Seventh/Final Meeting of the DFG Priority Program SPP 1145

Modern and Universal First-Principles Methods for Many-Electron Systems in Chemistry and Physics

Symposium 2010

March 29 - April 1, 2010

Haus der Kirche, Doblerstr. 51
D-76332 Bad Herrenalb, Germany

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Sponsor

The symposium is financed by the German Research Foundation (DFG).

Program

Start	Monday March 29th	Tuesday March 30th	Wednesday March 31th	Thursday April 1st
07:45	Arrival and Registration	Breakfast	Breakfast	Breakfast
09:00		I2 Cances	I4 Krylov	I6 Reiher
09:50		L5 Schneider	L15 Klopper	L24 Hanrath
10:20		Coffee	Coffee	Coffee
10:50		L6 Auer	L16 Kats	I7 Szalay
11:20		L7 Hamaekers	L17 Lüchow	
11:50		L8 Taut	L18 Saalfrank	Closing
12:30	Lunch	Lunch	Lunch	Lunch
14:00	I1 Ruud	I3 Baerends	I5 Yang	Departure
14:50	L1 Adler	L9 Görling	L19 Siedentop	
15:20	L2 Ochsenfeld	L10 Dreuw	L20 Groß	
15:50	Coffee	Coffee	Coffee	
16:20	L3 Usvyat	L11 Arbuznikov	L21 Ködderitzsch	
16:50	L4 Paulus	L12 van Wüllen	L22 Blöchl	
17:20	C1 Friedrich, J.	L13 Engel	L23 Schindlmayr	
17:50	C2 Soerensen	L14 Springborg	C3 Friedrich, C.	
18:30	Dinner	Dinner	Dinner	
20:00		Posters		

Location: talks SR 7/8, posters SR 6.

Monday, March 29 2010

12:00-12:30	**Arrival and Registration**
12:30-14:00	**Lunch**

Session 1, Chair: Christof Hättig

14:00-14:50	**Kenneth Ruud** Calculating vibrational contributions to molecular electric and magnetic properties
14:50-15:20	**Thomas Adler** Local explicitly correlated coupled cluster methods: DF-LCCSD(T)-F12
15:20-15:50	**Christian Ochsenfeld** Linear scaling AO-MP2 for large molecules
15:50-16:20	**Coffee**
16:20-16:50	**Denis Usvyat** Local and non-local density fitting in periodic methods
16:50-17:20	**Beate Paulus** Development of a wavefunction-based ab initio method for metals applying the method of increments
17:20-17:50	**Joachim Friedrich** Implementation of the incremental scheme
17:50-18:20	**Lasse Soerensen** General order coupled-cluster in the 4-component framework
18:30-20:00	**Dinner**

Tuesday, March 30 2010

07:45-09:00	**Breakfast**
Session 2, Chair:	**Wolfgang Hackbusch**
09:00-9:50	**Eric Cances** Some mathematical and numerical challenges in density functional theory
09:50-10:20	**Reinhold Schneider** Tensor approximation and quantum chemistry
10:20-10:50	**Coffee**
10:50-11:20	**Alexander Auer** Tensor decomposition in post-HF methods
11:20-11:50	**Jan Hamaekers** Tensor product multiscale many-particle spaces with finite-order weights for the electronic Schrödinger equation
11:50-12:20	**Manfred Taut** Violation of non-interacting v-representability in CDFT
12:30-14:00	**Lunch**
Session 3, Chair:	**Martin Kaupp**
14:00-14:50	**Evert Jan Baerends** Excitation energies with time-dependent density matrix functional theory
14:50-15:20	**Andreas Görling** Orbital-dependent kernels in time-dependent density-functional theory and new correlation functionals
15:20-15:50	**Andreas Dreuw** An additive long-range potential to correct for the charge-transfer failure of time-dependent density functional theory
15:50-16:20	**Coffee**
16:20-16:50	**Alexei Arbuznikov** Advances in local hybrid exchange-correlation functionals: from thermochemistry to response properties
16:50-17:20	**Christoph van Wüllen** DFT calculation of magnetic anisotropies for multinuclear complexes with antiferromagnetic coupling
17:20-17:50	**Eberhard Engel** Insulating Ground States of Transition-Metal Monoxides from Exact Exchange
17:50-18:20	**Michael Springborg** Extended systems in electrostatic fields
18:30-20:00	**Dinner**
20:00-22:00	**Posters**

Wednesday, March 31 2010

07:45-09:00	**Breakfast**

Session 4, Chair: Heinz-Jürgen Flad

09:00-9:50	**Anna Krylov** Electronic structure aspects of photoconversions of the green fluorescent protein chromophore
09:50-10:20	**Willem Klopper** Explicitly correlated molecular electronic wave functions: energies and analytic derivatives
10:20-10:50	**Coffee**
10:50-11:20	**Danylo Kats** Excited states from local methods
11:20-11:50	**Arne Lüchow** Quantum Monte Carlo: nodes, antisymmetry and how to get insight from QMC
11:50-12:20	**Peter Saalfrank** Correlated many-electron dynamics in real time using wavefunction methods
12:30-14:00	**Lunch**

Session 5, Chair: Hubert Ebert

14:00-14:50	**Weitao Yang** Insights and progress in density functional theory
14:50-15:20	**Heinz Siedentop** Ground State Energies of Coulomb Systems and One-Particle Reduced Density Matrices
15:20-15:50	**Eberhard K.U. Gross** Density functional theory at finite temperature: towards the ab initio description of phase transitions
15:50-16:20	**Coffee**
16:20-16:50	**Diemo Ködderitzsch** DFT and beyond using a multiple scattering approach
16:50-17:20	**Peter Blöchl** Density-matrix functionals with local interactions
17:20-17:50	**Arno Schindlmayr** Spin excitations in itinerant ferromagnets from first principles
17:50-18:20	**Christoph Friedrich** Efficient all-electron implementation of the GW approximation within the full-potential linearized augmented plane-wave method
18:30-20:00	**Dinner**

Thursday, April 1 2010

07:45-09:00	**Breakfast**
Session 6, Chair:	**Werner Kutzelnigg**
09:00-9:50	**Markus Reiher** New parametrizations of the electronic wave function: from DMRG to tensor network states
09:50-10:20	**Michael Hanrath** Properties of various MRCC-type approaches
10:20-10:50	**Coffee**
10:50-11:40	**Peter Szalay** Behind the Born-Oppenheimer approximation by coupled cluster methods
11:40-11:50	**Closing**
12:00-14:00	**Lunch and Departure**

List of Abstracts

Invited Talks

I 1

Calculating vibrational contributions to molecular electric and magnetic properties

Kenneth Ruud

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In this talk, I will discuss our recent work on developing analytic methods for calculating vibrational effects on electric and magnetic properties calculated using self-consistent field (SCF) wave functions, including Hartree-Fock and Kohn–Sham density functional theory [1]. Particular attention will be given to calculating higher-order derivatives of exchange-correlation kernels using automatic differentiation [2], including corrections from magnetic field or geometry dependence in the basis set. The extension of the formalism to calculating excited-state properties will also be addressed.
Different applications of the code will be presented, including calculations of Coherent Anti-Stokes Raman Scattering [3,4], pure vibrational corrections to nonlinear hyperpolarizabilities [5], as well as recent work on the vibronic effects in the Magnetic Circular Dichroism spectrum of ethylene [5].

Literature:

- [1] A. J. Thorvaldsen, K. Ruud, K. Kristensen, P. Jørgensen and S. Coriani, J. Chem. Phys. **129**, 214108 (2008)
- [2] U. Ekström, R. Bast, A. J. Thorvaldsen, K. Ruud and L. Visscher, J. Chem. Theor. Comput., submitted
- [3] A. J. Thorvaldsen, L. Ferrighi, K. Ruud, H. Ågren, P. Jørgensen and S. Coriani, Phys. Chem. Chem. Phys. **11**, 2293 (2009)
- [4] A. Mohammed, H. Ågren, A. J. Thorvaldsen and K. Ruud, Chem. Phys. Lett. **485**, 320 (2010)
- [5] A. J. Thorvaldsen, K. Ruud and M. Jaszuński, J. Phys. Chem. **A 112**, 11942 (2008)
- [6] H. Solheim, M. Nooijen, S. Coriani and K. Ruud, in preparation.

I 2

Some mathematical and numerical challenges in Density Functional Theory

Eric Cances

In this talk, I will present some recent achievements in the mathematical and numerical analysis of Kohn-Sham models.

In the first part of the talk, I will show how to derive a model describing the electronic structure of a crystal with local defects (a system with infinitely many electrons) from a Kohn-Sham model for atoms and molecules, by means of rigorously founded bulk limit arguments [E.C., A. Delerence and M. Lewin, Comm. Math. Phys. 2008 and J. Phys.: Condens. Matter 2008]. The resulting model has a subtle mathematical structure. An interesting feature of it is that the definition of the charge of the defect is not straightforward, and requires mathematical techniques similar to the renormalization techniques used in quantum electrodynamics. This models also allows to recover the electronic component of the macroscopic dielectric permittivity in the RPA approximation (Adler-Wiser formula), using homogenization techniques [E.C. and M. Lewin, Arch. Ration. Mech. Anal. 2009].

In the second part of the talk, I will focus on the construction and use of error estimates for Kohn-Sham calculations in planewave basis sets. I will present optimal a priori error estimates [E.C., R. Chakir and Y. Maday, 2010] and comment on the possible use of these error bounds to lower the computational effort in Kohn-Sham calculations.

I 3

Excitation energies with time-dependent density *matrix* functional theory

Evert Jan Baerends, Klaas J. H. Giesbertz, Oleg V. Gritsenko, Katarzyna Pernal
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Time-dependent density functional theory in its current adiabatic implementations exhibits three striking failures: a) totally wrong behavior of the excited state surface along a bond-breaking coordinate;[1] b) lack of doubly excited configurations, affecting again excited state surfaces; c) much too low charge transfer excitation energies. We address these problems with time-dependent density *matrix* theory (TDDMFT).[2,3] Frst, a brief introduction into density matrix functional theory will be given, reviewing the current state-of-the-art of functional development in an application to *E* vs *R* curves for bond dissociation of A-H bonds of the first row 10-electron hydrides.[4] For two-electron systems the exact exchange-correlation functional is known in DMFT, hence exact response equations can be formulated. This affords a study of the performance of TDDMFT in the TDDFT failure cases mentioned (which are all strikingly exhibited by prototype two-electron systems such as dissociating H_2 and HeH^+). At the same time, adiabatic approximations, which will eventually be necessary, can be tested without being obscured by approximations in the functional. We find:[5,6] a) In the fully non-adiabatic (ω-dependent, exact) formulation of linear response TDDMFT, it can be shown that LR-TDDMFT is able to provide exact excitation energies; in particular the first order (linear response) formulation does not prohibit the correct representation of doubly excited states; b) Within previously formulated simple adiabatic approximations[3] the bonding-to-antibonding excited state surface as well as charge transfer excitations are described without problems, but not the double excitations; c) An adiabatic approximation is formulated in which also the double excitations are fully accounted for.

1. K. J. H. Giesbertz, E. J. Baerends, Chem. Phys. Lett. **461** (2008) 338
2. K. Pernal, O. V. Gritsenko, E. J. Baerends, Phys. Rev. A **75**, 012506 (2007)
3. K. Pernal, K. J. H. Giesbertz, O. Gritsenko, E. J. Baerends, J. Chem. Phys. **127**, 21401 (2007)
4. D. Rohr, K. Pernal, O. Gritsenko, E. J. Baerends, J. Chem. Phys. **129** (2008) 164105
5. K. J. H. Giesbertz, E. J. Baerends, O. V. Gritsenko, Phys. Rev. Lett. **101** (2008) 033004
6. K. J. H. Giesbertz, K. Pernal, O. V. Gritsenko, E. J. Baerends, J. Chem. Phys. **130** (2009) 114104

I 4

Electronic structure aspects of photoconversions of the green fluorescent protein chromophore

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The unique properties of green fluorescent protein (GFP) exploited in novel bioimaging techniques have revolutionized many areas in life sciences, however, our mechanistic understanding of its function is still incomplete. I will present electronic structure calculations of the excited and ionized states of deprotonated 4'-hydroxybenzylidene-2,3-dimethylimidazolinone (HBDI anion). Our calculation offer a tentative structural explanation of the recently discovered oxidative redding of GFP. Relevant aspects of electronic structure methodology will also be discussed.

Literature:

1. E. Epifanovsky et. al., J. Chem. Theor. Comput. **5**, 1895 (2009)
2. Bogdanov et. al, Nature Chem. Biol. 5, 459 (2009)
3. E. Epifanovsky et. al., J. Chem. Phys., in press (2010)

Insights and Progress in Density Functional Theory

Weitao Yang
Department of Chemistry, Duke University

Density functional theory of electronic structure is widely and successfully applied in simulations throughout engineering and sciences. However, there are spectacular failures for many predicted properties. The errors include underestimation of the barriers of chemical reactions, the band gaps of materials, the energies of dissociating molecular ions and charge transfer excitation energies. Typical DFT calculations also fail to describe degenerate or near degenerate systems, as arise in the breaking of chemical bonds, and strongly correlated materials. These errors can all be characterized and understood through the perspective of fractional charges and fractional spins introduced recently. Standard approximations for the exchange-correlation functional have been found to give big errors for the linearity condition of fractional charges, leading to delocalization error, and the constancy condition of fractional spins, leading to static correlation error. These two conditions have been unified and extended to states with both fractional charge and fractional spin to give a much more stringent condition: the exact energy functional is a plane, linear along the fractional charge coordinate and constant along the fractional spin coordinate with a line of discontinuity at the integer. Violation of this condition underlies the failure of known approximate functionals to describe the gaps in strongly correlated systems. It is shown that explicitly discontinuous functionals of the density or orbitals that go beyond these currently used smooth approximations is the key for the application of density functional theory to strongly correlated systems. Understanding the errors of functionals in the simplest way possible --- as violations of exact conditions for fractional charges and fractional spins -- opens the path forward for reduction of the errors and for applications of density functional theory in new frontiers.

On the qualitative side, we have developed an approach to detect non-covalent interactions in real space, based on the electron density and its derivatives. The intricate non-covalent interactions that govern many areas of biology and chemistry are not easily identified from molecular structure. Our approach reveals underlying chemistry that compliments the covalent structure. It provides a rich representation of van der Waals interactions, hydrogen bonds, and steric repulsion in small molecules, molecular complexes, and solids. Most importantly, the method, requiring only knowledge of the atomic coordinates, is efficient and applicable to large systems, such as proteins or DNA. Across these applications, a view of non-bonded interactions emerges as continuous surfaces rather than close contacts between atom pairs, offering rich insight into the design of new and improved ligands.

References

A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, “Insights into current limitations of density functional theory,” Science, 321:792, 2008.

A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, “Fractional charge perspective on the band gap in density-functional theory,” Physical Review B, 77:115123, 2008.

P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, “Localization and delocalization errors in density functional theory and implications for band-gap prediction,” Phys. Rev. Lett. 100:146401, 2008.

A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, “Fractional spins and static correlation error in density functional theory,” Journal of Chemical Physics, 129:121104, 2008.

P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, “Discontinuous nature of the exchange-correlation functional in strongly correlated systems,” Phys. Rev. Lett. 102:066403, 2009.

A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, “Second-order perturbation theory with fractional charges and fractional spins,” J. Chem. Theory Comput., 5:786, 2009.

A. J. Cohen, P. Mori-Sanchez, and W. T. Yang, “Failure of the random phase approximation correlation energy,” J. Chem. Phys., 2009. submitted (arXiv:0903.4403v1).

E. R. Johnson1, S. Keinan, Paula Mori-Sanchez, J. Contreras-Garcia, A. J. Cohen, and W. T. Yang, “Revealing Non-Covalent Interactions”, J. Am. Chem. Soc., submitted, 2010.

New Parameterizations of the Electronic Wave Function: From DMRG to Tensor Network States

Markus Reiher

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Wolfgang-Pauli-Str. 10, 8093 Zurich, Switzerland

Over the last decade, we have witnessed the rise of the Density Matrix Renormalization Group (DMRG) algorithm in quantum chemistry [1] which had been successfully introduced in condensed matter physics. We showed that the DMRG algorithm is even applicable for non-linear, compact molecules like transition metal complexes and clusters [2] and proposed an extrapolation scheme that is able to control the error in the electronic energy during the iterations in order to provide an estimate for the converged energy and a criterion for terminating the iterations [3]. In the past few years, the DMRG algorithm has been discussed in terms of the parametrization of the wave function that is iteratively constructed. While we have decomposed the DMRG wave function in terms of a Slater determinant basis [4], which makes it comparable to a configuration-interaction (CI) wave function and thus analyzable, Rommer and Östlund showed already in 1995 that the DMRG wave function can be described as a matrix product state. Their work laid the foundations for a new family of states, the so-called tensor network states. The basic idea of tensor network states is to approximate the ground-state wave function of a strongly correlated system by constructing the complex high-dimensional CI coefficient tensor of a full-configuration-interaction wave function from a comparatively small set of coefficients relating the one-electron states. So far such states have been studied by several groups for simple spin Hamiltonians only. We have now analyzed electronic wave functions constructed in terms of such tensor network states for the full quantum chemical many-electron Hamiltonian [5].

Literature:

[1] Marti, K. H. and Reiher, M. *Z. Phys. Chem.* (2010), in press.
[2] Marti, K. H.; Malkin Ondík, I.; Moritz, G.; Reiher, M. *JCP* 128 (2008) 014104
[3] Marti, K. H. and Reiher, M. *Mol. Phys.* (2010), in press.
[4] Moritz, G. and Reiher, M. *JCP* 126 (2007) 244109.
[5] Marti, K. H.; Reiher, M.; Bauer, B.; Troyer, M.; Verstraete, F.; to be submitted.

I 7

Beyond the Born-Oppenheimer approximation by Coupled Cluster methods

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Enhancement of ab initio methods, in particular Coupled-Cluster (CC) methods allow the calculation of molecular properties with an accuracy which pushes the boundary of the Born-Oppenheimer approximation (BO). This is in particular true for binding energies, excitation energies, ionization potentials, structural parameters etc. On the other hand, we are now also able to treat processes associated with such electronic excitations which fall per se outside the boundary of BO approximation. After a short introduction into the joint treatment of electronic and nuclear coordinates, we will present two methods which enable us to perform calculations at the Coupled-Cluster level beyond the BO approximation.

The first one is the so called diagonal Born-Oppenheimer correction (DBOC) which considers the effect of the nuclear kinetic energy operator on the electronic wave function in an adiabatic fashion. Analytical formulae will be presented for use with general CC models. To reduce the computational resources required for the CC calculation of DBOC, a perturbational approach has also been developed. Calculations are reported to demonstrate the convergence of the DBOC with respect to electron correlation treatment and basis set as well as the accuracy of the perturbational approach.

The second method allows the calculation of the non-adiabatic coupling between electronic excited states at the Equation-of-Motion Coupled-Cluster Singles and Doubles (EOM-CCSD) level. Analytic formulae have been derived and implemented at the first time. Results are presented for the excitation spectrum of cytosine and pyrazine molecules showing that the coupling between the different states has an important effect on the spectrum.

Literature: [1] J. Gauss, A. Tajti, M. Kállay, J.F. Stanton and P.G. Szalay, *J. Chem. Phys.*, **125**, 144111 (2006). [2] A. Tajti and P.G. Szalay, *J. Chem. Phys.*, **131**, 124104 (2009).

Lectures

L 1

Local explicitly correlated coupled cluster methods: DF-LCCSD(T)-F12

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Recent developments in the DF-LCCSD(T)-F12x (x=a,b) methods [8] will be presented. For the first time ever the energies of large molecules with up to 100 light atoms can be calculated with an accuracy near the CCSD(T) basis set limit. It will be shown that neither the pair nor the domain approximations spoil the accuracy of the DF-LCCSD(T)-F12 methods significantly. Especially the domain error, which in severe cases could cause errors of several kcal/mol in DF-LCCSD(T), is efficiently cured by the local formulation of the strong orthogonality projector intrinsic in F12 theory [4,7]. The new local approximations of the additional F12x terms will be discussed in detail. These make it possible to achieve low order scaling of the computational resources (CPU, memory, and disk space) for the F12x terms. The DF-LCCSD(T)-F12x program relies on the linear scaling DF-LCCSD(T) program [1,2,3] and a linear scaling DF-LMP2-F12 program [5,6,7] developed in Stuttgart. Reaction energies of small, medium size and large molecules are studied. Enthalpies of a reaction set comprising 47 reactions are compared to experimental data and to the basis set limit. A QM/MM application will be presented.

Literature:

[1] C. Hampel and H.-J. Werner, J. Chem. Phys. **104**, 6286 (1996).

[2] M. Schütz and H.-J. Werner, Chem. Phys. Lett. **318**, 370 (2000).

[3] M. Schütz and H.-J. Werner, J. Chem. Phys. **114**, 661 (2001).

[4] H.-J. Werner, J. Chem. Phys. **129**, 101103 (2008).

[5] H.-J. Werner and F.R. Manby, J. Chem. Phys. **124**, 054114, (2006).

[6] H.-J. Werner, T. B. Adler and F.R. Manby, J. Chem. Phys. **126**, 164102, (2007).

[7] T. B. Adler, F. R. Manby, and H.-J. Werner, J. Chem. Phys. **130**, 054106 (2009).

[8] T. B. Adler, and H.-J. Werner, J. Chem. Phys. **130**, 241101, (2009).

L 2

Linear-Scaling AO-MP2 for Large Systems

Christian Ochsenfeld

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A linear-scaling AO-based MP2 method is presented that allows to avoid the $\mathcal{O}(\mathrm{M}^5)$ scaling with molecular size (M) of conventional MO-MP2 theory. We employ our multipole-based integral estimates (MBIE) for preselecting numerically significant contributions to the MP2 energy. Here, MBIE accounts for the 1/R coupling in two-electron integrals, which turns for transformed products to at least a $1/\mathrm{R}^4$ decay behavior. While the numerical accuracy is fully preserved, we were able to calculate as largest system sofar an RNA system comprising 1664 atoms and 19 182 basis functions at the SOS-MP2 level.

L 3

Local and non-local density fitting in periodic methods

Denis Usvyat, Marco Lorenz, Lorenzo Maschio, Martin Schütz

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Density fitting (resolution of the identity) approximation [1] is routinely used in molecular electronic structure methods, in order to speed up evaluation of 4-index integrals, which are factorized into products of 3- and 2-index ones. In the periodic context, this technique cannot be straight-forwardly applied due to the infinite nature of the systems. We discuss the possible schemes for periodic density fitting, namely longe-range reciprocal-space [2], short-range direct-space [3] and combined [3,4] treatment. The density fitting is employed within the periodic local MP2 and CIS methods.

Literature:

[1] B. I. Dunlap, J. W. D. Connolly and J. R. Sabin, Int. J. Quantum Chem. **S11**, 81 (1977)

[2] L. Maschio, D. Usvyat, F.R. Manby, S. Casassa, C. Pisani and M. Schütz, Phys. Rev. B, **76**, 075101 (2007)

[3] M. Schütz, D. Usvyat, M. Lorenz, C. Pisani, L. Maschio, S. Casassa and M. Halo, in *Accurate Condensed-Phase Quantum Chemistry*, ed. by F. Manby, (to be published in 2010)

[4] L. Maschio and D. Usvyat, Fitting of local densities in periodic systems, Phys. Rev. B, **78**, 073102 (2008)

Development of a wavefunction-based ab initio method for metals applying the method of increments

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Ab initio electron correlation calculations based on quantum-chemical methods are successfully applied to metallic systems via the method of increments. To deal with the two distinct problems that occur in metals, the difficulty of localization of the orbitals and the generation of clusters with neutral atoms in the center, we proposed an embedding scheme which has itself no metallic character but can mimic the metal in the internal region, where the atoms are correlated. The first application was made for solid mercury, where a very good agreement with experimental ground-state properties was achieved. Further the approach has been extended to other group 2 and 12 metals (Be, Mg, Zn, and Cd) where the metallic character is more pronounced than in mercury. Application of the method of increments to the investigated metallic systems allows us not only to obtain values close to experimental data but also to understand the influence of individual correlation-energy increments on cohesive properties and to clarify thereby some aspects of the structural features of the group 12 metals. Ongoing work on the group 2 metals Ca, Sr and Ba as well as on metallic ytterbium is presented.

Literature:

E. Voloshina and B. Paulus, *Wavefunction-based ab initio correlation method for metals: Application of the incremental scheme to* Be, Mg, Zn, Cd, and Hg, in Book Series: Chemical Modelling: Applications and Theory (Specialist Periodical Reports), Vol. 6, M. Springborg (ed.), R.S.C., Cambridge, 2009. (further references therein)

L 5

Tensor approximation in quantum chemistry

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The talk will present recent developments in tensor product approximations with a particular focus on problems in electronic structure calculations. Tensor product approximation is a tool for the treatment of high-dimensional problems. Low rank approximations of matrices, like SVD, partial Cholesky decomposition, RI techniques and pair natural orbitals have been proved to be powerfull instruments in quantum chemistry. However the genreralization to higher order tensors is not straightfroward. We will demonstrate some examples with the so-called canonical format. Recently, new tensor formats have been introduced by several groups which allow a stable approximation of any order d tensor into order three tensors! We will discuss perspectives of these new formats for wave function methods.

Literature:

L 6

Tensor decomposition in post-HF methods

Udo Benedikt[1]
Alexander A. Auer[1], **Mike Espig**[2], **Wolfgang Hackbusch**[2]

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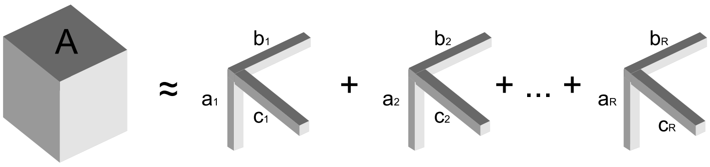
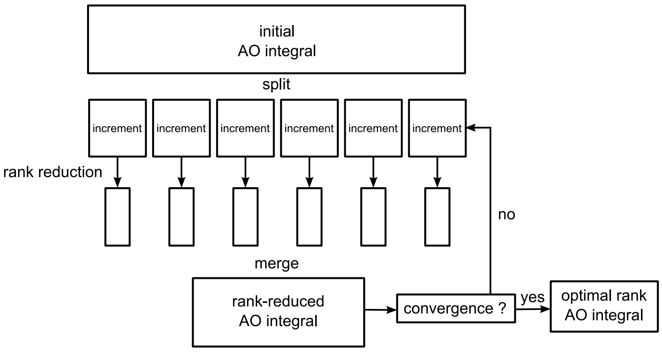
In this presentation details on the implementation and algorithm of the tensor decomposition technique for post-HF methods are presented (see contributed talk by Auer, Hamaekers and Schneider).



In typical applications of the tensor decomposition technique the time determining step in the original algorithm that was caused by processing highly-dimensional quantities vanishes and the actual tensor decomposition becomes dominant. If the decomposition is to be applied to quantities like the two-electron integrals or amplitudes special strategies have to be applied.



In this contribution we discuss details of the decomposition algorithm and examples for the decomposition of several quantities in post-HF methods. Furthermore, various strategies for the implementation of Coupled-Cluster methods using tensor decomposition are discussed.

L 7

Tensor Product Multiscale Many-Particle Spaces with Finite-Order Weights for the Electronic Schrödinger Equation

Michael Griebel and Jan Hamaekers

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We study tensor product multiscale many-particle spaces with finite-order weights and their application for the electronic Schrdinger equation. Any numerical solution of the electronic Schrdinger equation using conventional discretization schemes is impossible due to its high dimensionality. Therefore, typically Monte Carlo methods (VMC/DMC) or nonlinear model approximations like Hartree-Fock (HF), coupled cluster (CC) or density functional theory (DFT) are used. We present a new numerical method which combines the favorable properties of efficient Gaussian type orbitals basis sets, which are applied with good success in conventional electronic structure methods, and tensor product multiscale bases, which provide guaranteed convergence rates and allow for adaptive resolution. To this end, the approach is based on a modified adaptive sparse grid technique and a certain particle-wise decomposition with respect to one-particle functions obtained by a nonlinear rank-1 approximation. Sparse grids allow to overcome the exponential complexity exhibited by conventional discretization procedures. Here, we employ a multiscale Gaussian frame for the sparse grid spaces and we use Gaussian type orbitals to represent the rank-1 approximation. With this approach we are able to treat small atoms and molecules with up to six electrons.

Literature:

1. M. Griebel and J. Hamaekers. Tensor product multiscale many-particle spaces with finite-order weights for the electronic Schrödinger equation. Zeitschrift für Physikalische Chemie, 2009. (accepted).
2. M. Griebel and J. Hamaekers. Sparse grids for the Schrödinger equation. Mathematical Modelling and Numerical Analysis, 41(2):215-247, 2007.
3. M. Griebel and J. Hamaekers. A wavelet based sparse grid method for the electronic Schrödinger equation. In M. Sanz-Sol, J. Soria, J. Varona, and J. Verdera, editors, Proceedings of the International Congress of Mathematicians, volume III, pages 1473-1506, Madrid, Spain, August 22-30 2006. European Mathematical Society. Also as INS Preprint No. 0603.

L 8

Violation of non-interacting v-representability of the exact solutions of the Schrödinger equation for a parabolic two-electron quantum dot in a homogeneous magnetic field

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Keywords: Current density functional theory, quantum dots

In density functional theory it can be shown that the electron density of the ground state (GS) can be calculated from a model system of non-interacting particles in a properly chosen external potential, the Kohn-Sham (KS) system. This property is called non-interacting v-representability (NIVR). It follows from the fact that all mutual mappings between the external potential, many body wave function (WF) and electron density of the GS are invertible [1].

In the basic work on (non-relativistic) current density functional theory (CDFT) [2] NIVR of both densities (charge- and the paramagnetic current density) has been tacitly assumed, because the invertibility of the mapping of the external potentials (scalar- and vector potential) on the wave function has never been proven. In the contrary, in [3] has been shown, that different external potentials can provide the same WF. This rules the invertibility of the above mentioned mapping out, but does not say anything about NIVR.

We have shown by means of the exact solutions for the two-electron system in a parabolic confinement and a homogeneous magnetic field [4] that the exact densities are not always NIVR, or equivalently, that an exact KS system does not always exist. Whether it exists depends on the total angular momentum of the GS. (It is well known that the modulus of the orbital angular momentum L of the GS grows step-wise with increasing magnetic field connected with singlet-triplet oscillations.)

If the GS is a singulet (L is even) both densities are NIVR if the vorticity of the exact solutions vanishes. For L=0 this is trivially guaranteed because the paramagnetic current density vanishes in this state. (The gauge invariant mechanical current density does not vanish, though.) Fig.1 shows, that the vorticity based on the exact solutions for the higher L does not vanish, in particuler for small r.

If the GS is a triplet (L is odd) we can show, that there is no circular symmetric KS system which can provide the exact densities, except for L= – 1. Therefore, in this case NIVR cannot be ruled out in general, but it has been shown that common practise in self-consistent CDFT computations, where NIVR with a circular symmetcc KS system is assumed on the basis of the circular symmetry of the real system, is not rigorously justified. However, this does not mean, that all these results are completely wrong.

References

[1] P.Hohenberg, W.Kohn, Phys. Rev. **136B**, 864 (1964)

[2] G.Vignale, M.Rasolt, Phys. Rev. B **37**, 10685 (1988)

[3] K.Capelle, G.Vignale, Phys. Rev. B **65**, 113106 (2002)

[4] M. Taut, J. Phys. A **27**, 1045 (1994) and 4723 (1994)

[5] A.Wensauer, U.Rössler, Phys. Rev. B **69**, 155301 and 155302 (2004)

Figure 1: Vorticity for exact singlet states for effective confinement frequency (see [4]) =1 and total orbital angular momenta L= – 2 and L= – 4.

L 9

Orbital-dependent kernels in time-dependent density-functional theory and new correlation functionals

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A Time-Dependent Density-Functional (TDDFT) response equation for the effective Kohn-Sham potential instead of the electron densities is presented that enables the use of orbital-dependent exchange-correlation kernels. In combination with the frequency-dependent exact-exchange EXX kernel the new approach describes long-range charge-transfer excitations qualitatively correctly in contrast to standard TDDFT methods, as shown by formal analysis and applications to molecular systems. [1] The relation of TDDFT response methods based on the EXX kernel to time-dependent Hartree-Fock ist discussed. The fluctuation-dissipation theorem is used to construct new orbital-dependent correlation functionals within a random phase approximation using the EXX kernel. The new correlation functionals yield promising results in comparison with methods employing various other correlation functionals or compared to wave-function-based methods like Moller-Plesset perturbation theory or coupled cluster methods [2].

Literature:

[1] Andreas Heßelmann, Andrey Ipatov, and Andreas Görling, Phys. Rev. A 80, 012507 (2209).
[2] Andreas Heßelmann and Andreas Görling, Mol. Phys., in press.

An additive long-range potential to correct for the charge-transfer failure of time-dependent density functional theory

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Time-dependent density functional theory is one of the most widely used methods for the calculation of excited states of large molecules. However, it exhibits substantial problems with charge-transfer (CT) excited states when conventional exchange-correlation functionals are employed. Here, we introduce an additive long-range potential that can, in principle, be directly employed with any existing local, GGA or hybrid-functional, without re-fitting of the original functionals. The additive potential consists of two parts: (1) long-range Hartree-Fock is included by means of a switching function. Instead of using one error-function as is usually employed we utilize a linear combination of two error-functions that allows us to switch on non-local Hartree-Fock exchange at larger electron-electron distances than zero. The inclusion of Hartree-Fock exchange at long-range recovers the correct 1/R-asymptote along charge separation coordinates.(2) The quality of excitation energies of CT states strongly depends on the extend of charge transfer, i.e. on the spatial overlap of the electron donating and accepting orbitals. Therefore we calculate the spatial overlap and use it as a measure of how large the excitation energies of CT states need to be shifted to higher eneergies. Both corrections have been implemented together into a development version of the Q-Chem programme package. First examples of its successful application are presented.

L 11

Advances in local hybrid exchange-correlation functionals: From thermochemistry to response properties

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Our progress in the construction and validation of local hybrid functionals, [1] attained during the last years within the DFG SPP-1145 is reviewed. Local hybrids provide a very promising new generation of exchange-correlation functionals for the simultaneous accurate description of various properties within Kohn-Sham DFT. Compared to traditional (global) hybrids (e.g., B3LYP, PBE0, TPSSh) local hybrids exhibit larger flexibility, due to the replacement of a constant exact-exchange admixture by a position-dependent one. The latter is governed by a so-called *local mixing function* (LMF), and this is the crucial quantity which controls the overall performance of local hybrids.

The most successful LMFs have been derived partially in a semi-empirical way, based on a physically justified balance between the elimination of Coulomb self-interaction and efficient simulation of nondynamical correlation. Such LMFs may be built of the dimensionless density gradient [2], the ratio of von Weizsäcker kinetic energy density to local kinetic energy density [1,3], spin polarization [4], etc. On the other hand, LMFs can be derived within a purely *ab initio* approach based, for instance, on the adiabatic connection (AC) formalism [5] that provides valuable insights into the performance and limits of various local hybrids while being less practically successful than a semi-empirical approach.

Our best local hybrids include a minimal number of adjustable parameters (one or two) and turn out to be superior in the description of atomization energies, reaction barrier heights [2-4,6], NMR chemical shifts [7], EPR g tensors [8], and electric response properties (polarizabilities and hyperpolarizabilities) compared to traditional hybrids that often suffer from being overparametrized. Important implementation aspects (nonlocal vs. localized exchange-correlation potentials) and an outlook on the further improvement of local hybrid functionals, and their extension to computation of other properties are discussed as well.

Literature:

[1] J. Jaramillo, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **118** (2003) 1068.
[2] A. V. Arbuznikov, M. Kaupp, *Chem. Phys. Lett.* **440** (2007) 160.
[3] H. Bahmann, A. Rodenberg, A. V. Arbuznikov, M. Kaupp *J. Chem. Phys.* **126** (2007) 011103.
[4] A. V. Arbuznikov, H. Bahmann, M. Kaupp, *J. Phys. Chem. A*, **113** (2009) 11898.
[5] A. V. Arbuznikov, M. Kaupp, *J. Chem. Phys.* **128** (2008) 214107.
[6] M. Kaupp, H. Bahmann, A. V. Arbuznikov, *J. Chem. Phys.*, **127** (2007) 194102.
[7] A. V. Arbuznikov, M. Kaupp, *Chem. Phys. Lett.* **442** (2007) 496.
[8] A. V. Arbuznikov, M. Kaupp, *J. Chem. Theory Comput.* **5** (2009) 2985.

L 12

DFT calculation of magnetic anisotropies for multinuclear complexes with antiferromagnetic coupling

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The density functional treatment of systems where the true many-electron wave function is multideterminantal faces a problem. This arises, for example, if one considers the low-energy manifold of states that arises from antiferromagnetic couplings between several open-shell transition metal centers. This low-energy manifold can faithfully be described by a phenomenological Heisenberg Spin Hamiltonian $\hat{H}_{iso} = \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$ where $\hat{S}_i$ is the spin operator representing the single-site (local) spin of a metal center. One can obtain a relation between the exchange coupling constants J_{ij} and energy expectation value differences of Ising-type configurations (where all local spins have either maximum or minimum spin projection). The latter are then identified with DFT energy differences from *broken symmetry* calculations. This way, DFT provides the parameters of $\hat{H}_{iso}$ whose diagonalization finally yiels the "true" energy differences.

The spin-orbit contribution to magnetic anisotropy (or zero-field splitting) can phenomenologically be described by adding single-site terms to the Spin Hamiltonian which then assumes the form

$$\hat{H} = \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j + \sum_i \hat{S}_i \cdot \mathbf{D}_i \cdot \hat{S}_i \tag{1}$$

The problem is now that all Ising configurations have the same magnetic anisotropy, and DFT calculations also show very similar magnetic anisotropies for all the different broken symmetry situations: not enough information is generated to get a hold on the magnetic anisotropies of the true many-electron states, which e.g. must be zero for singlets.

To generalize the broken symmetry approach to the calculation of zero field splittings or magnetic anisotropies, one must extract somehow the single-ion tensors $\mathbf{D}_i$ which can be done in numerical experiments by "switching on/off" the spin-orbit interaction at specific sites. Togehter with the J_{ij} calculated by the standard procedure, the Spin Hamiltonian can be set up and diagonalized which gives the "true" magnetic anisotropies for the individual spin states. Two-center contributions to the magnetic anisotropy have to be treated separately, but this can be well treated with a point-dipolar approximation.

Insulating Ground States of Transition-Metal Monoxides from Exact Exchange

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The exact exchange of density functional theory is used to calculate the electronic structure of the antiferromagnetic (type II) phases of the transition-metal monoxides MnO, FeO, CoO and NiO at $T = 0$. In contrast to the local density (LDA) and generalized gradient approximation, the exact exchange (combined with LDA correlation) correctly yields insulating ground states for all four compounds. The values for the band gaps and magnetic moments obtained with this parameter-free *first principles* method are in good agreement with the experimental data. While correlation plays a major role for the electronic structure, these results demonstrate that the mere opening of a gap in FeO and CoO is already obtained on the level of density functional theory, if the exact, multiplicative exchange potential is combined with a full potential method. State-dependent potentials are not required for obtaining a gap.

Literature:

E. Engel, R. N. Schmid, PRL **103**, 036404 (2009).

L 14

Extended Systems in Electrostatic Fields

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The basic principles behind a theoretical method for treating infinite, periodic systems exposed to an external electrostatic field are outlined. The approach, based on the vector-potential description of the external field, leads to single-particle Hartree-Fock or Kohn-Sham equations that differ from the field-free counterparts in several aspects. In particular, solving them is only possible through a careful so-called smoothing procedure. In that case it is possible to derive a numerically stable and efficient approach. Results of model studies as well as of the first *ab initio* calculations, in both cases for quasi-one-dimensional systems, are reported in order to illustrate the approach. Although the approach is based on the treatment of infinite, periodic systems, it is demonstrated that effects of the terminations are included. Finally, extensions to two- and three-dimensional systems are discussed, where surfaces and shapes turn out to have surprising effects.

Details of the work are presented in the following references:

1. M. Springborg, B. Kirtman, and Y. Dong, Chem. Phys. Lett. **396** (2004) 404.
2. M. Springborg and B. Kirtman, J. Chem. Phys. **126** (2007) 104107.
3. M. Springborg and B. Kirtman, Phys. Rev. B **77** (2008) 045102. Eratum: Phys. Rev. B **77** (2008) 209101.
4. M. Springborg and B. Kirtman, Chem. Phys. Lett. **454** (2008) 105.
5. M. Springborg and B. Kirtman, Can. J. Chem. **87** (2009) 984.
6. B. Kirtman, M. Ferrero, M. Rérat, and M. Springborg, J. Chem. Phys. **131** (2009) 044109.
7. A. Pomogaeva, M. Springborg, B. Kirtman, F. L. Gu, and Y. Aoki, J. Chem. Phys. **130** (2009) 194106.

L 15

Explicitly correlated molecular electronic wave functions: Energies and analytic derivatives

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In wave function-based quantum chemistry, molecular electronic wave functions are expanded in a basis of antisymmetrized products of one-particle functions, that is, orbitals. In practical calculations, this basis is incomplete, and basis-set truncation errors occur. The basis can be increased in a systematic and optimal fashion, but nevertheless, the basis-set truncation errors vanish only slowly as n^{-1}, where n is the number of orbitals per atom. This slow convergence represents a major obstacle for accurate wave function-based quantum chemistry, as computation times grow at least as n^4. The convergence of computational results to the limit of a complete basis can be accelerated by utilizing extrapolation procedures or by seeking alternatives to the expansion in a basis of antisymmetrized products of one-particle functions. In the present talk, the F12 method will be discussed, which represents such an alternative. In the F12 methods, not only one-particle functions are used, but also two-particle functions (Slater-type geminals), which depend explicitly on the interparticle distances between the electrons in the molecule.

In previous work by Kordel *et al.*, we have discussed the implementation—in the Dalton program—of the analytic calculation of first-order molecular properties at the explicitly correlated second-order Møller–Plesset level, including nuclear gradients. In the present talk, we report our progress in the corresponding implementation in the Turbomole program. Results will be presented for the analytic calculation of relaxed first-order properties and nuclear gradients.

Literature:

E. Kordel, C. Villani, and W. Klopper, *J. Chem. Phys.* **122**, 214306 (2005).

E. Kordel, C. Villani, and W. Klopper, *Mol. Phys.* **105**, 2565 (2007).

S. Höfener, C. Hättig, and W. Klopper, Z. Phys. Chem. (in press).

EXCITED STATES FROM LOCAL METHODS

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The calculation of excitation energies and first-order properties of excited states with *a-priori* restricted local methods is a challenging task, since one needs information about the state-character *before* the calculation. One possibility is to take it from an initial lower level method calculation like CCS [1, 2, 3]. Yet such an approach is too strongly dependent on the quality of this initial calculation.

With the Laplace-transform formalism [4, 5] we are able to solve this problem by adapting the local approximations on-the-fly during the calculation [6]. As a further advantage, the Laplace-transform technique considerably speeds up the convergence, reduces the I/O rate and memory usage. Furthermore, it permits multi state calculations and a new type of local approximations from Laplace transformed quantities.

Test calculations on various molecules demonstrate robustness and accuracy of the new method.

Literature:

[1] T.Korona, H.J.Werner, *J. Chem. Phys.* 118 (2003) 3006

[2] D.Kats, T.Korona, and M.Schütz, *J. Chem. Phys.* 125 (2006) 104106

[3] D.Kats, T.Korona, and M.Schütz, *J. Chem. Phys.* 127 (2007) 064107

[4] J. Almlöf, *Chem. Phys. Letters* 181 (1991) 319

[5] D.Kats, D.Usvyat, and M.Schütz, *Phys. Chem. Chem. Phys.* 10 (2008) 3430

[6] D.Kats, M.Schütz, *J. Chem. Phys.* 131 (2009) 124117

L 17

Quantum Monte Carlo: Nodes, Antisymmetry, and How To Get Insight from QMC

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Quantum Monte Carlo is a wave function based method that employs accurate wave functions that are nonetheless very compact. In the diffusion quantum Monte Carlo variant (DMC), the energy depends solely on the accuracy of the nodal hypersurface of this wave function. For ground states the nodal hypersurface describes the antisymmetry of the wave function and connects the coalescence points of two electrons with like spin. Recent progress in the optimization of the hypersurface with respect to the DMC energy is reported and compared with optimizations based on an energy criterion. Antisymmetry and the Coulombic attraction of the electrons by the nuclei determine the electronic structure of molecules and, to a somewhat lesser extent, the electron electron repulsion. With quantum Monte Carlo, an efficient sampling of the many-body distribution $|\Psi|^2$ of the electrons is possible allowing to obtain detailed information about the distribution. Single electron densities that add up to the total electron density are defined based on the many-body distribution allowing to obtain insight into the details of the chemical bond and in particular into the effect of the antisymmetry on chemical bonding. First examples of this analysis are presented.

L 18

Correlated many-electron dynamics in real time using wavefunction methods

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In recent years, in part due to the progress made in generating and controlling intense laser fields, the timescale of dynamical processes in atomic and molecular systems has been pushed into the so-called attosecond domain. In parallel to the experimental work, theoretical methods are being developed to treat explicitly time-dependent electronic motion after photoexcitation. This talk describes correlated, explicitly time-dependent wavefunction-based N-electron methods and their application to selected molecular problems.

The focus of the talk is on many-electron methods in which the time-dependent N-electron wavefunction is represented as a sum of Slater determinants. The first approach of this type to be used here is time-dependent configuration interaction (TD-CI), where only the coefficients of the determinants are time-dependent. The second approach adopted here is the time-dependent complete active space SCF method (TD-CASSCF), for which both the coefficients of, and the Slater determinants themselves are time-dependent. Extensions of the methods to include ionization, dissipation, and optimal control strategies for excited electron dynamics, are also presented.

The methods will then be applied (i) for laser-pulse excitation and switching of real molecules without [1,2,3] and with [4] a dissipative environment, (ii) for the calculation of response properties of small molecules [5], (iii) for long-range intermolecular charge transfer [6], and (iv) for controlled electron dynamics in molecules [7].

[1] P. Krause, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **123**, 074105 (2005).
[2] M. Nest, R. Padmanaban, and P. Saalfrank, J. Chem. Phys. **126**, 214106 (2007).
[3] F. Remacle, M. Nest, and R.D. Levine, Phys. Rev. Lett. **99**, 183902 (2007).
[4] J.C. Tremblay, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **129**, 0843201 (2008).
[5] P. Krause, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **127**, 034107 (2007).
[6] S. Klinkusch, T. Klamroth, and P. Saalfrank, PCCP **11**, 3875 (2009).
[7] J.C. Tremblay and P. Saalfrank, Phys. Rev. A **78**, 063408 (2008).

Ground State Energies of Coulomb Systems and One-Particle Reduced Density Matrices

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Functionals of the one-particle reduced density matrix are a tool for the computation of quantum ground state energies. Together with appropriate correlation inequalities they yield controlled approximations. We will discuss such functionals and will show, in particular, that the basic functional introduced by Müller (1984) and rediscovered in quantum chemistry describes the ground state energy of atoms of nuclear charge Z correctly up to terms of order $o(Z^{5/3})$.

Literature: H. Siedentop: J. Phys. A: Math. Theor. 42, 085201 (2009)

L 20

Density functional theory at finite temperature: Towards the ab-initio description of phase transitions

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Density functional theory (DFT) at finite temperature has the potential to describe phase transitions in an ab-initio way. How close to this goal we are with presently available approximate exchange-correlation functionals will be explored in this lecture. Two recent developments in finite-temperature DFT will be presented: In the first part, we develop a density functional formalism which describes superconductors at thermal equilibrium in terms of three quantities: the ordinary electronic density, the superconducting order parameter, and the nuclear N-body density. These three “densities” are determined self-consistently by a set of Kohn-Sham equations. The formalism can be viewed as the superconducting version of the multi-component density-functional theory for electrons and nuclei. Approximations of the universal exchange-correlation functional are derived on the basis of many-body perturbation theory. In this way, a true ab-initio description is achieved which does not contain any adjustable parameters such as the μ^* of Eliashberg theory. Numerical results for the critical temperature, the isotope effect, the gap function and the jump of the specific heat will be presented for simple metals, for MgB_2 , and for Li, Al, K and H under pressure. At the heart of finite-temperature DFT is the exchange-correlation part of the grand canonical potential which, in practice, needs to be approximated. Knowing the exact properties of this functional is essential to make good approximations. In the second part of the lecture, we will deduce exact features of this functional such as virial theorems and scaling laws. An interesting aspect in the formulation of scaling laws is that their formulation is possible only if the density and the temperature are scaled simultaneously.

L 21

DFT and beyond using a multiple scattering approach

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The versatility of the multiple scattering KKR-Green's function (KKR-GF) method as a powerful tool for the determination of the electronic structure of solids is illustrated with two developments.

We present the formalism and implementation of a relativistic optimized effective potential method in the framework of exact exchange (EXX) within spin-DFT. All ingredients of the integral equation are expressed in terms of the KKR-GF, thereby avoiding a basis set formulation. The real-space static Kohn-Sham response function as well as the inhomogeneity of the integral equation are expressed in terms of the GF. In the all-electron formulation, core, valence and their respective cross terms are treated explicitly. By imposing appropriate boundary conditions the associated core part of the code can be used to calculate free (open-shell) atoms. [1,2] A formulation of the RPA within the scheme is sketched. We further give examples of the application of the method to solids using EXX. [3]

In the second part we present the formalism and an implementation of total energy calculations in the local density plus dynamical mean field theory (LDA+DMFT) method within KKR-GF. Applications of the scheme to fcc-Nickel and γ-Manganese are shown. [4,5]

Literature:

[1] D Ködderitzsch, H Ebert, E Engel, Phys. Rev. **B 77**, 045101 (2008)
[2] E Engel, D Ködderitzsch, H Ebert, Phys. Rev. **B 78**, 235123 (2008)
[3] D Ködderitzsch, H Ebert, H Akai, E Engel, J. Phys: Condens. Matter, **21**, 064208 (2009)
[4] I Di Marco, J Minár, S Chadov, M I Katsnelson, H Ebert and A I Lichtenstein, Phys. Rev. **B 79**, 115111 (2009)
[5] I Di Marco, J Minár, J Braun, M I Katsnelson, A Grechnev, H Ebert, A I Lichtenstein and O Eriksson, Eur. Phys. J. B**72**, 472 (2009)

L 22

Density-matrix functionals with local interactions

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Dynamical-Mean-Field-Theory (DMFT) calculations have shown that local interactions, i.e. the Anderson impurity model, capture a range of interesting correlation effects. We present first developments towards a method that incorporates such correlation effects into the standard methodology of DFT-based ground-state first-principles calculations. The method is based on density matrix functional theory with a functional obtained on the fly with a full CI ansatz. The validity of the methodology has been explored using simple model Hamiltonians. As a first step towards a full implementation into the CP-PAW code, the density-matrix functional has been approximated by a hybrid functional, namely PBE0. This corresponds to a PBE0 calculation with completely screened intersite interaction, i.e. PBE0(r). Not only a d- or f-shell, but all orbitals including core states from a given site participate in the explicit Fock term. Compared to a complete implementation of hybrid functionals, the computational overhead of this method is neglegible. Results for transition metal oxides are presented.

Spin excitations in itinerant ferromagnets from first principles

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The long-range order of the electron spins in magnetic solids gives rise to additional excitation modes that preserve the charge density but change the total spin of the electron system. While Stoner excitations, which correspond to spin-flip transitions between the majority and minority channels, can be described within a single-particle picture, spin waves are collective modes that result from the spin-dependent exchange interaction between the electrons. Here we discuss different approaches that we have explored for material-specific spin-wave calculations from first principles. All of these methods focus on the non-local and dynamic transverse spin susceptibility, whose spectral function can be directly related to experimental spectroscopies, but employ either time-dependent density-functional theory or many-body perturbation theory to treat dynamic exchange and correlation effects. In the latter case, maximally localized Wannier orbitals are used to efficiently obtain the electron-hole vertex of the multiple-scattering T matrix, which is constructed with the full frequency and wave-vector dependence [1]. Our implementation uses the full-potential linearized augmented-plane-wave (FLAPW) method [2]. For the ferromagnetic transition metals Fe, Co and Ni our results are in good agreement with experimental data and reproduce all important spectral features.

Literature:

[1] E. Şaşıoğlu, A. Schindlmayr, C. Friedrich and S. Blügel, Phys. Rev. B **81** (2010).
[2] C. Friedrich, S. Blügel and A. Schindlmayr (submitted to Phys. Rev. B).

L 24

Properties of Various MRCC Type Approaches

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The talk will briefly introduce various MRCC methods (SRMRCC [1, 2], SUMRCC [3], MkMRCC [4, 5], RMRCC [6, 7], and MRexpT [8, 9]) and discuss properties regarding

- symmetry adaption
- universality
- extensivity, consistency
- accuracy
- wavefunction quality
- cost.

Subsequently numerical examples are presented.

References

[1] N. Oliphant, L. Adamowicz, J. Chem. Phys. 95 (1991) 6645.

[2] P. Piecuch, N. Oliphant, L. Adamowicz, J. Chem. Phys. 99 (1993) 1875.

[3] B. Jeziorski, H. J. Monkhorst, Phys. Rev. A 24 (1981) 1668.

[4] U. S. Mahapatra, B. Datta, D. Mukherjee, Mol. Phys. 94 (1998) 157.

[5] U. S. Mahapatra, B. Datta, D. Mukherjee, J. Chem. Phys. 110 (1999) 6171.

[6] X. Li, J. Paldus, J. Chem. Phys. 107 (1997) 6257.

[7] X. Li, J. Paldus, J. Chem. Phys. 108 (1998) 637.

[8] M. Hanrath, J. Chem. Phys. 123 (2005) 84102.

[9] M. Hanrath, Chem. Phys. Lett. 420 (2006) 426.

Contributed Short Lectures

Implementation of the incremental scheme

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A fully automated parallelized implementation of the incremental scheme[1-4] for coupled-cluster singles-and-doubles (CCSD) energies has been extended to treat MP2-F12 and CCSD(F12) energies [5] and to treat molecular (unrelaxed) first-order one-electron properties such as the electric dipole and quadrupole moments [6]. The convergence and accuracy of the incremental approach for the dipole and quadrupole moments has been studied for a variety of chemically interesting systems.
For the explicitly correlated methods the numerical accuracy of the approach is explored for a set of 15 chemical reactions using the limiting case of single orbital one-site domains as a worst case scenario. The results are analyzed by the maximum absolute deviation, the mean absolute error and the root mean squared error, with respect to the standard MP2-F12 and CCSD(F12) results.

Literature:

[1] H. Stoll, *Chem. Phys. Lett.* **91**, 548 (1992)
[2] R. K. Nesbet, *Adv. Chem. Phys.* **14**, 1 (1969)
[3] J. Friedrich, M. Hanrath and M. Dolg, *J. Chem. Phys.* **126**, 154110 (2007)
[4] J. Friedrich, M. Hanrath and M. Dolg, *J. Phys. Chem. A* **111**, 9830 (2007)
[5] J. Friedrich, D. P. Tew, W. Klopper and M. Dolg, *J. Chem. Phys.* submitted
[6] J. Friedrich, S. Coriani, T. Helgaker and M. Dolg, *J. Chem. Phys.* **131**, 154102 (2009)

C 2

General Order Coupled-Cluster in the 4-Component Framework

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We present the initial implementation of a string-based general-order coupled cluster [1] method which fully accounts for relativistic effects within the four-component framework [2]. The method opens the way for the treatment of multi-reference problems through a state-selective expansion of the model space. Unlike the previously reported version[3], where the evaluation of the coupled cluster vector function is carried out via relativistic configuration interaction expansions, the current version is commutator-driven and therefore has the correct scaling.

We demonstrate some of the capabilities of the new method in calculations of complete potential energy curves of the HBi molecule. The inclusion of spin-orbit interaction and higher excitations than coupled cluster double excitations, either by multi-reference model spaces or the inclusion of full iterative triple and quadruple excitations, leads to highly accurate results for spectral constants of HBi.

Due to the correct scaling, the new code also opens the possibility doing inner-valence/outer-core correlation/polarization which is often be very significant if high accuracy is desired. The importance of these effects on HBi are demonstrated.

Additional truncation schemes of the coupled cluster hierarchy not only based on excitation level n but also on the flipping of the Kramers projection ΔM_k is shown along with additional schemes exploiting the Generalized Active Space (GAS) concept to achieve a more compact representation of the wavefunction.

[1] L. K. Sørensen, J. Olsen and T. Fleig, *In Preparation*
[2] DIRAC, a relativistic ab initio electronic structure program, Release DIRAC08 (2008), written by L. Visscher, H. J. Aa. Jensen, and T. Saue, with new contributions from R. Bast, S. Dubillard, K. G. Dyall, U. Ekström, E. Eliav, T. Fleig, A. S. P. Gomes, T. U. Helgaker, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, P. Norman, J. Olsen, M. Pernpointner, K. Ruud, P. Sałek, and J. Sikkema (see http://dirac.chem.sdu.dk)
[3] T. Fleig, L. K. Sørensen and J. Olsen, *tca* 118 (2007) 347

Efficient all-electron implementation of the *GW* approximation within the full-potential linearised augmented-plane-wave method

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The *GW* approximation for the electronic self-energy yields quasiparticle band structures in very good agreement with experiment, but almost all implementations so far are based on the pseudopotential approach, which limits their range of applicability. We have developed an implementation within the full-potential linearised augmented-plane-wave (FLAPW) method, which treats core and valence electrons on an equal footing. Within this method a large variety of materials can be treated, including d- and f-electron systems, oxides and magnetic systems. Our implementation employs a mixed product basis for the representation of basis-function products in the interstitial and muffin-tin regions. An expansion of the wave functions around the Γ point using $\mathbf{k} \cdot \mathbf{p}$ perturbation theory allows us to treat the divergence of the Coulomb interaction analytically leading to fast convergence with respect to the $\mathbf{k}$-point sampling. The anisotropy of the dielectric screening is fully taken into account. A basis transformation to the eigenfunctions of the Coulomb potential allows a reduction of the basis-set size without compromising the accuracy, which leads to a considerable speed-up in computation time. As a demonstration we show results for prototype semiconductors and insulators, perovskite transition-metal oxides, and ferromagnetic nickel. Financial support from the DFG through the Priority Programme 1145 is gratefully acknowledged.

Posters

P 1

Tensor decomposition in post-HF methods

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A new approximation for post-HF methods is currently being developed applying recent developments in tensor decomposition techniques [1-3]. In contrast to established approaches such as Cholesky decomposition, RI or density fitting [4-7] the tensor decomposition applied in this ansatz yields tensors of dimension $orbitals \cdot rank$ ($rank$ being the expansion length of the tensor decomposition) as a representation for higher dimensional tensors like integrals, amplitudes and intermediates.
This approach has the potential to decrease the computational effort and the memory requirements of the algorithm drastically while allowing for rigorous truncation and error estimation. For methods from the Coupled-Cluster hierarchy for example, storage is reduced to $d \cdot rank \cdot orbitals$ (d being the dimensionality of the full tensor) and the computational effort is for all levels of approximation $rank^2 \cdot orbitals$. In this contribution first results for the the decomposition of the two electron integrals, the AO-MO transformation and the Coupled-Cluster amplitudes equations are presented. Furthermore, the scaling of the decomposition rank with system and basis set size is discussed for various quantities like integrals and amplitudes.

Literature:

[1] U. Benedikt,M. Espig, W. Hackbusch, A. A. Auer, *to be submitted*
[2] S. R. Chinnamsetty et al. *J. Chem. Phys.* 127 (2007) 084110.
[3] M. Espig, *PhD thesis* (2007) Universität Leipzig.
[4] N. H. F. Beebe, J. Linderberg, *Int. J. Quantum Chem.* 12 (1977) 683–705.
[5] H. Koch, A. S. de Meras, T. B. Pedersen, *J. Chem. Phys.* 118 (2003) 9481–9484.
[6] T. Kinoshita, O. Hino, R. J. Bartlett, *J. Chem. Phys.* 119 (2003) 7756–7762.
[7] O. Hino, T. Kinoshita, R. J. Bartlett, *J. Chem. Phys.* 121 (2004) 1206–1213.

P 2

Electronic and nuclear fluxes during pericyclic reactions: Quantum simulations for the Cope rearrangement of Semibullvalene

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Chemical reactions and molecular vibrations involve simultaneous fluxes of the coupled nuclei (F_{nuc}) and electrons (F_{el}) in molecules. Here, we use a general quantum method, recently developed in [1], in order to calculate F_{nuc} and F_{el} during the degenerate Cope rearrangement of Semibullvalene (SBV) (Fig. 1a). We present high level ab-initio data (CCSD(T)/cc-pVTZ) for the calculation of the potential energy curve and compare to less expensive DFT methods (Fig. 1a). We also present visualizations of the coupled time dependent nuclear- and electronic densities during the Cope rearrangement, providing new means for analysis and comprehension of the detailed mechanism underlying the coupled electronic- and nuclear fluxes (Fig. 1b, c).

Our new approach combines the fields of quantum chemistry for stationary molecular properties and quantum reaction dynamics for electronic and nuclear fluxes, hence allowing us to answer questions like: How many electrons are flowing during the Cope rearrangement of SBV? Are they traveling unidirectionally? On which time scale? Do accurate quantum simulations support traditional rules which are used ubiquitously, e.g. in organic chemistry?

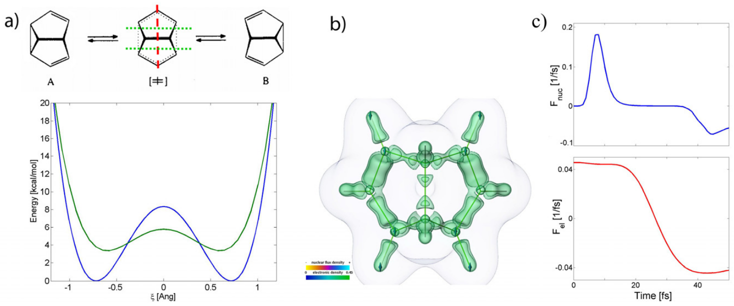

Figure 1 a) Top: Degenerate Cope rearrangement of Semibullvallene (SBV) "with planes of observers" for the electronic (red) and nuclear (green) fluxes. Bottom: Two one dimensional cuts through the potential energy surface calculated at the B3PW91/cc-pVTZ level. One cut goes from Minimum A to B along the coordinate ξ (blue), the other one (green) goes parallel to ξ but passing through the transition state. b) Snapshot of electronic- and nuclear densities. c) Nuclear (top) and electronic (bottom) fluxes.

[1] Barth, I.; Hege, H.-Ch.; Ikeda, H.; Kenfack, A.; Koppitz, M.; Manz, J. Marquardt, F.; Paramanov, G.; *Chem. Phys. Lett.* **2009**, 481, 118

Cholesky-Decomposed Densities in Laplace-Based Second-Order Møller-Plesset Perturbation Theory

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We present a modification of our linear-scaling AO-MP2 method [1-3] employing Cholesky-decomposed [4,5] pseudo-density (CDD) matrices [6]. This leads to an energy expression involving only fully transformed integrals (FTIs) over localized pseudo-MOs. Using an integral screening procedure based on rigorous Schwarz and MBIE upper bounds [1], the asymptotic scaling of the number of required FTIs is reduced to linear for non-delocalized systems. Due to the restriction of indices to the occupied and virtual subspaces, important performance gains are obtained as compared to standard AO-MP2, in particular for large basis sets. Results for both the pure CDD-MP2 algorithm as well as the corresponding approach employing the 'resolution of the identity' (RI) technique [6,7] for the formation of integrals are presented. In contrast to CDD-MP2, the RI-CDD-MP2 approach sacrifices the linear-scaling behavior in favor of a significant prefactor reduction, effectively leading to higher performance for medium-sized and even relatively large molecules.

Literature:

[1] D. S. Lambrecht, B. Doser, C. Ochsenfeld, *J. Chem. Phys.* **123**, 184102 (2005).
[2] B. Doser, D. S. Lambrecht, C. Ochsenfeld, *Phys. Chem. Chem. Phys.* **10**, 3335 (2008).
[3] B. Doser, D. S. Lambrecht, J. Kussmann, C. Ochsenfeld, *J. Chem. Phys.* **130**, 064107 (2009).
[4] N. H. F. Beebe, J. Linderberg, *Int. J. Quantum Chem.* **12**, 683 (1977).
[5] F. Aquilante, T. B. Pedersen, A. Sánchez de Merás, H. Koch,
J. Chem. Phys. **125**, 174101 (2006).
[6] J. Zienau, L. Clin, B. Doser, C. Ochsenfeld, *J. Chem. Phys.* **130**, 204112 (2009).
[7] O. Vahtras, J. Almlöf, M. W. Feyereisen, *Chem. Phys. Lett.* **213**, 514 (1993).

Efficient Implementation of Highly Excited Coupled Cluster

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We present recent advances of our coupled cluster implementation, which can treat in principle arbitrary excitation levels. Several other implementations of highly excited coupled cluster have been published so far, e.g. [1-4].

We focus here on the calculation of the residuals, which is the time determining step for the solution of coupled cluster equations. The key step with respect to efficiency is the implementation of the tensor contraction which is used for this calculation. We illustrate our approach based on matrix multiplication combined with an optimized rearranging of tensor entries [5].

In addition, we implemented a new method for the factorization of the expressions for the residuals [6]. Factorization here means the definition of a sequence of binary tensor contraction operations for the evaluation of these expressions. This includes the choice of the contractions to be carried out – in particular the order of the factors in each product –, the addition of compatible tensors before contraction, and the identification of reusable intermediates. All these steps are treated simultaneously as a coupled optimization problem. This optimization is carried out by a genetic algorithm.

We also show exemplary timings and analyze the performance of different program parts.

Literature:

[1] S. Hirata and R. J. Bartlett, Chem. Phys. Lett. **321** (2000) 216
[2] J. Olsen, J. Chem. Phys. **113** (2000) 7140
[3] M. Kállay and P. R. Surján, J. Chem. Phys. **113** (2000) 1359
[4] S. Hirata, J. Phys. Chem. A **107** (2003) 9887
[5] M. Hanrath and A. Engels-Putzka, *"An Efficient Matrix-Matrix Multiplication Based Antisymmetric Tensor Contraction Engine"*, manuscript in preparation
[6] M. Hanrath and A. Engels-Putzka, *"The (Highly Excited) Coupled Cluster Factorization Problem: A Genetic Approach"*, manuscript in preparation

Analytical nuclear gradients for RI-MP2-F12

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We present analytical nuclear gradients for explicitly correlated MP2 using density fitting (RI-MP2-F12) in Turbomole [1-2]. Compared to previous results of Kordel *et al.* [3], the implementation has been accomplished in Turbomole for Ansatz 2* [4] without coupling terms, standard approximation A using CABS, a Slater-type geminal (STG-6G), and robust density-fitting. Additionaly, a second-order perturbation theory correction for single excitations into a complementary auxiliary basis set (CABS singles) is included to reduce the Hartree-Fock error [5]. Smooth convergence towards the basis set limit is observed for all investigated molecules. For dimers to be computed with small basis sets, RI-MP2-F12 outperforms conventional RI-MP2 clearly, since basis set superposition errors (BSSE) are avoided.

Literature:

1. S. Höfener, F. A. Bischoff, A. Glöß, W. Klopper, *Phys. Chem. Chem. Phys.* **10**, 3390 (2008).
2. F. A. Bischoff, S. Höfener, A. Glöß, W.Klopper, *Theor. Chem. Acc.* **121**, 11 (2008).
3. E. Kordel, C. Villani, W. Klopper, *Mol. Phys.* **105**, 2565 (2007).
4. E. Valeev, *Chem. Phys. Lett.* **395**, 190 (2004).
5. T. B. Adler, G. Knizia, H.-J. Werner, *J. Chem. Phys.* **127**, 221106 (2007).

Investigation of Electronic Structure and Properties of Solid EuC_2 and YbC_2

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EuC_2 crystallizes in a different space group (C 2/c) in comparison to all other rare earth carbides (I 4/mmm) [1] that have been synthesized.

In addition the unit cell volumes of solid EuC_2 and YbC_2 do not fit in the lanthanide row. It has been proposed that this effect might be caused by a difference in the valence of the lanthanide atoms (Ln^{2+} vs. Ln^{3+}). Generally rare earth atoms prefer a valence of 3+ in molecules and crystals. It is possible that the rare earth atoms in EuC_2 and YbC_2 may better be described as a Ln^{2+} than a Ln^{3+} since a half and fully occupied 4f-shell (Eu^{2+}: $4f^7$, Yb^{2+}: $4f^{14}$) is favoured.

In our work we focussed on the structures of EuC_2 and YbC_2. The calculations were carried out with the CRYSTAL06 program [2]. Geometries of both carbide compounds have been fully optimized. Band structures were derived and frequencies were analyzed. Our results agree with experimental presumtions. We could show that Eu is more likely to show a 2+ valence in the carbide compound and Yb a 3+ valence, respectively.

Literature:

[1] D. Wandner, U. Ruschewitz, M. Abd Elmeguid, M. A. Ahmida and O. Heyer, *Z. Anorg. Allg. Chem.*, **632**, 2099 (2006).

[2] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, M. Llunell **CRYSTAL06**, University of Torino, Torino, Italy (2006).

P 7

Laser-induced electron dynamics including photoionization: A heuristic model within TD-CI theory

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We report simulations of laser-pulse driven many-electron dynamics by means of a simple, heuristic extension of the time-dependent configuration interaction singles (TD-CIS) approach. The extension allows for the treatment of ionizing states as non-stationary states with a finite, energy-dependent lifetime to account for above-threshold ionization losses in laser-driven many-electron dynamics. The extended TD-CIS method is applied to the following specific examples: (i) State-to-state transitions in the LiCN molecule which correspond to intramolecular charge transfer and (ii) creation of electronic wavepackets in LiCN including wavepacket analysis by pump-probe spectroscopy.

Literature:

T. Klamroth, *Phys. Rev. B* **68**, 245421 (2003) and references therein.

P. Krause, T. Klamroth, and P. Saalfrank, *J. Chem. Phys.* **123**, 074105 (2005).

S. Klinkusch, T. Klamroth, and P. Saalfrank, *Phys. Chem. Chem. Phys.* **11**, 3875 (2009).

S. Klinkusch, P. Saalfrank, and T. Klamroth, *J. Chem. Phys.* **131**, 114304 (2009).

PERIODIC DENSITY FITTED LOCAL CIS

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A new density fitted local CIS method for periodic systems as implemented in the CRYSCOR [1] code is presented. In its current implementation it can describe Frenkel and intermediate-ranged Γ-point excitons in one-dimensional periodic systems. The procedure it partly performed in direct and partly in reciprocal space. The periodic CIS method is able to capture the electron-hole-interaction and constitutes a first step towards correlated optical band gaps in periodic systems.

Literature:

[1] M. Schütz, D. Usvyat, M. Lorenz, C. Pisani, L. Maschio, S. Casassa, M. Halo, *Accurate Condensed-Phase Quantum Chemistry*, will be published in May 2010.

P 9

Calculation of intermolecular interaction energies using explicitly correlated coupled-cluster methods

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The CCSD(T)-F12a method is used to compute highly accurate interaction energies of molecular dimers. Comparison with extrapolated conventional CCSD(T) calculations for the S22 benchmark set shows excellent agreement. Using augmented triple zeta basis sets the CCSD(T)-F12 interaction energies agree within 0.02 kcal with the estimate complete basis set (CBS) values. Furthermore, a dispersion weighted variant of spin component scaling MP2-F12 (DW-MP2-F12) is employed to correct approximately for higher-order correlation effects in intermolecular interactions. In this method a weighted average of the MP2-F12 and SCS-MP2-F12 correlation energies is used, and the weight factors are determined on the basis of the Hartree-Fock and MP2-F12 correlation contributions to the interaction energies. This yields good agreement with CCSD(T)-F12a results of the same basis set quality for the description of all types of weak interactions. For the S22 set, the maximum deviation from the CCSD(T)-F12a results is reduced from 3.27 kcal/mol (MP2-F12/aug-cc-pVDZ) to 0.41 kcal/mol (DW-SCS-MP2-F12/aug-cc-pVDZ). This allows computing interaction energies of near CCSD(T)/CBS quality for much larger clusters than can be treated with CCSD(T). Furthermore, DW-MP2-F12 optimized geometry properties are compared with CCSD(T) results.

Literature:

[1] H.-J. Werner, T. B. Adler, and F.R. Manby, J. Chem. Phys. **126**, 164102 (2007).
[2] T. B. Adler, G. Knizia and H.-J. Werner, J. Chem. Phys. **127**, 221106 (2007).
[3] G. Knizia, T. B. Adler, and H.-J. Werner, J. Chem. Phys., submitted (2008).
[4] O. Marchetti and H.-J. Werner, Phys. Chem. Chem. Phys., DOI:10.1039/B804334E (2008).
[5] P. Jurečka, J. Černy, J. Šponer, and P. Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006).
[6] O. Marchetti and H.-J. Werner, J. Phys. Chem. A **113**, 11580 (2009).

Application of the Method of increments for the investigation of electron correlation effects in physisorbed systems

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Physisorption plays an important role in many different contexts of surface chemistry. In these weakly bound systems the interaction consists of two parts: electron dispersion and classical electrostatics. Dispersion is non-local electron correlation. It is neglected in Hartree-Fock (HF) theory, not included in common DFT functionals, but recovered by Møller-Plesset Perturbation (MP2) or Coupled Cluster (CC) theory. Classical electrostatic interactions are in principle well described already at the HF or DFT level, however for some molecules e.g. CO and N_2O these methods fail to reproduce the small dipole moments and consequently fail to reproduce the electrostatic interactions, too. It is therefore important to apply very accurate computational methods in order to obtain reliable data for the adsorption energy that could be compared to experiment. Due to the high computational costs of the ordinary MP2 and CC methods we here apply these theories in the framework of a local correlation scheme called The Method of Increments [1-4]. In this scheme, which can be applied for all size-consistent methods, the correlation energy is calculated as a many-body expansion in terms of localized orbital groups. Due to the local character of the electron correlation this expansion converges quite fast with much lower requirements on computational time and resources than standard implementations of post-HF methods. We have extended the method of increments to adsorption problems and investigated the systems $CO/CeO_2(110)$ [5], $CO/CeO_2(111)$ [6], $N_2O/CeO_2(111)$ [7], and H_2S/Graphene [8]. We found that in all four systems electron correlation effects contribute to a large amount to the adsorption energy. On top of the large speed-up the method of increments yields some interesting insights into the nature of the molecule-surface bond in weakly bound systems.

Literature:

- [1] H. Stoll, Phys. Rev. B 46, 6700 (1992).

P 11

Calculations on Small Test Systems Employing Multi-Reference Coupled-Cluster Schemes

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Previously described Multi-Reference Coupled-Cluster (MRCC) schemes (namely SRMRCC [1], RMRCC [2] and MRexpT [3]) have been applied to the hetero-nuclear LiH system and the H4 model system. The qualities of the energy expectation values and the wave-functions have been investigated as a function of the internuclear distance, respectively. The set up of the above mentioned MRCC ansätze will be briefly revisited and discussed with a focus on their intrinsic relationships and their properties. The results of the Coupled-Cluster calculations are discussed in comparison to full configuration interaction as an exact method concerning the given many-particle basis set. A focus is set on near-degeneracy and degeneracy problems such as the D_{4h} geometry in H4 since the treatment of these states is the major intention for the set up of multi-reference schemes. It will be shown that the RMRCC and SRMRCC implementations suffer from inherently symmetry broken wave-functions and are very sensitive to changes in the Fermi vacuum, while MRexpT provides reasonable results although it is neither valence- nor core-valence connected [4].

Literature:

[1] N. Oliphant, L. Adamowicz, *J. Chem. Phys.* **94**, 1229 (1991).
[2] X. Li, J. Paldus, *J. Chem. Phys.* **107**, 6257 (1997).
[3] M. Hanrath, *J. Chem. Phys.* **123**, 084102 (2005).
[4] M. Hanrath, *Theo. Chem. Acc.* **121**, 187 (2008).

P 12

DEVELOPMENT AND FIRST TESTS FOR AN ADDITIVE LONG RANGE CORRECTED XC-FUNCTIONAL

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Time dependent density functional theory (TDDFT) has become a powerful and widely used tool for the description of excited states of large molecules with up to several hundreds of atoms and is often considered the method of choice due to its low computational cost. While the theoretical treatment of low lying optically allowed locally excited electronic states is usually in good agreement with experimental data, the description of 'dark' states on the other hand is problematic: Doubly and higher excited states are not included at all in the TDDFT framework and the energy of charge transfer (CT) states is usually drastically underestimated by up to several eV due to the so called 'self interaction error'. Furthermore, CT states do not exhibit the correct 1/R behavior when looking at the potential energy curves of a dimer along an intermolecular separation coordinate R.

It has been shown that the 1/R behavior of CT states may be regained by using coulomb attenuated functionals, but the energy of CT states is still drastically underestimated. The ansatz for our new xc-functional is to correct the excitation energy of every transition according to the amount of charge transfer character character of the given transition. Local excitations should not be shifted while CT excitations should be shifted upwards in energy. The 'amount' of charge transfer character for a given transition may be estimated by the orbital overlap of the molecular orbitals involved in the specific transition. The lower the orbital overlap, the higher the charge transfer character of the transition. The energy of the lowest charge transfer excitation of a dimer at infinite distance is given to zeroth order by the difference between electron affinity (EA) and ionization potential (IP), thus it is possible to estimate and correct for the self interaction error if EA and IP are known.

Since this energy correction is an additive functional it may in principle be added to every existing functional without the need of refitting the functional parameters.

P 13

Influence of methyl substitution and bond length alternation on the lowest excited states of linear polyenes

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Due to their central role in biophysical photo-processes and technical applications, linear polyenes are frequent targets of experimental and theoretical research. However, the understanding of the nature of their lowest excited electronic states still poses a challenging task. Here the influence of methyl substitution on the vertical excitation energies and excited state geometries of linear polyenes and the influence of bond length alternation strongly affecting computed vertical excitation energies have been investigated.

The performance of various levels of theory in the description of the electronic ground state geometry of linear polyenes is studied in detail. In addition, the algebraic diagrammatic construction (ADC)[2] scheme is used to calculate vertical excitation energies. The results obtained are compared with experimental absorption and fluorescence data, which have recently been published for 1,1'-dimethylpolyenes[1]. The best agreement is achieved when B3LYP/cc-pVTZ equilibrium structures are used, most likely due to most fortuitous cancellation of error. Moreover, the vertical excitation energies of methyl substituted linear polyenes strongly depend on the position and the rotational conformation of the methyl groups. While butadiene and the two isomers of dimethyl-butadiene were used to study the effect of different substitution schemes in detail, longer polyenes with up to seven double bonds are also included in our theoretical investigation.

Literature:

[1] R. L. Christensen et al, *Journal of Physical Chemistry* 112 (2008) 12629-12636
[2] J. Schirmer, *Physical Review A* 26 (1982) 2395

P 14

Implementation of a vector potential method in an *ab initio* Hartree-Fock code

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For extended systems exposed to an external, electrostatic field, the presence of the field leads to an extra term ($\vec{E}$. $\vec{P}$) to the Hamiltonian, where $\vec{E}$ is the field vector and $\vec{P}$ is the polarization of the system of interest. In order to find out how a polymer chain responds to an external electric perturbation, a field with a charge and a current term for the polarization is added to an *ab initio* Hartree-Fock Hamiltonian. The polarization expression is taken from an efficient vector potential approach (VPA) for calculating electronic and nuclear responses of infinite periodic systems to finite electric fields and is implemented in the *ab initio* LCAO-SCF algorithm, which computes band structure of regular or helical polymers, taking into account the one-dimensional translational symmetry.

Literature:

M. Springborg and B. Kirtman, Phys. Rev. B 77, 045102 (2008).

J. M. André, D. H. Mosley, B. Champagne, J. Delhalle, J. G. Fripiat, J. L. Brédas, D. J. Vanderveken, and D. P. Vercauteren, METECC-94 B 423 (1993).

P 15

Perturbative explicitly correlated basis set imcompleteness corrections

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Explicitly correlated R12 methods [1] are a means to overcome the slow convergence of the (dynamic) correlation energy of determinant-based methods with the size of the one-particle basis set. The well-known MP2-R12 method, already introduced at the beginning of R12 theory [2], treats the explicitly correlated part of the wave function together with the conventional doubly excited contributions as a part of the first-order perturbation theoretical wave function with the Hartree Fock wave function being of zeroth order. Here we present a generalization of perturbative explicitly correlated R12 theory at the level of state-of-the-art R12 theory [1] to other zeroth order wave functions based on the Löwdin partitioning technique [3]. The application of this method to CCSD, invoking further simplifications, is the CCSD(2)$_{\overline{\text{R12}}}$ method [4] and it's fixed-coefficient version [5]. In the case of CCSD(T), we get the CCSD(T)$_{\overline{\text{R12}}}$ method [6], considering the (T) and the $_{\overline{\text{R12}}}$ correction as perturbative corrections of CCSD. The advantage of these methods is that they are virtually as simple and computationally cheap as MP2-R12, still yielding about the accuracy of a conventional aug-cc-pV5Z calculation with an aug-cc-pVTZ orbital basis set. By employing a second quantization formalism for general multideterminantial wave functions [7], an universal perturbative explicitly correlated basis set imcompleteness correction applicable to any multideterminantial wave function yielding one- and two-particle density matrices can be derived with our approach [8]. By neglecting terms with higher-than two-electron cumulants [9] as well as terms, where two r_{12} matrix elements or one r_{12} and one g_{12} matrix element are connected via a two-electron cumulant [9], the $[2]_{\text{R12}}$ correction [8] is obtained, yielding results with the quality of conventional aug-cc-pVQZ caculations with an aug-cc-pVDZ basis set in first tests [8]. The $[2]_{\text{R12}}$ correction is internally contracted and employs state-of-the-art [1] R12 theory: when supplied with Hartree-Fock density matrices it recovers the explicitly correlated part of the projector 2 version of MP2-R12. With this, it is suited as a R12 correction to intricate wave functions, such as multireference configuration interaction.

[1] W. Klopper, F. R. Manby, S. Ten-no, E. F. Valeev *Int. Rev. Phys. Chem.* **25** (2006) 427.

[2] W. Kutzelnigg *Theor. Chim. Acta* **68** (1985) 445; W. Klopper, W. Kutzelnigg *Chem. Phys. Lett.* **134** (1987) 17; W. Kutzelnigg, W. Klopper *J. Chem. Phys.* **95** (1991) 1985.

[3] P.-O. Löwdin *J. Math. Phys.* **3** (1962) 969.

[4] E. F. Valeev *Phys. Chem. Chem. Phys.* **10** (2008) 106.

[5] M. Torheyden, E. F. Valeev *Phys. Chem. Chem. Phys.* **10** (2008) 3410.

[6] E. F. Valeev, T. D. Crawford *J. Chem. Phys.* **128** (2008) 244113.

[7] W. Kutzelnigg, D. Mukherjee *J. Chem. Phys.* **107** (1997) 432.

[8] M. Torheyden, E. F. Valeev *J. Chem. Phys.* **131** (2009) 171103.

[9] W. Kutzelnigg, D. Mukherjee *J. Chem. Phys.* **120** (2004) 7350.

BSSE correction for N-body clusters within an approximate treatment of the Site-Site Function Counterpoise Scheme

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The accurate quantum chemical evaluation of intermolecular interactions is a highly demanding task, especially for weak interactions and for large interacting systems. The supermolecular approach suffers from the so-called basis set superposition error (BSSE), which arises due to the more significant incompleteness of the basis sets used for the calculation on the monomers than for the one of the N-mers. The most widely used prescription to correct for BSSE effects is the counterpoise (CP) correction of Boys and Bernardi. In the framework of the counterpoise method Wells and Wilson proposed the so called site-site function CP (SSFC) approach, which corrects for BSSE in aggregates with various subunits.

In this work we present a simplification of the SSFC scheme, which aims at a reduction of the size of the one-particle basis set. The accuracy of the proposed approach is investigated for the water cluster series: $(H_20)_n$ with n=10,12,14,16,18 and 20 at SCF, MP2, CCSD and CCSD(T) level of theory. Additionally we present MP2, CCSD and CCSD(T) correlation energies of the water series (up to n=18) obtained with the incremental scheme using the domain-specific basis set approach.

Literature:

B. H. Wells, S. Wilson, Chem. Phys. Lett. **101**, 429 (1983).

S. F. Boys, F. Bernardi, Mol. Phys. **19**, 553 (1970).

J. Friedrich, M. Dolg, J. Chem. Phys. **129**, 244105 (2008).

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The Algebraic Diagrammatic Construction Scheme for the Calculation of Electronic Excited States Employing Localized Orbitals

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The algebraic diagrammatic construction (ADC) scheme provides a way to derive methods for the calculation of electronic excited states based on perturbation theory. By employing the scheme for a given order in perturbation theory a hermitian, CI-like ADC matrix is obtained whose eigenvalues and eigenvectors yield the energies and transition moments of excited states, respectively. The second order variant ADC(2) performs similar to CIS(D) or CC2 producing reliable results for most optically allowed excited states. Yet, neither ADC(2) nor CC2 are sufficient to correctly describe highly correlated states, as they are e.g. present in the low-energy region of linear polyenes. An improved description of such states can be obtained by using an extended second order scheme ADC(2)-x which represents a compromise between the accuracy of higher order methods and the computational costs of ADC(2). It has been shown recently [1] that ADC(2)-x yields acceptable results for the energies of the lowest excited states in small linear polyenes.

To reduce the computational scaling of the ADC(2)-x method we have developed and implemented it in the Q-Chem package of programs employing localized occupied and virtual orbitals. By exploiting the locality of the orbitals a significant amount of doubles amplitudes can be neglected in the calculation which reduces the scaling of the method significantly without sacrificing accuracy. Several distinct models for neglecting doubles amplitudes based on orbital distances have been implemented and evaluated. The most promising model has been applied to a set of test molecules. Compared to non-local ADC calculations the results of the local version showed less than 0.15 eV deviation in the excitation energies of any of the calculated excited states.

Literature:

[1] J. H. Starcke, M. Wormit, J. Schirmer and A. Dreuw, *Chem. Phys.*, **329**, 39 (2006)

P 18

Linear scaling open-shell local correlation methods

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The local correlation methods as originally proposed by Pulay [1, 2] and implemented previously for closed-shell methods in our group [3, 4, 5] have been generalized and implemented for spin-restricted high-spin open-shell MP2 (RMP2) and unrestricted coupled cluster (UCCSD) theory, using ROMP2 orbitals. Two different localization schemes are compared and discussed. In the first case localization is performed separately in the closed-shell and open-shell orbital spaces. In the second case localization is performed separately for the alpha and beta spin orbitals. The excitations are restricted to domains, and only strong pairs are treated at the highest level. Local density fitting approximations [6] are used to compute all integrals. Provided that the orbitals can be well localized, this leads to linear scaling of the computational effort with molecular size and extends the applicability of the local RMP2 and UCCSD methods to systems with 100-150 correlated orbitals and 2000-4000 basis functions. The methods are tested for computing ionization potentials, electron affinities and reaction energies. The accuracy is found to be comparable to the corresponding canonical methods.

References

[1] P. Pulay, Chem. Phys. Lett. **100**, 151 (1983).

[2] S. Saebø and P. Pulay, J. Chem. Phys. **88**, 1884 (1988).

[3] C. Hampel and H.-J. Werner, J. Chem. Phys. **104**, 6286 (1996).

[4] M. Schütz and H.-J. Werner, Chem. Phys. Lett. **318**, 370 (2000).

[5] M. Schütz and H.-J. Werner, J. Chem. Phys. **114**, 661 (2001).

[6] H.-J. Werner, F. R. Manby, and P.J. Knowles, J. Chem. Phys. **118**, 8149 (2003).

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