | Lunch | |
| Chairman: | Einar Uggerud | |
| 14:00 | Hans Sverre Smalø | Stretching polymer molecules using mechanical force |
| 14:20 | Kai Lange | A paramagnetic bonding mechanism for diatomics in strong magnetic fields |
| 14:40 | Nazanin Davari | Ionization potential and excitation energy of molecules in high electric fields |
| 15:00 | Harald Møllendal | Microwave and quantum chemical investigations of cyanoacetaldehyde ($CH_2(CN)CHO$), a potential prebiotic precursor of pyrimidines found in DNA and RNA |
| 15:20 | Artur Wodynsky | Calculations of spin-spin coupling constants and NMR shielding constants of transition metal cyanides |
| 15:40 | Coffee break | |
| Chairman: | Knut Børve | |
| 16:00 | Thomas Jagau | Analytic Evaluation of Electrical Anharmonicities in Møller- Plesset Perturbation Theory and Coupled-Cluster Theory |
| 16:20 | Dan Jonsson | Gauge-origin independent calculations of Jones birefringence |
| 16:40 | Heike Fliegl | Aromatic pathways in porphyrin type molecules |
| 17:00 | Eirik Hjertenæs | Benchmark data and DFT evaluation for sodium-graphite interactions |
| 17:20 | Trinh Thaut | Simulating CO_2 adsorption and transport on graphite surface |
| 17:40 | End of session | |
| 17:45 | Break | Annual meeting in Computational Chemistry |
| 18:00 | | Outdoor jacuzzi – suits for rent!! |
| 20:00 | Dinner | |

Wednesday 13.06.2012

| | | |
|----------|-------------------|--|
| Chairman | Kenneth Ruud | |
| 09:15 | Xin Xu | Development of New Density Functionals for Accurate Descriptions of Nonbond Interactions, Thermochemistry, and Thermochemical Kinetics |
| 10:00 | Kathrin Hopmann | Iridium-Catalyzed Enantioselective Imine Hydrogenation: Mechanism and Stereocontrol |
| 10:20 | Taye Demissie | Four-Component Relativistic Chemical Shift Calculation Combined with Atomic Force Microscopy for the Structural Elucidation of Breitfussin A and B |
| 10:40 | Coffee break | |
| Chairman | Ole Swang | |
| 11:00 | Bin Gao | Plasmon resonances in linear noble metallic chains |
| 11:20 | Simen Reine | Efficient and parallel Kohn-Sham DFT developments for large molecular systems |
| 11:40 | Stella Stopkowicz | Relativistic Corrections via Fourth-Order Direct Perturbation Theory |
| 12:00 | Magnus Ringholm | A general open-ended response code |
| 12:20 | Stig-Rune Jensen | Chemistry at the basis set limit using multiwavelets |
| 12:40 | Lunch | |
| 14:00 | Departure | Bus transport to Bardufoss and Tromsø |

DFT-D Studies of Transition Metal-Catalyzed Reactions: Accuracy and Insight

Vidar R. Jensen

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Density functional methods are applied routinely in the study of structure, bonding, reactivity, and other properties of transition metal (TM) systems, and have achieved a particularly strong position as a source of information on reaction mechanisms, not least of catalytic reactions.¹ Even though considerable trust is often put in results from such DFT calculations, it is important to realize that computational TM chemistry, including DFT, still faces a number of challenges and that all the particular challenges may add up to significant errors.² For example, most catalysts and other functional TM compounds contain large organic ligands, and London dispersion forces, not accounted for by standard DFT, are important to describe correctly both the intra and inter-molecular interactions of such groups. Fortunately, significant progress with respect to development of schemes for inclusion of dispersion effects has been made in recent years,³ with a particularly simple and practical approach being that of adding an empirical term, running over all atom pairs, to the conventional DFT energy, known as DFT-D.

Complementing standard GGA and hybrid-GGA functionals with such an empirical term basically always leads to more accurate calculated relative energies,⁴ and in the presentation we will see that the improvement in some cases may be dramatic. For example, when calculating the bond enthalpy of a seemingly “harmless” TM–ligand bond, namely that of the ubiquitous phosphine class of ligands, the simple DFT-D approach, remarkably, corrects a systematic, gross underestimation on the part of standard DFT and brings the bond enthalpies into very nice agreement with experiment.⁵ Next, we will move on to explore the performance of DFT-D in more challenging tasks, such as that of calculating barriers to association/dissociation of phosphine ligands as well as to other reactions frequently involved in catalytic cycles. Importantly, the increased accuracy offered by DFT-D in calculating relative energies opens for the extraction of new mechanistic information.⁶ Finally, even if the effects of dispersion are more easily visible in relative energies, they may also manifest themselves in geometries, such as in the relative arrangements of large organic ligands frequently found in homogeneous catalysts and other TM complexes of practical use.⁷

References

- 1 Fey, N.; Ridgway, B. M.; Jover, J.; McMullin, C. L.; Harvey, J. N. *Dalton Trans.* **2011**, 40, 11184.
- 2 Harvey, J. N. *Annu. Rep. Prog. Chem., Sect. C, Phys. Chem.* **2006**, 102, 203.
- 3 Grimme, S. *Wiley Interdiscip. Rev.-Comput. Mol. Sci.* **2011**, 1, 211.
- 4 Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, 132, 154104.
- 5 Minenkov, Y.; Occhipinti, G.; Jensen, V. R. *J. Phys. Chem. A* **2009**, 113, 11833.
- 6 Heyndrickx, W.; Occhipinti, G.; Minenkov, Y.; Jensen, V. R. *Chem.-Eur. J.* **2011**, 17, 14628. Minenkov, Y.; Occhipinti, G.; Heyndrickx, W.; Jensen, V. R. *Eur. J. Inorg. Chem.* **2012**, 1507. Minenkov, Y.; Occhipinti, G.; Jensen, V. R. **2012**, to be submitted.
- 7 Minenkov, Y.; Singstad, Å.; Occhipinti, G.; Jensen, V. R. *Dalton Trans.* **2012**, 41, 5526.

Wild and tame density functional theories

Ulf Ekström

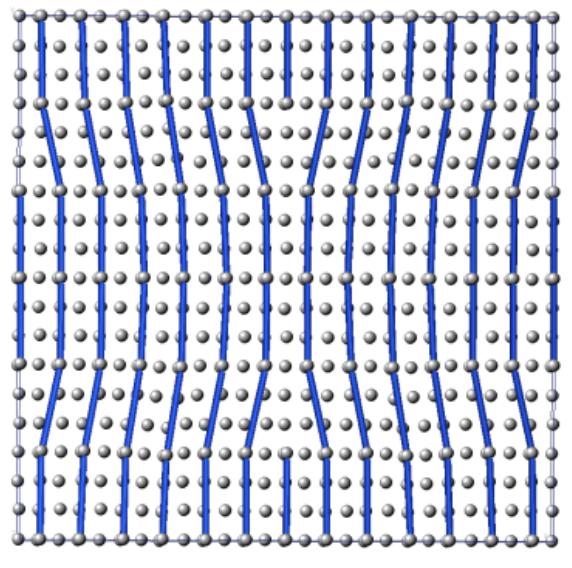
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Computational chemistry for a better society: Atom-scale modeling at SINTEF Materials and Chemistry.

Ole Swang

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Following rapid development in available computer resources and efficient formalism and software alike, our methods have become highly useful also outside academia. In the present contribution, an overview of the present activities in atom-scale modeling at SINTEF will be given, followed by some, hopefully provocative, scenarios for the future of industrially applied atom-scale modeling. Finally, some suggestions for future co-operation between academia and institute sector in Norway will be made.



Model for dislocations in metallic aluminium, keeping translational symmetry.

Theoretical investigation of a model system for molecular photoswitch functionality

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Abstract

The ground and five lowest-lying electronically excited singlet states of 2-(4-nitropyrimidin-2-yl)ethenol (NPE) have been studied theoretically using the complete active space self-consistent-field (CASSCF), Mller-Plesset second-order perturbation theory (MP2) and second-order multiconfigurational perturbation theory (CASPT2) methods. The molecule can be regarded as being composed of a frame and crane component and is characterized by the existence of two planar minima of similar energy on the ground-state potential energy (PE) surface. This work explores the possibility of a photoinduced rotation of the crane by 180° around the bond connecting both fragments, leading to the transfer of a H atom from a specific site on the frame to another one. We assess the performance of electronic structure models for the description of photoisomerization and analyze vibronic interactions between the low-lying states that are induced by the frame-crane torsion. A hypothetical reaction coordinate has been constructed for NPE. State-averaged CASSCF and CASPT2 calculations of the six lowest-lying singlet states have been performed for the isomerization. Adiabatic and simplified quasi-diabatic PE and transition dipole moment functions have been constructed. The computations indicate that there exist substantial barriers for the rotation process on the adiabatic PE surfaces of all the five excited states investigated.

Proton hopping through water wires in clusters $\text{MH}^+(\text{H}_2\text{O})_n$ ($\text{M} = 2,2'\text{-BiPy}, 4,4'\text{-BiPy}, 2,2'\text{-EtBiPy}, 4,4'\text{-EtBiPy}$)

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b) *AstraZeneca R&D Mölndal, Pepparedsleden 1, SE-431 83 Mölndal, Sweden*

Microsolvation of ions possesses many interesting aspects of fundamental nature, bridging the transition from bare ions in gas phase to ions in solution. Proton mobility in water occurs quickly, and the basic mechanism is usually referred to as the Grotthuss mechanism. Elementary steps of this process can be studied by applying suitable mass spectrometric methods to ionic water clusters, in combination with analysis of cluster size trends in hydrogen/deuterium isotope exchange rates.

According to our previous experiments of hydrogen/deuterium exchange in reactions between protonated pyridine water clusters $\text{H}^+(\text{pyridine})_m(\text{H}_2\text{O})_n$ ($m = 0 - 3$, $n = 0 - 38$) with D_2O [1], there is a completely different reaction scenario for clusters with different m . For protonated single pyridine water clusters, $\text{H}^+(\text{pyridine})(\text{H}_2\text{O})_n$, the main reaction is $\text{D}_2\text{O}/\text{H}_2\text{O}$ ligand swap. For clusters containing two pyridines, $\text{H}^+(\text{pyridine})_2(\text{H}_2\text{O})_n$, the H/D exchange is observed to be swift. A series of quantum-chemical calculations [1] showed that extra proton in $\text{H}^+(\text{pyridine})_1(\text{H}_2\text{O})_n$ clusters is bound in the form of a pyridinium ion, limiting proton scrambling. While for $\text{H}^+(\text{pyridine})_2(\text{H}_2\text{O})_n$ clusters the computational study shows that the two pyridines could transfer the site of protonation between the two bases, assisting proton mobility and H/D exchange.

Our present investigation aims at understanding of proton transfer processes inside clusters $\text{MH}^+(\text{H}_2\text{O})_n$ (where M^+ can be 2,2'-bipyridine, 4,4'-bipyridine, 2,2'-ethylenebipyridine or 4,4'-ethylenbipyridine, $n = 0 - 30$) which can be seen as a continuation of our original study of $\text{H}^+(\text{pyridine})_m(\text{H}_2\text{O})_n$ [1]. The $\text{MH}^+(\text{H}_2\text{O})_n$ are expected to deeply resemble $\text{H}^+(\text{pyridine})_2(\text{H}_2\text{O})_n$ in a structural sense, and may exhibit similar H/D-exchange characteristics due to participation of extra proton in relay mechanism through a bridge of hydrogen bonds formed between nitrogen atoms – in case of favorable position of nitrogen atoms and possible cooperation between them. This was tested by examining H/D exchange in reactions of $\text{MH}^+(\text{H}_2\text{O})_n$ clusters with D_2O in the gas phase.

[1] M.J. Ryding, A.S. Zatula, P.U. Andersson, E. Uggerud, Isotope exchange in reactions between D_2O and size-selected ionic water clusters containing pyridine, $\text{H}^+(\text{pyridine})_m(\text{H}_2\text{O})_n$, *Physical Chemistry Chemical Physics*, (2011).

Optical rotatory dispersion (ORD) and circular dichroism (CD) of lactamide and 2-amino-1-propanol

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The main aim of the project is to model the optical rotation (OR) and circular dichroism spectra (CD) of lactamide and 2-aminopropanol. To do these we need to take account the presence of the solvent (water) in our computations. There are two main approaches used for evaluating the effects of a solvent surrounding an optically active molecule on its chiroptical properties: implicit, where the solute molecule is treated quantum-mechanically (QM) and the solvent is treated as a source of a potential (PCM), and explicit, where both the solute molecule and the solvent molecules are treated at the same level. In the latter approach, solute-solvent structures can be generated by molecular dynamics (MD) or by adding explicit water molecules. In our calculations we used both explicit and implicit (employing MD and microsolvation) methods and density functional theory with B3LYP functional and aug-cc-pVTZ basis set. In molecular dynamics approach we investigate how the number of water molecules used in the model influences the calculated electronic chirooptical spectra, and what is their convergence with the number of MD snapshots. The calculated properties are compared with experimental results, also obtained in our group.

MOLECULAR DYNAMIC STUDY OF CARBOXYLIC ACIDS AT THE WATER/OIL INTERFACE

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Research problem: The present study addresses the naphthenate deposition problem that is encountered during pressure reduction, where degassing of the carbon dioxide from the production water results in an increased pH and dissociation of naphthenic acids at the water/oil interface followed by reaction with the salt ions in the aqueous phase leading to a precipitation.

Goal of present study: Understanding the factors influencing the interfacial organization and composition of tetra-naphthenic acids at the interface as well as understanding the nature of interactions between surfactants in mixed interfacial systems.

Methods and results: Molecular dynamic simulations were used to study the adsorption dynamics (Fig.1) and interfacial structure (positioning at the interface and interfacial arrangement) of a model compound (BP10) that mimics an indigenous tetra-naphthenic acid, a fatty mono-acid, and mixture of these two surfactants. The present work is mainly focused on determining the molecular parameters such as the area per molecule (A) and the second virial coefficient (B_2) of the molecules at the interface. The value of B_2 is related to the strength and nature of molecular interactions at the interface which is important when considering complex mixed interfaces. The MD results will be employed to predict the multi-component equilibrium concentration and composition of the interfacial adsorbed compounds through the use of a molecular-thermodynamic equation of state. Other physicochemical aspects such as effect of solvent nature, pH and adsorption dynamics of the model tetra naphthenic acid compound will also be addressed.

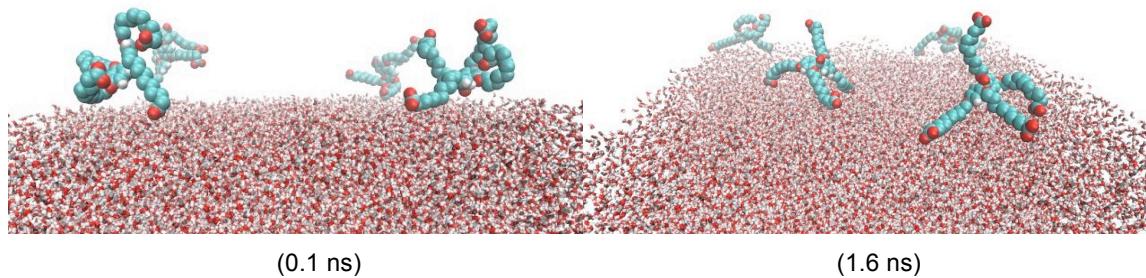


Fig.1: Adsorption process of model compound of tetra naphthenic acid at water/oil interface

Linear and non-linear absorption in fluorescent proteins

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Green fluorescent protein (GFP) and its mutants and homologs are popular tools for biochemists to study protein expression and localization in living cells. Mutations can improve the absorption cross section and can shift the excitation wavelength to allow for multi-colour imaging. We will here explore to what extent theory can reproduce differences among fluorescent proteins in both linear excitation energies and non-linear two-photon absorption cross sections.

Absorption properties are calculated using a polarizable embedding approach combined with DFT (PE-DFT), as described in Ref. [1] and applied previously to GFP in Ref. [2]. Structures are obtained from a molecular dynamics simulation on GFP and several of its mutants. The effect of structural optimization — both classical energy minimization and QM/MM optimization — is investigated. Results are presented for both one-photon and two-photon absorption on the neutral chromophore of GFP and both resonance structures of its anionic counterpart. PE-DFT calculations on the whole protein are compared to DFT calculations on the chromophore to examine the effect of the protein surrounding on the absorption properties of the chromophore.

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Stretching polymer molecules using mechanical force

Hans Sverre Smalø and Einar Uggerud,
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May 21, 2012

Abstract

Mechanochemistry is a general concept covering all aspects of how application of an external mechanical force may influence chemical properties and reactivity.¹ For example it has been demonstrated that a polymer molecule may be anchored between the tip and the base of an atomic force microscope (AFM) and then mechanically manipulated by the motion of the cantilever to which the tip is attached.

In this work mechanochemistry is investigated theoretically using a constrained geometry optimization. A previous study has shown that the DFT with the B3LYP functional works good up to moderate bond elongations,² which we also apply in this work.

Stretching a polymer may be divided into three stages, first the polymer is unfolded. This stage is not of main interest here. In the second and more interesting stage, the angles between the bonds and the bond lengths are increased. When approaching the critical force, the *weakest* bond in the polymer cannot take any more strain and the bond is broken.

One of the question tried to be answered in this work is what bond is broken and why? Butane has two kinds of C-C bonds, one central and two outer C-C bonds (which are similar due to symmetry). According to the bond dissociation energies, the central C-C bond should be the *weakest*. Therefor it might be surprising that, when pulling on butane by constraining the distance between two none-bonded C-atoms, it is actually the outer C-C bond which breaks. And the same trend also holds for larger hydrocarbon chains. The external force is not necessarily parallel to the bonds, and in the case of butane, it is seen that the external force is more parallel to the outer bond compared to the central bond. In fact it is a general trend that the outermost C-C bond easier aligns in the direction of the external force. Thus it is concluded that mechanochemical strength of a bond is not necessarily the same as chemical strength, and results indicate that the direction of the external force compared to the direction of the bond is important.

Calculation beyond the critical point may be viewed as a transition state, and thus critical energies may be calculated using constrained geometry optimization, but only for the bond which actually breaks. How close are the other bonds to breaking? When stretching a bond, the harmonic constants changes and approaches zero as we approach the critical force. The harmonic constants may be calculated for all bonds, and calculating the harmonic constants for the different bonds is an simple way to categorize the different bonds.

References

- [1] M. K. Beyer and H. Clausen-Schaumann. Chem. Rev., **105**, 2921-2947, (2005).
- [2] M. F. Iozzi, T. Helgaker, and E. Uggerud. Mol. Phys., **107**, 2537-2546, (2009).

A paramagnetic bonding mechanism for diatomics in strong magnetic fields

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Elementary chemistry distinguishes two kinds of strong bond between atoms in molecules: the covalent bond, where bonding arises from valence electron pairs shared between neighboring atoms; and the ionic bond, where transfer of electrons from one atom to another leads to Coulombic attraction between the resulting ions. We here present a third, distinct bonding mechanism: perpendicular paramagnetic bonding, generated by the stabilization of antibonding orbitals in their perpendicular orientation relative to an external magnetic field. In strong fields such as those present in the atmospheres of white dwarfs (of the order of 10^5 T) and other stellar objects, our calculations suggest that this mechanism underlies the strong bonding of H₂ in the $^3\Sigma_u^+(1\sigma_g1\sigma_u^*)$ triplet state and of He₂ in the $^1\Sigma_g^+(1\sigma_g^21\sigma_u^{*2})$ singlet state, as well as their preferred perpendicular orientation in the external field.

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Ionization potential and excitation energy of molecules in high electric fields

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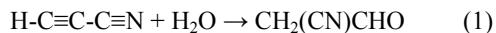
Insulating liquids are often used as a part of the dielectric barrier between two conductors in high voltage electrical equipments and may suffer a dielectric breakdown in high electric fields. Breakdown happens when a conductive plasma channel, which is created in the high field regions, propagates through the entire dielectric barrier and bridges the gap between two conductors. This phenomena is influenced by the molecular properties of the insulating liquids. Electrons are the main charge carriers in dielectrics at high fields and the concentration of free electrons depends on the ionization potential and excitation energy of the molecules. In this study, the effect of electric field on the ionization potential is investigated by density functional theory (DFT) and a field-dependent model is used which is based on the interaction between a negative point charge and a molecular cation [1]. In addition, the 20 lowest singlet-singlet excitation energies are calculated as a function of the electric field with time-dependent density functional theory (TD-DFT). Results are presented for *trans*-azobenzene, glyceryl tributyrate, N,N-dimethylaminoethylene, trichloroethylene, tetrakis(dimethylamino)ethylene and 9,10-dimethyloctadecane. It is shown that the electric field facilitates ionization processes, i.e., the ionization potential decreases by increasing the field. Furthermore, most of the excitations remain relatively constant in the field while a few of them shows a reduction. It is important to identify if an "excited state" is a bound or an unbound state, in particular at high electric fields. It is demonstrated that for some of the excitations, the unoccupied molecular orbital becomes an ionized state by increasing the field.

- [1] H. S. Smalø, Ø. Hestad, S. Ingebrigtsen and P.-O. Åstrand *J. Appl. Phys.*, **109**, 027601 (2008)

Microwave and quantum chemical investigations of cyanoacetaldehyde ($\text{CH}_2(\text{CN})\text{CHO}$), a potential prebiotic precursor of pyrimidines found in DNA and RNA

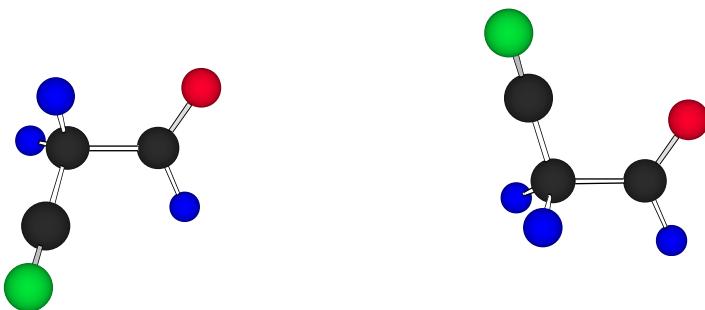
It is now well established that “small” molecules containing up to about 20 atoms are generated in the gas phase in interstellar space at temperatures often slightly above 0 K and at very low pressures. The small interstellar molecules formed in this manner may condense out on dust and other particles forming an “ice”. The ice may be bombarded by ultraviolet radiation from nearby stars setting off a series of reactions and the formation of a wide variety of larger molecules. In a recent analysis of meteorites, tens of thousands, even millions, of different compounds were found. Comets are other celestial bodies where large amounts of interstellar molecules settle down. Early Earth was bombarded by comets and meteorites with their loads of a wide variety of molecules. A better starting point for life can hardly be envisaged.

Two of the compounds found in meteorites are the pyrimidines cytosine and uracil. The first of these two molecules is part of both DNA and RNA, while uracil is found in RNA. Pyrimidines have been found in meteorites, and this shows that a prebiotic route to them indeed exists. One mechanism for the formation of pyrimidines could be the following: Cyanoacetylene ($\text{H-C}\equiv\text{C-C}\equiv\text{N}$) is a prominent interstellar compound found in many sources in space and in the atmospheres of planets. Addition of water to cyanoacetylene could produce cyanoacetaldehyde



Urea and guanidine are two well-known and relatively prevalent prebiotic compounds. They react readily forming pyrimidines.

We have modeled the uncatalyzed gas-phase addition mechanism of eqn. (1) by ab initio quantum chemistry at the MP2/6-311++G** level of theory. A reaction mechanism consisting of several steps was found in these calculations, but the activation energy of the second crucial step is relatively high (216 kJ/mol), which makes it unlikely that cyanoacetaldehyde is formed in an uncatalyzed reaction. Similar calculations were performed for an uncatalyzed reactions of water and protonated cyanoacetylene ($\text{H-N}\equiv\text{CCH}_2\text{CHO}^+$), which is known to exist in space. A significantly smaller activation energy of the second step (114 kJ/mol) was found in this case, as expected, but this activation energy is still so high that this reaction too seems unlikely. A catalyzed reaction therefore seems to be probable for the formation of cyanoacetaldehyde under interstellar conditions.



Conformers of cyanoacetaldehyde. The OCCC dihedral angle is 151(3)° in the conformer to the left and 0° in the other conformer. The 0° conformer less stable by 2.9(8) kJ/mol according to the microwave spectrum.

A detection of cyanoacetaldehyde in interstellar space would of course strengthen the hypothesis that cytosine and uracil indeed is formed in the way indicated above, or by a similar mechanism. We have made a series of quantum chemical calculations of the two conformers of cyanoacetaldehyde shown in the figure, as well as of several tautomeric forms of this compound. It is concluded from these calculations that the two forms shown here are indeed the low-energy forms of this molecule. Thousands of microwave transitions have been assigned by us and could form the basis for the detection of cyanoacetaldehyde anywhere in the Universe.

Calculations of spin-spin coupling constants and NMR shielding constants of transition metal cyanides

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Relativistic density functional (DFT) calculations of nuclear spin-spin coupling constants and shielding constants have been performed for selected transition metal (11th, 12th group of periodic table) and thallium cyanides. The calculations have been carried out using zeroth-order regular approximation (ZORA) Hamiltonian and four-component Dirac-Kohn-Sham (DKS) Hamiltonian with different nonrelativistic exchange-correlation (XC) functionals. Two recent approaches for representing the magnetic balance (MB) between the large and small components of four-component spinors, namely mDKS-RMB and sMB, have been employed for shielding tensor calculations and their results have been compared. Relativistic effects have been also analysed in terms of scalar and spin-orbit contributions at the two-component level of theory, including discussion of heavy-atom-on-light-atom (HALA) effects for ${}^1J_{CN}$, σ_C and σ_N . The results for molecules containing metals from 4th row of periodic table show that relativistic effects for them are small (especially for spin-spin coupling constants). The biggest effects are observed for the 6th row where nonrelativistic theory reproduces only about 50-70% of the two-component ZORA results for ${}^1J_{MeC}$ and about 75% for heavy metal shielding constants. It is important to employ a full Dirac picture for calculations of heavy metal shielding constants, since ZORA reproduces only 75-90% of DKS results. Smaller discrepancies between ZORA-DFT and DKS were observed for nuclear spin-spin coupling constants. Finally it has been shown that influence of the exact exchange in the relativistic calculation of heavy metal shielding constants is rather small, unlike for the coupling constants.

Analytic Evaluation of Electrical Anharmonicities in Møller-Plesset Perturbation Theory and Coupled-Cluster Theory

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The consideration of electrical and mechanical anharmonic effects is known to be crucial for the accurate theoretical description of IR spectra [1]. Electrical anharmonicities are of particular importance for the intensities of overtone and combination bands in IR spectra. The theoretical treatment of electrical anharmonicities is made possible by expanding the dipole moment operator in the normal-coordinate space. Such an expansion shows that the leading anharmonic contribution to the dipole moment is given by the second derivative of the dipole moment with respect to nuclear displacements. Hence, its evaluation requires the calculation of third-order energy derivatives.

While analytic first and second derivatives are available for use in coupled-cluster (CC) calculations with arbitrary excitation level and can be considered as quantum-chemical standard tools [2,3], only selected third derivatives of the CC energy have been calculated analytically. Most noteworthy are implementations of hyperpolarizabilities and Raman intensities [4,5]. However, fully analytic techniques for the evaluation of electrical anharmonicities have, so far, only been implemented at the Hartree-Fock level of theory[6], but are worthwhile to be extended to electron-correlated approaches.

In this presentation, we derive the theory necessary for the analytic evaluation of electrical anharmonicities at the second-order Møller-Plesset and coupled-cluster levels of theory. We demonstrate how the implementation of Raman intensities at the CC level of theory in the CFOUR program package [7] needs to be extended to cover electrical anharmonicities. In particular, third-order integral derivatives are evaluated by interfacing the GEN1INT library [8] to CFOUR.

The resulting implementation will allow for a thorough investigation of the impact of electron correlation on electric anharmonicities and may also serve as a benchmark for corresponding studies at lower levels of theory [9].

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Gauge-origin independent calculations of Jones birefringence

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When linearly polarized monochromatic light passes through a sample exposed to external uniform electric and magnetic fields that are applied parallel to each other and perpendicular to the direction of propagation of the light beam, an anisotropy of the refractive index of the sample is observed.

This anisotropy in the refractive index was first theoretically predicted in 1948 by Jones [1], from which the anisotropy now bears its name, Jones birefringence. The quantum mechanical theory of Jones birefringence was later developed by Graham and Raab [5]. More than 50 years after its first prediction Jones birefringence was observed experimentally in liquids by Rikken and coworkers [2, 3, 4].

In this talk, we present the extension of our analytic scheme for the calculation of derivatives of the electronic quasienergy for time- and perturbation-dependent basis sets [6] to the study of Jones birefringence using London atomic orbitals [7]. The use of London atomic orbitals [8] ensures that the calculated birefringence is origin independent, in contrast to earlier theoretical calculations of Jones birefringence, and particular attention will here be given to investigate the convergence of the numerical results with and without London orbitals.

Results will be presented for two non-dipolar molecules, carbon tetrachloride and naphthalene, and the dipolar molecule chlorobenzene.

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Aromatic pathways in porphin type molecules

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Magnetically induced current densities have been calculated for free-base porphyrinoids [1] using the gauge including magnetically induced current (GIMIC) method.[2] Numerical integration of the current density passing selected chemical bonds yields current pathways and the degree of aromaticity according to the magnetic criterion.[3] The calculations show that the 18π [16]annulene inner cross is not the correct picture of the aromatic pathway for porphyrins. All conjugated chemical bonds participate in the current transport independently of the formal number of π electrons. The ring current branches at the pyrrolic rings taking both the outer and the inner route. The traditional 18π [18]annulene with inactive NH bridges is not how the ring-current flows around the macroring either. The GIMIC method and its applicability has recently been reviewed in a perspective article.[4]

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Benchmark data and DFT evaluation for sodium-graphite interactions

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Diffusion of sodium through graphite materials is a contributing factor to the wear of cell linings in aluminium production [1, 2]. Atomistic modelling is a suggested approach to understanding the underlying mechanisms of sodium mobility. In order to model systems large enough to represent bulk graphite, our goal is to employ DFT. To quantify the accuracy of future DFT calculations, the description of sodium-benzene interactions by various density functionals is evaluated against benchmark coupled cluster calculations. We present CCSD(T)/aug-cc-pVTZ potential energy curves of benzene with a sodium atom and a sodium dimer. Fifteen functionals from literature have been investigated and compared to CCSD(T) results with respect to binding energy and bond length. Many of the functionals are studied with and without the D3 dispersion correction by Grimme [3]. In general, DFT underestimates the bonding between sodium and benzene, while DFT-D3 overestimates the bond strength. The relative error in binding energy is greater when D3-corrections are applied. The functionals tested that give the smallest overall error are PBE [4] and PBE0 [5]. These functionals will be used in simulations of larger and more complex system. The benchmark dataset of CCSD(T) energies provide a comparison for other functionals and corrections tested in the future.

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Simulating CO₂ adsorption and transport on graphite surface

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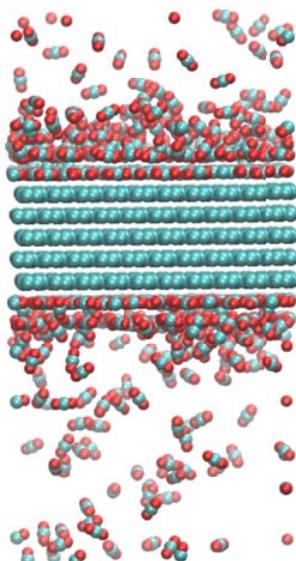
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The production of cheap membranes for CO₂ separation is of primary importance, for realization of carbon capture and sequestration technologies.¹ Nano-porous, fibrous, carbonaceous materials are promising such candidates from an experimental point of view. In order to make further progress to produce molecular sieve membranes, better knowledge of several issues are needed. Central for good membrane functionality are pore size, surface binding, surface wall transport, pore inlet control, carbon structure and composition.

Previous simulation investigated adsorption of hydrogen on graphite² and found that the pore surface plays a surprising role, pointing to a possibility to create a mobile gas layer on top of a more bounded layer. In order to compare with H₂ transport, this talk aims to study CO₂ transport and adsorption on graphite surface using Molecular Dynamic simulation (see figure 1 for an illustration).



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Development of New Density Functionals for Accurate Descriptions of Nonbond Interactions, Thermochemistry, and Thermochemical Kinetics

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Density functional theory (DFT) has become the method of choice for first principles quantum chemical calculations of the electronic structure and properties of many chemical systems. Based on the number of occurrences of functional names in the journal titles and abstracts analyzed from the ISI Web of Science (2007), B3LYP is by far the most popular density functional in chemistry, representing 80% of the total of occurrences of density functionals in the literature, in the period 1990-2006.

Is B3LYP good for everything? There is growing evidence, showing that B3LYP (1) degrades as the system becomes larger, (2) underestimates reaction barrier heights, (3) yields too low bond dissociation enthalpies, (4) gives improper isomer energy differences, (5) fails to bind van der Waals systems, etc.

How can we go beyond B3LYP? Recently, we have developed a doubly hybrid functional, XYG3, based on the adiabatic connection formalism and the Görling-Levy coupling-constant perturbation expansion to the second order (PT2). The new functional was shown to surmount some known difficulties of B3LYP, leading to a general functional with more predictive power for molecular systems of main group elements.

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Iridium-Catalyzed Enantioselective Imine Hydrogenation: Mechanism and Stereocontrol

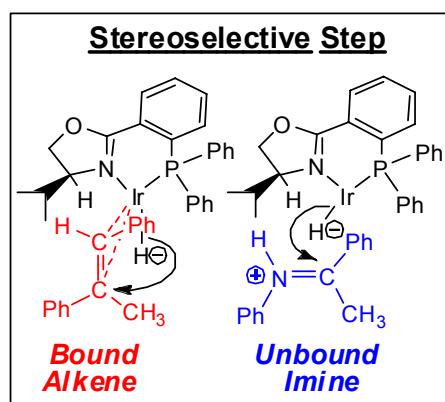
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Enantioselective imine hydrogenation is an essential synthetic process for generation of chiral amines that can be used as building blocks in pharmaceutical and fine chemical industries. A number of transition-metal catalysts for imine hydrogenation have been developed, which provide good yields and selectivities. However, from a mechanistic point of view, imine hydrogenation is generally poorly understood and much less explored than hydrogenation reactions involving alkene substrates. Imine substrates display a number of complicating factors, including the possibility of *E/Z* isomerization, η^1 or η^2 coordination of the substrate (or also lack of coordination), and the inherent asymmetry of the C=N double bond compared to the C=C counterpart, implying that the number of mechanistic possibilities is at least doubled.

We have used DFT to investigate imine hydrogenation reactions with different iridium complexes and propose a novel outer sphere mechanism, which is fundamentally different from the generally accepted inner sphere mechanism through which alkenes are hydrogenated. The imine hydrogenation mechanism exhibits feasible barriers and, equally important, predicts the correct enantioselectivities for hydrogenation reactions employing iridium complexes with different electronic and steric properties. The factors controlling the stereoselectivity of imine hydrogenation can be identified to include mainly steric interactions with the catalyst backbone, but appear also to involve interactions with a coordinated solvent molecule.



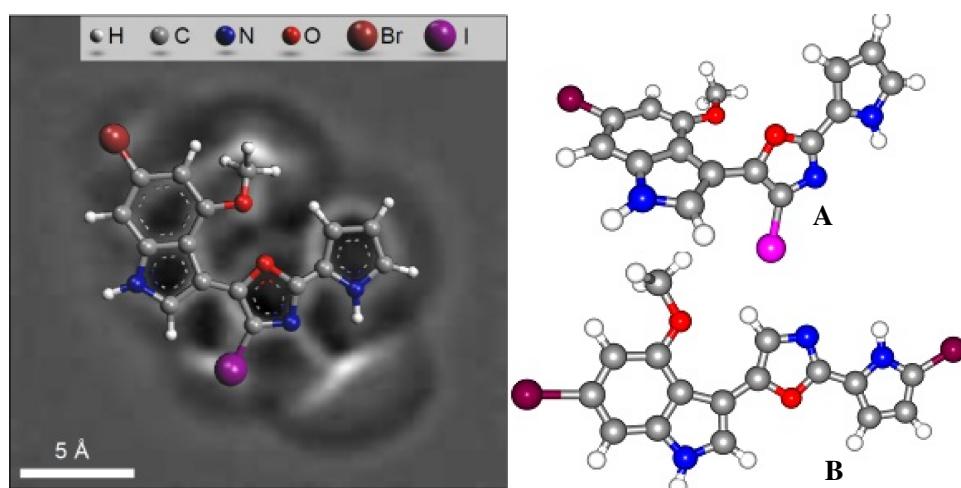
Four-Component Relativistic Chemical Shift Calculation Combined with Atomic Force Microscopy for the Structural Elucidation of Breitfussin A and B

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When only limited quantities of an isolated natural organic compound is available, it is difficult to propose a single unequivocal structure which is consistent with all the data using X-ray crystallography or spectroscopy data alone. In this study, two halogenated dipeptides, breitfussin A and B, isolated from *Thuiria breitfussi* from the underinvestigated class Hydrozoa were considered. Due to a limited quantity of the two compounds, structure determination was made based on a combination of AFM, CASE and DFT calculations, none of which were able to propose a unique solution individually.

Among the screened possible structures for the two compounds, the oxazole unit of the two compounds got further attention due to a possible swap of the atoms in the ring, which cannot be directly assessed by AFM and CASE, but is accessible by DFT calculations. Due to the presence of the heavy atom in the structures, non-relativistic shielding constant calculations were unable to choose a structure that fits well with the experimental data. Four-component relativistic calculations were performed on the screened possible structures for both compounds. The shielding constants from the four-component relativistic calculations identified the structure which fit best to the experimental results. The method and procedure followed to determine the structure of these two compounds could be a novel route for organic structure analysis in the future.



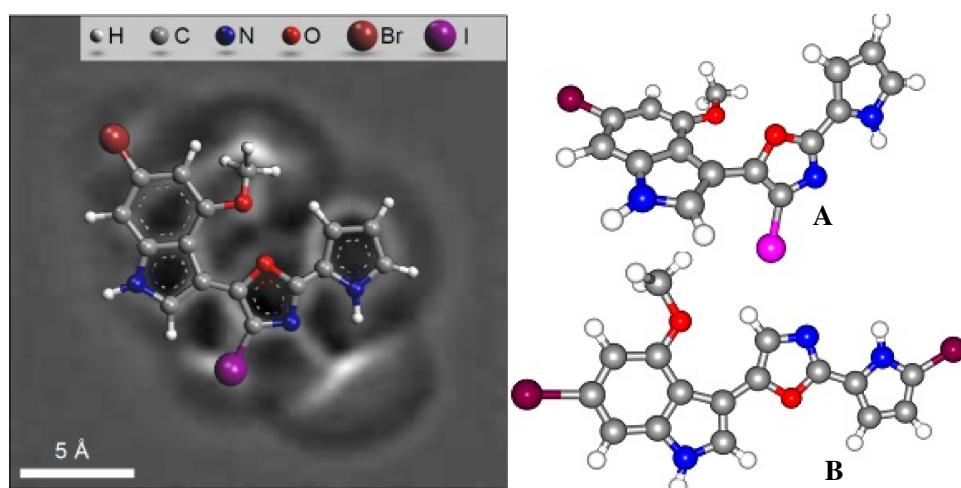
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Plasmon resonances in linear noble metallic chains

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We have investigated the electronic excitations of three noble metallic chains—copper, silver and gold using the reduced single-electron density matrix based time-dependent density functional theory. Instead of solving the linear response equation in frequency domain, the reduced single-electron density matrix is propagated in real-time domain according to the Liouville-von Neumann equation after an impulse excitation at initial time. The formation and size evolution of electronic excitations in these chains have been investigated with different number of atoms, from 2 up to 26. The longitudinal oscillations are dominated by *s* electrons at lower excitation energies, while (*d* → *p*) transitions appear at higher energies and collective resonances are involved in the first peak of (*d* → *p*) transitions. In contrast, (*d* → *p*) transitions usually appear in every resonances of transverse oscillations. Different types of resonances—collective, central and end resonances—have been observed in longitudinal and transverse polarizations, which may help to understand the surface plasmons in practice.

Efficient and parallel Kohn-Sham DFT developments for large molecular systems

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The LSDALTON program is designed to treat large molecular systems both efficiently and in a linear-scaling fashion by employing state-of-the-art methodology. In this talk we present ongoing developments in LSDALTON for the robust and efficient evaluation of Kohn-Sham DFT on contemporary supercomputer architectures, with emphasis on recent parallelization strategies.

Relativistic Corrections via Fourth-Order Direct Perturbation Theory

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In order to reach high-accuracy in quantum-chemical calculations consideration of relativistic effects in systems containing light elements can be essential. Perturbative schemes such as direct perturbation theory (DPT) [1] represent an attractive and cost-effective option in these cases where relativistic effects are small. While DPT in lowest-order, i.e. DPT2, already has evolved to a standard tool for the calculation of relativistic corrections to energies, higher-order treatments are so far scarce. For this reason, the DPT treatment is extended to the next higher order (DPT4). To facilitate the implementation, the theory is developed using analytical derivative theory [2]. In this general formulation, wave function and operators are expanded with respect to the relativistic perturbation $\lambda_{\text{rel}} = c^{-2}$, with c being the speed of light. The DPT4 correction is then given as a second derivative of the energy with respect to $\lambda_{\text{rel}} = c^{-2}$. Scalar-relativistic as well as spin-orbit contributions can be separated using Dirac's identity and calculated using the usual one-component formulations. To investigate the convergence of the DPT series, results are presented at the Hartree-Fock level as well as at the correlated level using second-order Møller-Plesset perturbation theory.

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A general open-ended response code

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In recent years, there has been a renewed interest in calculating high-order properties of relevance in chemistry. The ability to calculate high-order response properties is essential in order to treat a wide range of nonlinear experimental spectroscopic techniques computationally. In many current codes, the support for the calculation of a given property is implemented by a routine specifically designed for this property. For high-order properties, such routines can quickly become cumbersome to code and increasingly error-prone simply due to the increasing size of the routines.

A recent open-ended formulation of response theory allows the calculation of any response property at SCF levels of theory in the atomic orbital basis [1]. We present a general code based on this formulation. The principal idea behind the code is the use of recursive routines. Assuming that the necessary one-electron [2], two-electron [3-5] and exchange/correlation [6,7] contributions are available from integral routines, the code can derive the required contributions to a property, collecting the necessary information from integral and response equation solver routines and constructing the response tensor. The code can use any rule between and including the $(n + 1)$ and $(2n + 1)$ rules for determining the highest non-truncation order of (perturbed) matrices used in the calculation, notably (perturbed) density, Fock, and overlap matrices. In addition, a general caching scheme for contributions to the response tensor has been implemented, leading to significant computational savings.

With the current support of the integral routines used, the code can support the analytic calculation of geometric derivatives of the energy up to and including the quartic force field and the geometric derivatives from zeroth to third order of any polarization property (i.e. the molecular dipole moment and (hyper)polarizabilities) at the Hartree-Fock level of theory. Support for the calculation of these properties at DFT levels of theory is under development.

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Chemistry at the basis set limit using multiwavelets

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We present the performance of our Multi-Resolution Chemistry Program Package (MRCPP), which is a code using the multiwavelet (MW) basis for all-electron Density Functional Theory (DFT) calculations on molecular systems.

The MW basis is similar to the Finite Element (FE) basis, in that the 3D coordinate space is partitioned into cubic cells, and a low-order polynomial basis is assigned to each cell. One of the main advantages of the MW basis over FE, is that the formalism allows for rigorous error control in the representation of functions and operators: the resolution of the grid cells is locally adjusted to guarantee the precision of each function.

The coupled Kohn-Sham DFT equations are recast into an integral form [1]:

$$\varphi_i(r) = \int H^{(\varepsilon_i)}(r,s)V_{\text{eff}}(s)\varphi_i(s)ds$$

which is solved self consistently. Each component of the above equation is defined on its own multi-resolution grid, to guarantee the precision of the result. This allows, within a predefined accuracy, to obtain basis set limit results at the DFT level of theory, as was shown by Harrison and coworkers [2]. As the integral equation above can be viewed as a preconditioned steepest descent, acceleration techniques such as DIIS or KAIN [3] can be applied to speed up convergence. The most time-consuming step of the method, namely the application of integral operators has been highly optimized by computing explicitly all 64 components of the non-standard form of the operator and devising a linearly scaling, massively parallel scheme for the operator application.

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