

**Sat, Apr 22 9:30 0:45 Andreas Köster**

*Response theory in deMon*

Abstract not available.

**Sat, Apr 22 10:15 0:35 Tom Ziegler**

The application of TDDFT to systems with a spin or space degenerate ground state

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Ordinary time-dependent density functional theory (TDDFT) is not able to treat single excitations involving spin-flips and can thus not treat systems with spin degenerate ground state. We introduce in the first part of our talk a formulation of TDDFT based on a non-collinear representation of the XC potential. Within the non-collinear representation, we are able to apply TDDFT to atoms and molecules with a spin-degenerate ground state and thus study spin-multiplet splittings. The second part of the talk deals with spatially degenerate ground states using time-dependent density functional theory (TDDFT). We propose here a new “Transformed reference via an intermediate configuration Kohn-Sham TDDFT (TRICKS-TDDFT) method. This method avoids the complications caused by the multi-reference nature of spatially degenerate ground state by taking a non-degenerate excited state with desirable properties as the reference for the TDDFT calculation. The scope and practical application of the method is discussed.

**Sat, Apr 22 11:05 0:45 Alberto Vela**

*The Lieb-Oxford bound and the large gradient limit in the  
exchange-correlation energy*

Abstract not available.

**Sat, Apr 22 11:50 0:25 Mark E. CASIDA**

*Progress on TDDFT in deMon2k*

Abstract not available.

Sat, Apr 22 12:15 0:25 Mike Seth

*The Calculation of MCD Spectra with TDDFT*

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Magnetic Circular Dichroism (MCD) is defined as the difference in absorption intensity of left and right circularly polarized light in the presence of a magnetic field. If the MCD as a function of the energy of the incident light is measured then an MCD spectrum is obtained. MCD spectroscopy has been shown to be capable of providing much useful information including insight into the symmetry, the structure and the magnetic moment of the molecule of interest and also can aid in the assignment of the corresponding absorption spectrum. In more recent applications, the selectivity of MCD has been utilized in studies of complicated systems such as enzymes.

In the last few years we have been working on methods of calculating MCD spectra using time-dependent density functional theory. This talk will summarize our progress so far. MCD can be shown to arise due to several different contributions, each with its own physical origin. We have considered the MCD that appears when degenerate excited states are split by the applied magnetic field (A terms) and the MCD caused by breaking the degeneracy of the ground state (C terms). The calculation of C terms further required the ability to perform TDDFT calculations on systems with a degenerate ground state. Finally, it has been shown that spin-orbit coupling introduces further contributions to the MCD that can dominate the spectra when the system has little symmetry or a ground state that is only spin degenerate. Our most recent work deals with calculating these spin-orbit contributions.

Sat, Apr 22 16:30 0:35 Florian Janetzko

*Ab initio CCM: Inclusion of long-range interactions*

Florian Janetzko and Andreas M. Köster

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The SCF behavior of Cyclic Cluster Model (CCM) calculations within the deMon2k code is analyzed. The imposing of periodic boundary conditions by the CCM introduces fictitious orbitals and auxiliary functions, which cause problems for the transformation of the Kohn-Sham matrix into the orthogonal basis and the variational fitting of the Coulomb potential. A solution to these problems is (a) the use of a canonical orthogonalization of the Kohn-Sham matrix and (b) the transformation of the fitting equation into the diagonal basis of the auxiliary functions. It is shown that these modifications considerably improve the stability of the SCF in molecular calculations, too.

Finally, the Cyclic Cluster formalism for *ab initio* Kohn-Sham DFT is derived from the full periodic ansatz and the inclusion of the long-range interactions is presented.

**Sat, Apr 22 17:05 0:25 Hongjuan Zhu**

*A Theoretical Study of the Original Shilov Reaction Involving Methane Activation by Platinum Tetrachloride (PtCl<sub>4</sub><sup>2-</sup>) in an Acidic Aqueous Solution*

Hongjuan Zhu and Tom Ziegler

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Density functional theory (DFT) has been employed to investigate the rate-determining step for the Shilov reaction in which PtCl<sub>4</sub><sup>2-</sup> can catalyze H-D exchange of alkanes in acidic aqueous solution. C-H activation and methane uptake are the two possible candidates. Associative and dissociative pathways are both considered in the methane uptake step. It was not possible to determine whether methane uptake followed an associative or dissociative mechanism due to uncertainties in the calculated contributions to the free energy of activation from entropy and solvation. The active species in the Shilov reaction are PtCl<sub>4</sub><sup>2-</sup>, PtCl<sub>3</sub>H<sub>2</sub>O<sup>-</sup> and PtCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>. We have shown that PtCl<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> is the most active catalyst for H/D exchange. Rate expressions for the Shilov reaction have been derived for different reaction conditions.

**Sat, Apr 22 17:30 0:25 Jorge Martín del Campo Ramírez**

*Structure Optimization with Levenberg-Marquardt Methods*

Jorge Martín del Campo Ramírez and Andreas M. Köster

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Restricted step methods are widely used for molecular structure optimizations. In this presentation we show the implementation of a restricted step method based on the Levenberg-Marquardt step selection [1]. We will demonstrate that this step selection is superior to the RFO algorithm [2] currently implemented in deMon2k. We will also derive the extension of the Levenberg-Marquardt step selection for a potential energy walking algorithm as well as for the transition state search [3]. The relation to the intrinsic reaction coordinate algorithm from Schlegel [4] is worked out. Selected examples are presented.

References

- [1] K. Levenberg, *Quart. Appl. Math.* 2, 164 (1944). D. W. Marquardt, *SIAM J.* 11, 431 (1963). R. Fletcher, *Practical Methods of Optimization*, Vol. 1 (John Wiley and Sons, Salisbury, 1980).
- [2] A. Banerjee, N. Adams, J. Simons, R. Shepard, *J. Phys. Chem.* 89, 52 (1985).  
J. Baker, *J. Comp. Chem.* 7, 385 (1986).
- [3] P. Culot, G. Dive, V. H. Nguyen, J. M. Ghuyssen, *Theor. Chim. Acta.* 82, 189 (1992). J. M. Bofill, *J. Comp. Chem.* 15, 1 (1994).
- [4] C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* 94, 5523 (1990).

**Sat, Apr 22 17:55 0:25 Alicija Haras**

*DFT Study on the Copolymerization of Ethylene with Polar Monomers Catalyzed by Transition Metal Complexes*

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DFT method is well proven to be valuable tool in analyzing compounds containing transition metal atoms. Herein we present our theoretical study on the copolymerization of ethylene with polar monomers in the presence of the neutral Pd(II) complexes proposed by Drent et al. [CHEM. COMMUN. 2002, 744–745]. Based on experimental findings by the authors, the catalytic systems are capable to provide a linear topology of copolymers composed of ethylene and methacrylate but the origins of this phenomenon remain unclear. Our computational data on processes involved in chain propagation and migration of catalytic active center along the formed polymer chain allow to rationalize the experimentally observed behavior of the Drent systems and to propose some modifications of the catalyst in order to obtain its higher efficiency.

**Sun, Apr 23 9:00 0:35 Tomasz A. Wesolowski**

*Subsystem formulation of DFT: Recent formal developments and applications of the orbital-free embedding formalism -deMon2K perspective.*

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We will focus on our recent works, in which the deMon2K implementation of the orbital-free embedding effective potential of Wesolowski and Warshel [Eqs. 20 in J. Phys. Chem. vol. 97, 8050] was used. As far as formal issues are concerned, the numerical consequences of the divergence of the embedding potential at the position of the nuclei will be discussed [1] and new benchmarking studies for weak and hydrogen-bonded intermolecular complexes will be presented [2,3]. New applications of the formalism to study: spin-state of the transition-metal containing enzymatic centres [4] and the electronic structure of the manganese impurities in fluoroperovskites [5]. Examples of the recent applications of our first-principles based orbital-free embedding effective potential in multi-level computer simulations [6,7] using other-then-deMon2K numerical implementation of will be overview to illustrate our objectives as far as the deMon2K code is concerned.

[1] M. Dulak and T.A. Wesolowski, J. Chem. Phys. (2006) in press

[2] J. Chem. Phys. vol.124 (2006) 024104.

[3] M. Dulak and T.A. Wesolowski, to be published

[4] Chem. Eur. J. vol. 12 (2006) 2532-2541.

[5] J. Phys.: Condens. Matter, vol. 18 (2006) 1519-1534.

[6] J. Chem. Phys. vol. 123 (2005) 114101.

[7] J. Phys. Chem. A. vol. 109 (2005) 7805.

Sun, Apr 23 9:35 0:35 Annick Goursot

*Hydrophobic interactions, evaluation and understanding*

Abstract not available.

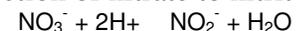
Sun, Apr 23 10:10 0:35 Nino Russo

*Mechanism of nitrate reduction by desulfovibrio desulfuricans nitrate reductase. A theoretical investigation.*

Monica Leopoldini<sup>a</sup>, Nino Russo<sup>a</sup>, Marirosa Toscano<sup>a</sup>, Marcin Dulak<sup>b</sup>, and Tomasz Adam Wesolowski<sup>a</sup>

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Nitrate reductases have an important role in nitrogen assimilation, by catalyzing the reduction of nitrate to nitrite:



Reaction starts with the five coordinated Mo<sup>IV</sup> (Mo<sup>IV</sup>SCys(SR)<sub>4</sub>) that, in this oxidation state, can coordinate a nitrate ion. The latter binds to the metallic centre by one of its oxygen atoms. Then, through an associative transition state with a substantial M—OX bond-making character, the Mo<sup>IV</sup> is oxidized to Mo<sup>VI</sup> and NO<sub>2</sub> is released. Mo<sup>IV</sup> is restored in another step, by two protons coming from water molecules present in the active site, and two electrons coming from a Fe<sub>4</sub>S<sub>4</sub> cofactor cluster. In this work, the oxidative half-reaction of the oxygen atom transfer from nitrate molecule substrate to a Mo<sup>IV</sup> complex, was investigated at density functional level. Two models were used for enzyme active site simulation that differ by the presence of a number of amino acidic residues that can have an important role in determining the catalytic efficiency. The influence of these nearest amino acids claimed out as the most well conserved ones among nitrate reductases, was investigated using a two layered ONIOM (B3LYP/UFF) method extensively used to compute potential energy profiles for biological large systems, and the Orbital-Free Embedding approach.

**Sun, Apr 23 11:00 0:35 Thomas Heine**

*Multi-scale simulations with deMon*

Thomas Heine, Serguei Patchkovskii, and Helio A. Duarte

The experimental version of deMon has been extended with DFTB and MM methods (DFTB, SCC-DFTB, UFF). The efficient implementation of periodic boundary conditions allows to treat some 10000 or even 100000 atoms on regular computers, and OpenMP parallelisation makes efficient use of modern multi-core and multi-CPU machines. The consequent continuation of our present strategy puts special needs for to the 'master' code. A possible directions for further development will be discussed. Examples of the present simulations include electromechanical properties of nanotubes and nanostructures and guest-host interactions of biological molecules in aqueous solution.

**Sun, Apr 23 11:35 0:25 Patrizia Calaminici**

*Applications on Large Systems with deMon2k*

Patrizia Calaminici

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Calculations on large systems like zeolites models and fullerenes have been performed using the density functional theory deMon2k code. Different zeolites models like mordenite-type zeolites containing up to more than 400 atoms as well as different fullerenes containing up to 540 atoms have been considered. The structures of all studied models have been optimized. In the zeolites systems the only restriction that the position of the hydrogens atoms terminating the zeolites models are kept fixed is introduced. The calculations were of all-electron type. Local and gradient corrected functionals have been used. Optimized geometries, energetic parameters and molecular electrostatic potential maps will be presented. The obtained results will be compared with available experimental and theoretical data.

**Sun, Apr 23 12:00 0:25 Tzonka Mineva**

*On the applicability of numerical algorithms based on Slater sum rule to atomic multiplets within DFT*

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Two possibilities to use the Slater sum rule were implemented in deMon code: the first numerical scheme consists of writing the term energies as a weighted sum of the non-equivalent by symmetry single-determinant energies; the second scheme consists of writing the term energies as functions of Racah or Slater-Condon parameters. The latter being obtained from the least square fitting over the density functional (DF) energies of all single determinants within a full manifold of a given electron configuration. This second algorithm is incorporated in deMon program for the 3d atoms. Within the use of Racah parameters the redundancy problem inherent to the first computational scheme is overcome.

A comparison from the results obtained with both computational schemes will be presented. Multiplet energies for various electron configurations of atoms and ions of the first transition metal row will be critically discussed. The performance of the method was examined using several GGA exchange-correlation functionals and basis sets.

**Sun, Apr 23 12:25 0:35 Sourav Pal**

*Density functional response approach: deMON implementation of approximate CPKS scheme*

Abstract not available.

Sun, Apr 23 16:30 0:25 Max Dion

*A Density Functional for Dispersion Forces*

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Rutgers University

H. Rydberg and B.I. Lundqvist  
Chalmers University

A non-empirical density functional that accounts for long range dispersion interactions will be presented [*Phys. Rev. Lett.* **92**, 246401 (2004)]. The functional is also seamless, meaning that the system does not have to be arbitrarily divided in interacting fragments. It is based on the linear response of the electrons to an electric field. To obtain such a response, the occupied and unoccupied orbitals are usually needed. However our approximation treats the response as a pure density functional, so that no cumbersome orbital interactions are needed. Some results on simple systems will be presented.

Sun, Apr 23 16:55 0:35 Sandro Chiodo

*Solvent Effect by a quasilinear RISM approach*

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The need to reliably model chemical reactions and biological processes in aqueous solution forces theoretical chemists to use computational approaches based mainly on a Continuum Model description. We present an alternative and computationally efficient method to treat free energies of hydrated systems by resolution of integral equations. The reference interaction site model (RISM) is representative of the methods based on the integral equations theory. In this approach solvation free energies can be expressed as a function of the radial distribution functions (RDF) and the direct correlation function. The model provides detailed information on the solute-solvent interaction in terms of statistically averaged site-site distribution functions. In the basic model the electronic structure of the solute and the solvent distribution around the solute can be obtained self-consistently. A set of partial charges of the gas-phase quantum mechanical system is determined as first step. These charges are used to calculate the solvent distribution around the solute. The electrostatic potential produced is added to the Fock operator to obtain the partial charges of the solvated species. The procedure is repeated up to convergence is achieved. These iterations are expensive for *ab-initio* calculations. We have modified the RISM approach by introducing repulsive bridge functions and quasilinear response solvent effects. We have applied this method for the calculation of the solvation free energies of ionic species.

**Sun, Apr 23 17:30 0:25 Simone Tomasi**

*Methyl Acrylate Group Transfer Polymerizations with Early d-Block and f-Block Metallocenes*

The monometallic Group Transfer Polymerization (GTP) of methyl acrylate (MA) catalyzed by Sm-based and Zr-based metallocenes has been studied with DFT methods. The processes examined are the generation of the catalytically active species, the subsequent C-C coupling reaction and the ring opening of a metallacyclic stable intermediate, resting state of the polymerization process, obtained from the C-C coupling. The mechanism for a neutral zirconocene, a cationic zirconocene and a neutral samarocene are compared. The isoelectronic neutral samarocene and cationic zirconocene systems share many features, which explains their similar behavior in both the C-C coupling (no energy barrier on the potential energy surface) and the MA-assisted opening of the metallacycle. An analysis of the factors driving polymer stereoregularity in the processes catalyzed by the neutral samarocene and the cationic zirconocene has led to identifying a relationship between stereoregularity and the relative disposition of the acrylate and enolate ligands, as well as the direction of the incoming MA molecule in the opening of the metallacycle resting state. Based on these discoveries a kinetic model has been developed, which has proved successful in qualitatively predicting stereoregularity.

**Sun, Apr 23 17:55 0:25 Marcin Dułak**

*Accuracy of Coulomb based density fitting approaches for the calculation of intermolecular electrostatic energies*

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Three different Coulomb based density fitting approaches to the calculation of intermolecular electrostatic energies are investigated, employing the input electron densities from the self-consistent field Kohn-Sham procedure with variational density fitting. It is found that the constraint on the approximated densities to integrate to the number of the electrons in each subsystem is not necessary, and that with the monomolecular expansion of the basis and auxiliary sets, the three-term corrected expression for the calculation of the electron-electron repulsion energy together with "exact" (calculated using the density matrices) electron-nuclear attraction energies result in the average absolute errors of the intermolecular electrostatic energy smaller than  $10^{-5}$  Hartree (averaged from ten geometries of the water dimer). The approximated (calculated using fitting procedures) intermolecular electrostatic energies do not show any important deterioration of the accuracy with the increasing size of the interacting subsystems, the drawback present in the Kohn-Sham intramolecular ones, as tested on the chains formed by increasing number of Ne atoms.

**Mon, Apr 24 9:00 0:35 Lars G.M. Pettersson**

*X-ray spectroscopy calculations in StoBe*

Abstract not available.

**Mon, Apr 24 9:35 0:35 Klaus Hermann**

*Recent developments of StoBe and application to systems of catalytic interest*

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The computer code demon-StoBe (STOCKHOLM/BERLIN) is a quantum chemical tool to calculate electronic parameters and spectroscopic data for free and adsorbed molecules as well as for local sites at substrate surfaces and in the bulk. The calculations are based on Density-Functional Theory (DFT) together with gradient corrected functionals where electronic excitations are treated at different levels of approximation. The corresponding theoretical results can help to interpret experimental spectra and can provide a detailed understanding of excitation phenomena and other physical behavior on a microscopic scale. This applies, in particular, to electron spectroscopy experiments using synchrotron radiation such as X-ray absorption (XAS/NEXAFS). Here we describe recent improvements of the demon-StoBe code including the implementation of Dolg pseudopotentials and parallel computing strategies to evaluate polarization tensors and vibrational modes. Further, examples of recent applications to systems of catalytic interest will be discussed: experimental angle-resolved NEXAFS spectra for phenylpropene adsorbates on Cu(111) together with theoretical StoBe results have been used to determine the adsorbate geometry quantitatively. Further, differently coordinated oxygen sites in vanadium and molybdenum oxides could be discriminated by comparing experimental angle-resolved NEXAFS spectra with theoretical excitation spectra obtained by StoBe calculations.

**Mon, Apr 24 10:10 0:25 Bernardo Zuniga**

*Implementation of an NMR Module in deMon2k*

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In this presentation we report the status of the implementation of an NMR module in deMon2k [1]. The aim of this work is to merge the integral and orbital localization routines from deMon2k with the chemical shift calculation of the MASTER code [2]. The main features of the angular momentum and spin-orbit integral calculations and the orbital localization procedure will be discussed. The new implementation lifts the current restrictions in the  $l$  quantum numbers for the basis and auxiliary functions in the MASTER code. Validation results will be presented.

[1] A.M. Köster, P. Calaminici, M.E. Casida, R. Flores-Moreno, G. Geudtner, A. Goursoot, T. Heine, A. Ipatov, F. Janetzko, S. Patchkovskii, J.U. Reveles, A. Vela And D.R. Salahub, The deMon Developers (2005).

[2] V.G. Malkin, O.L. Malkina, M.E. Casida, D.R. Salahub, J. Am. Chem. Soc. 116, 5898 (1994).

**Mon, Apr 24 10:35 0:20 Gerald Geudtner**

*Technical notes on the parallel deMon code*

A short introduction in the parallelization of the deMon source code will be given. The focus will not be on how to parallelize but what are consequences because it was parallelized. Furthermore, an introduction of the installation of the parallel deMon code will be given.

**Mon, Apr 24 11:10 0:25 11:35 Rui Zhu**

*Water clusters by QM/MM using deMon+Tinker*

Besides carrying out complete DFT calculations for a system, the deMon program can also perform QM/MM hybrid calculations based on the ONIOM method. On the QM part of the system, a variety of DFT methods can be specified in the current deMon program; on the MM part of the system, however, only the Universal Force Field (UFF) is available so far. This imbalance strongly limits the application of QM/MM in deMon. The Tinker program is a molecular mechanics program which includes 19 different force fields, such as MM3, CHARMM, and AMBER. The primary purpose of this study is to make Tinker-provided force fields available to deMon so that the 19 force fields could be arbitrarily combined with the DFT methods in the QM/MM calculations. In this short talk, I will first briefly state the method for incorporating Tinker into deMon. Then, I will explain some keywords for the deMon & Tinker (dT) program. Also, some practical issues, such as how we make input files for the dT, are also involved. Finally, some results from the QM/MM study of small water clusters by using the dT will be presented.

**Mon, Apr 24 11:35 0:25 12:00 Yue Zhang**

*Implementation of meta-GGA in deMon code*

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Meta-GGA (meta generalized gradient approximation) obtained improvement over normal GGA. The subroutine of the kinetic energy density was added to the demon code. The subroutines of the kinetic energy density and Laplacian were validated by obtaining the same exchange and correlation energies of BmT1 functionals. Combining the PKZB and TPSS meta-GGA exchange with PBE and tau1 correlations, the calculated results are presented using non-self consistent method.

**Mon, Apr 24 12:00 0:25 12:25 Jan Andzelm**

*Multiscale modeling of sulfonated copolymers*

An important class of thermoplastic elastomers involves styrenic and polyisobutylene blocks (SIBS). Sulfonated SIBS Triblock Copolymers (S-SIBS) are of particular interest because of potential applications for fuel cell and textile applications, where breathable, protective clothing is required. We have used multiscale modeling to gain an understanding of the static and dynamic properties of these polymer systems at detailed atomistic and mesoscale levels. Quantum chemistry tools were used to elucidate the bonding of water molecules and sulfonate groups. In addition, Molecular Dynamics was applied to calculate the polymer density at various levels of sulfonation. The structure of polymer with ions and also water and alcohol was studied and the channels allowing for diffusion were identified. The diffusion coefficients were calculated and compared to experimental data. Next, the mean-field dynamic density functional theory was utilized to obtain the morphology of SIBS block copolymers and their blends with polystyrene and polyisobutylene. Using these results permeability of water was calculated via the finite element method. A comparison between the theoretical results and recent experimental work will be presented.

**Mon, Apr 24 12:25 0:25 12:50 Anastassiia Moussatova**

*Theoretical study of the mechanism of catalysis by adenosine deaminase*

Biological processes are commonly catalyzed by metalloenzymes, containing transition metals in the active site. It is hoped that the investigation of the action of the metal during these processes will allow better understanding of the mechanism of reaction with further application of the knowledge towards rational design and development of more efficient catalysts in biological/chemical settings.

The current theoretical study uses density functional theory to explore the mechanism of reaction by Zn-metalloenzyme *adenosine deaminase* (ADA). ADA catalyzes the irreversible hydrolysis of adenosine and deoxyadenosine to inosine and deoxyinosine, respectively. The energy profile of reaction steps suggested in experimental literature was investigated by localization and structural, electronic and energetic characterization of the reactant, products and key intermediate and transition-state structures. The proposed mechanism of reaction will be discussed.

**Tue, Apr 25 9:00 0:25 Petr Jurecka**

*Density Functional Theory Augmented with an Empirical  
Dispersion Term*

Standard density functional theory is augmented with a damped empirical dispersion term. The damping function is optimized on a small, well balanced set of 22 van der Waals complexes and verified on a validation set of 58 vdW complexes. Both sets contain biologically relevant molecules such as nucleic acid bases. Results are in remarkable agreement with reference high-level wave function data based on the CCSD(T) method. The geometries obtained by full gradient optimization are in very good agreement with the best available theoretical reference. In terms of the standard deviation and average errors, results including the empirical dispersion term are clearly superior to all pure density functionals investigated – B-LYP, B3-LYP, PBE, TPSS, TPSSh, and BH-LYP and even surpass the MP2/cc-pVTZ method. The combination of empirical dispersion with the TPSS functional performs remarkably well. The most critical part of the empirical dispersion approach is the damping function. The damping parameters should be optimized for each density functional/basis set combination separately. To keep the method simple, we optimized mainly a single factor,  $sR$ , scaling globally the vdW radii. For good results a basis set of at least triple zeta quality is required and diffuse functions are recommended, since the basis set superposition error seriously deteriorates the results. On average, the dispersion contribution to the interaction energy missing in the DFT functionals examined here is about 15% and 100% for the hydrogen-bonded and stacked complexes considered, respectively.

**Tue, Apr 25 9:25 0:25 K. B. Sophy**

*Implementation of the numerical-analytic CPKS procedure in the  
deMon 2k*

K. B. Sophy and Sourav Pal

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We discuss our implementation of the linear response approach to the density functional theory (DFT) in the Kohn-Sham (KS) framework for the linear and non-linear electric properties of molecules. The equations involved are single-particle orbital equations which are solved using Gaussian basis sets. Hence, the density derivative can be obtained using coupled-perturbed Kohn-Sham (CPKS) procedure. Our method requires the derivative of the KS operator matrix to be obtained numerically using a finite-field approach. Further the orbital response is obtained using the analytical coupled-perturbed Kohn-Sham (CPKS) equations for each of the x, y and z directions. These equations have a single step solution. The orbital response obtained from them can be used to get the polarizability and first hyper polarizability tensor components. The approach is viable, especially for larger molecules. Earlier, we had integrated our formalism in the version 3.5 of deMon-KS. We have now incorporated this idea of ours in the deMon 2k, version 1.7, and would discuss the algorithm and present preliminary results for some test cases.

**Tue, Apr 25 9:50 0:25 Serguei Patchkovskii**

*Calculation of heat conductivities with non-equilibrium MD*

Andre Erwan<sup>a</sup>, Emile Bevillon<sup>a</sup>, and Serguei Patchkovskii<sup>b</sup>

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Heat conductivities are of both crystalline and amorphous materials are of a considerable fundamental and technological interest. The standard equilibrium molecular dynamics approaches to calculations of heat conductivities, based on Green-Kubo formalism, have proven difficult in practical applications. Through lack of attention to the relevant literature, we have re-discovered the “heat pipe” non-equilibrium molecular dynamics technique (HP-NEMD) [T. Ikeshoji and B. Hafskjold, Mol. Phys. 81, 251 (1994)].

We improve the robustness, ease of use, and convergence of the HP-NEMD approach in several key areas: a) we impose a momentum-conserving constant heat flux on the system, allowing easy separation of contributions due to mass transfer and heat conductivity; b) we employ multi-zone sensing, improving convergence of the results and giving additional insight for heterogeneous systems; and c) we derive statistical tolerances of the heat conductivities in the HP-NEMD approach. Taken together, these improvements allow robust, black-box calculations of heat conductivities of complex systems.

**Tue, Apr 25 10:30 0:35 Alexei Arbuznikov**

*Local hybrid functionals: recent progress in their development, and thermochemical tests*

A. V. Arbuznikov, M. Kaupp, and H. Bahmann

The concept of hybrid functionals has been generalized recently by introducing “local hybrid functionals” [1] with the position-dependent exact-exchange (EXX) admixture governed by a so-called “local mixing function” (LMF). Since such functionals are clearly more flexible than traditional hybrids (with the constant EXX admixture), one may expect superior accuracy of local hybrid functionals provided that the LMF is chosen well from a physical point of view.

For the first time, we have implemented local hybrid functionals in a self-consistent fashion, within the framework of the optimized effective potential (OEP). The resulting “localized local-hybrid” (LLH) potentials with two different choices of the LMF have been tested in calculations of atomization energies. Our thermochemical results, together with careful analysis of the spatial distribution of the LMFs have provided substantial new insight that will help to improve local hybrid functionals and the corresponding LLH potentials.

LLH potentials based on the improved LMFs seem to be very promising for precise calculations of a wide range of properties beyond thermochemistry.

[1] J. Jaramillo, G. E. Scuseria, M. Ernzerhof, J. Chem. Phys. 118, 1068 (2003).

**Tue, Apr 25 11:05 0:25 Victor Dominguez**

*An Iterative Solver for the Coulomb Fitting*

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An iterative solution for the variational Coulomb fitting based on automatic preconditioning by quasi-Newton updating [1] is presented. In our implementation we combine the inverse BFGS update [2] with a quadratic line search. The memory demand of the algorithm, previously a bottleneck in deMon2k [3], is drastically reduced. A detailed analysis of the performance of the iterative Coulomb solver is given. Large scale validations will be presented.

References

- [1] J.L. Morales, J. Nocedal, SIAM J. OPTIM, 10, 1079,(2000).
- [2] R. Fletcher, Practical Methods of Optimization, Volume 1, Unconstrained Optimization, (John Wiley and Sons, New York, 1980).
- [3] A.M. Köster, P. Calaminici, M.E. Casida, R. Flores-Moreno, G. Geudtner, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, S. Patchkovskii, J.U. Reveles, A. Vela and D.R. Salahub, The deMon Developers (2005).

**Poster 1. Nicolas Jardillier**

*Capping Electron Core Potential as link atoms : Methodology and Application.*

Abstract not available.

**Poster 2. Giovanni Morales**

*Static Modeling of Ketene Dimerization Reaction using ADF*

Tom Ziegler, and Giovanni Morales

We carried out calculations on the ketene dimerization reaction using ADF software considering the following product dimers: [1] diketene, [2] 1,3-cyclobutanodione, [3] 2,4-dimethylene-1,3-dioxetane and [4] 2-methyleneoxetan-3-one. The last one has not been considered before as a product of this reaction. Structures were optimized using the exchange functional PW86x, the correlation functional PBEc and the DZP Slater-type basis set. Vibrational frequencies were obtained with the same functionals and basis set. Single points calculations were applied on the optimized structures using the hybrid functional B3LYP. Transition states were calculated for each kind of dimer and intrinsic reaction coordinate methodology was applied to confirm the link between the reactants and the products.

Energy barriers for product dimers [1], [2], [3] and [4] were calculated to be 29.44, 26.98, 54.45 and 233.42 kcal/mol respectively. Dimers No 3 and No 4 are less stables than the starting ketenes by having a heat of reaction of 12.62 kcal/mol and 3.40 kcal/mol respectively. Dimers 1 and 2 have much greater stabilization with a heat of reaction of -16.20 kcal/mol and -11.54 kcal/mol respectively. Experimentally dimer [1], the diketene, is the major product, this suggest that the reaction is controlled thermodynamically.

**Poster 3. Victor Manuel Medel Juárez**

*Conformational Analysis of the naturally occurring  $\alpha$ -amino acids*

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To gain insight on the role played by the intramolecular interactions in the conformational distribution of naturally occurring  $\alpha$ -amino acids, we have under-taken the task of determining the conformational spectrum of the most common  $\alpha$ -amino acids. Different theoretical methodologies, ranging from molecular mechanics with the MMFF and SYBYL force fields, semiempirical with the PM3 parameterization, both as implemented in Spartan<sup>1</sup> and deMon2k<sup>2</sup> calculations with the PBE exchange-correlation energy functional, a DZVP orbital basis set and the GEN-A2\* auxiliary basis set, are presented and discussed.

<sup>1</sup><http://www.wavefun.com/>

<sup>2</sup>A.M. Köster, P. Calaminici, M.E. Casida, R. Flores-Moreno, G. Geudtner, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, S. Patchkovskii, J.U. Reveles, A. Vela and D.R. Salahub, The deMon Developers (2005).

**Poster 4. Serguei Patchkovskii**

*Evidence of intramolecular dynamics in X-ray adsorption spectra of high density amorphous ice*

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A remarkable variety of solid and liquid phases is formed by hydrogen-bonded water. Understanding dynamics and structure of these phases is of essential in such diverse areas as origin of life, planetary evolution, and natural gas industry. One of the most important tools in studies of hydrogen bonding is near-edge X-ray adsorption (NEXAFS). Recently, two of us (DDK and JST) measured a high-resolution NEXAFS spectrum of high-density amorphous (HDA) ice, which is suggested to be qualitatively similar to that of dense liquid water. We simulate the HDA spectrum based on molecular dynamics trajectories. Site variations are treated by averaging over a large number (100) embedded cluster models. Quantum-mechanical calculation are performed using the StoBe code. The “HDA” spectrum calculated for rigid water (SPC/E model) does not resemble the experimental spectrum, but is similar to that of ice I<sub>h</sub>. Once the internal molecular motion is included (Clementi model), the simulated spectrum comes into a good qualitative agreement with experiment. Both potentials produce essentially identical simulated spectra for liquid water. We speculate that the more confined environment of the HDA phase induces a qualitative change to the coupling between intra- and inter-molecular motions. HDA may therefore not be an appropriate model for hydrogen bonding in liquid water.

**Poster 5. Jan Andzelm**

*TDDFT study of silicon phthalocyanine*

Abstract not available.

**Poster 6. Ruslan Kevorkyants**

*Modelling behavior of amphiphils in water*

Abstract not available.

**Poster 7. Helio Anderson Duarte**

*Structure and Dynamics of B-cyclodextrin and Ang1-7 in aqueous solution at quantum-mechanical level*

Abstract not available.