Oral contributions **C1**

DFT modeling of the polymerization and co-polymerization processes catalyzed by the late-transition metal complexes

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Modeling complex catalytic processes with many elementary reactions by quantum chemical calculations is often not practical without the aid of statistical methods; this is especially important when addressing the influence of macroscopic reaction conditions (*T, p*). A possible approach is a 'mesoscopic' scheme, in which the results of the DFT calculations are used as input data for a stochastic modeling of the process. In the present investigations we have applied such a procedure to model polymer growth in the processes of the α-olefin polymerization catalyzed by the late-transition-metal-complexes. The DFT calculations (static and MD) performed for elementary reactions present in the catalytic cycle provided the reaction energies and the activation barriers that were further used as input data for simulations of the polymer growth and branching. The major goal of this study was to draw conclusions about the influence of the catalyst structure and the reaction conditions (temperature and pressure) on the polyolefin branching and microstructure. Further, DFT was used to understand the influence of the metal and the polar monomer on the chain isomerization energetics, and thus, on the copolymer microstructure.

Molecular weight is one of the crucial characteristics of the polymer, that directly influence its properties. In the polymerization processes catalyzed by some late-transition-metal based catalyst the molecular weight can be controlled not only by the ligand structure but as well by the thermodynamic parameters of the process. The DFT-based studies have been focused on understanding the pressure dependence of molecular weight in the processes catalyzed by Ni-based anilinotropone complexes.

Oral contributions **C2**

New correlation energy functional : a modified Colle-Salvetti approach

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The Colle and Salvetti approach [1] to the calculation of the correlation energy of a system is modified in order to explicitly include into the theory the kinetic contribution to the correlation energy. This is achieved by deducing from a many electrons wave function, including the correlation effects via a Jastrow factor, an approximate expression of the one-electron reduced density matrix. Applying the latter to the homogeneous electron gas, an analytic expression of the correlation kinetic energy is derived. The total correlation energy is then deduced from the kinetic contribution inverting a standard procedure. At variance of the original Colle-Salvetti theory, the parameters entering in both the kinetic correlation and the total correlation energies are determined analytically, leading to a satisfactory agreement with the results of Perdew and Wang for the homogeneous electron gas [2]. The resulting (parameter-free) expressions give rise to a modified-local-density approximation that can be used in self-consistent density-functional calculations. We have performed such calculations for a large set of atoms and ions and we have found results for the correlation energies and for the ionization potentials which improve those of the standard local-density approximation [3].

[1] R. Colle and O. Salvetti, Theor. Chim. Acta, **37**, 329 (1975).
[2] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[3] S. Ragot and P. Cortona, J. Chem. Phys. **121**, 7671 (2004).

Oral contributions **C3**

Off-centre instabilities of impurities in solids explained through ab initio calculations

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Off-center instabilities of impurities in solids have been detected in many systems including some with technological applications. Magnetic resonance measurements demonstrate the existence of big off-centre motions (≈ 1 Å) from the substitutional position in cases like d^9 (Ni^+, Cu^{2+} or Ag^{2+}) and d^4 (Cr^{2+}) Jahn-Teller (JT) impurities in some fluorite type crystals. Some authors have suggested that these displacements would be due to size effects while other works have tried to explain them through JT coupling. Nevertheless, recent ENDOR experiments [1] carried out on $SrCl_2$: Fe^+ clearly demonstrate that the d^7 ion undergoes a big off-centre motion along <001> type directions. Moreover, no evidence of any close defect to Fe^+ has been detected experimentally [1]. As Fe^+ in $SrCl_2$ exhibits a value S=3/2 [1] its ground state in a perfect cubal symmetry would be $^4A_2$ ($e_g{}^4t_{2g}{}^3$) with *no orbital degeneracy*, a situation which is thus different to that for d^9 ions in fluorite type lattices.

Searching to investigate the origin of the off-centre motion in $SrCl_2$:Fe^+ and in Cu^{2+} doped $SrCl_2$ and SrF_2 DFT calculations on clusters involving up to 51 atoms have been performed [2]. For $SrCl_2$:Fe^+ a (0,0,Z) equilibrium position with Z = 1.3 Å is obtained. The well depth related to this spontaneous distortion is found to be 0.28 eV. The microscopic origin of this huge distortion is shown to be very subtle as it cannot be understood looking only to the half filled t_{2g} shell [2]. The polarization of the electronic cloud through admixtures of ligand and 4s and 4p orbitals of Fe^+ is found to play a key role together with the electrostatic field due to the rest of the lattice which acts against the distortion.

[1] D. Ghica et al., Phys. Rev. B **70**, 024105-1 (2004)
[2] P. García Fernández et al., Phys. Rev. B **69**, 174110-1 (2004)

Oral contributions **C4**

DNA-BINDING OF RUTHENIUM-ARENE ANTICANCER DRUGS

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The discovery of cisplatin as an anticancer drug led to considerable interest in metallopharmaceuticals. Problems remain associated with their use, including general toxicity, drug resistance and low selectivity. Recently, organometallic ruthenium(II)-arene complexes showed their potential to overcome this drawback. Rational design requires a detailed understanding of structure-property relationships at an atomistic level.

We performed classical MD and mixed QM/MM Car-Parrinello MD simulations[1] to rationalize the binding mode of two series of anticancer ruthenium(II) arene-complexes to double-stranded (ds) DNA. The bifunctional[2] $[Ru(\eta^6\text{-arene})X_2(PTA)]$ (**1**) and the monofunctional[3] $[Ru(\eta^6\text{-p-cymene})Xen]^+$ (**2**) series of compounds were both bound to the DNA sequence d(CCTCTG*G*TCTCC)/d(GGAGACCAGAGG), where G* are guanosine bases that bind to the ruthenium compounds through their N7 atom. As reference, the same sequence was also simulated without any drug and in its canonical, unperturbed B-DNA form.

The local and global structural modifications of DNA upon complexation were analysed in detail. The differences of the DNA-interaction-properties between the two series of compounds as well as with respect to the canonical B-DNA are discussed and linked to experimental observations. In particular, an atomistic description of a Watson-Crick base-pair break upon binding of **2** to dsDNA is proposed, that has been recently suggested on the bases of experimental results. Fundamental differences between binding of **1** or **2** to single stranded DNA (ssDNA) or dsDNA are rationalized.[4]

[1] Laio, VandeVondele, Rothlisberger *J. Chem. Phys.* **2002**, *116*, 6941.
[2] Allardyce, Dyson, Ellis, Heath *Chem. Commun,* **2001**, 1396.
[3] Sadler et al. *J. Med. Chem.* **2001**, *44*, 3616.
[4] Dorcier, Dyson, Gossens, Rothlisberger, *Organometallics* (in press).

Oral contributions **C5**

Quantum Mechanical/Molecular Mechanical investigation of bacteriorhodopsin proton pumping

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A key event in the proton transporting photocycle of bacteriorhodopsin is the transfer of the retinal Schiff base proton to the nearby Asp85 on the ~10 μs time-scale. Due to difficulties in the experimental characterization of the transition states, the mechanism of this transfer step remained highly controversial. To understand why the photocycle follows some pathways and not others, we investigated the retinal configurations that are compatible with a productive proton pumping and computed the energy barriers of the proton transfer paths. Minimum-energy reaction pathways were calculated on a Quantum Mechanical/Molecular Mechanical potential energy surface using Density Functional Theory methods to describe the quantum mechanical region. The results show that active proton pumping can be achieved with 13-*cis*, 15-*anti* retinal, but not with 13-*cis*, 15-*syn* [1]. Three very different transfer pathways were found that have barriers consistent with the experiment [2]. Detailed analysis of the proton transfer energy profiles reveals the important role of specific protein groups in stabilizing the ion-pair state formed by the protonated Schiff base and the negatively charged Asp85 [1].

[1] A.-N. Bondar, S. Fischer, J. C. Smith, M. Elstner, and S. Suhai, *J. Am. Chem. Soc.* **2004**, *126*, 14668.
[2] A.-N. Bondar, M. Elstner, S. Suhai, J. C. Smith, and S. Fischer, *Structure* **2004**, *12*, 1281.

Oral contributions **C6**

Non-local interactions in naphthalene, anthracene, and pyrene dimers

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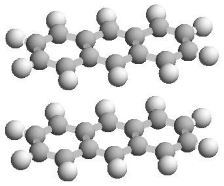
We study the interactions of dimers consisting of naphthalene, anthracene or pyrene molecules stacked on top of each other. These molecules are members of the polycyclic aromatic hydrocarbon (PAH) family, and consist of aromatic rings where the peripheral carbon atoms are bonded to a hydrogen atom. The figure below shows an anthracene dimer in AA (or sandwich) stacking, with dark grey and light grey circles denoting the positions of the carbon and hydrogen atoms, respectively.



The van der Waals forces, which are weak but long-ranged, have important effects on the binding of the dimers. However, these forces are not included in the standard implementations of density functional theory (DFT). By modifying a recently developed van der Waals density functional for planar geometry [1] to treat finite size molecules, we calculate the van der Waals interactions between the molecules. Combining this with standard electronic structure calculations, we are able to obtain binding energies and distances consistent with those of experiments and other theoretical studies [2].

[1] H. Rydberg, M. Dion, N. Jacobson, E. Schröder, P. Hyldgaard, S.I. Simak, D.C. Langreth, and B.I. Lundqvist, *Phys. Rev. Lett.*, **2003**, *91*, 126402.
[2] S.D. Chakarova and E. Schröder, *J. Chem. Phys.*, **2005**, *5*, 05410.

Oral contributions **C7**

Density Functional Methods with Auxiliary Functions

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Abstract

The use of auxiliary functions has a long history in the development of density functional theory (DFT) methods. In this presentation the extension of the variational fitting of the Coulomb potential to the calculation of the exchange-correlation potential is discussed. The accuracy and reliability of the resulting energy expression is demonstrated. An efficient parallel implementation scheme using Hermite Gaussian auxiliary functions is described. Applications to systems with up to 10,000 contracted basis functions are shown.

Oral contributions **C8**

Applications of the Reduced Density Matrix Functional Theory to periodic systems and open shell finite systems

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Reduced Density Matrix Functional Theory is based on Gilbert's theorem[1] according to which every observable is a functional of the one-body-reduced density matrix (1-RDM). Only implicit functionals of the 1-RDM have been introduced so far [2]. They depend explicitly on the natural orbitals and occupation numbers, i.e. the eigenfunctions and eigenvalues of 1-RDM. In the present work, we generalize these functionals (a) to the case of periodic systems and (b) to the case of open shell systems.

In the case of periodic systems, our functional formulation is based on a Wannierstates description of the system [3]. We apply this formalism to the calculation of correllation energy of prototype 1-dimensional periodic systems like LiH chain. Furthermore in a similar fashion to DFT we explore the possibility of using the discontinuity of the chemical potential as a function of the number of electrons in the calculation of the electronic gap.

In the case of open-shell atomic and molecular systems, we based our formulation of 1-RDM functional[2] on the Restricted Open-Shell Hartree-Fock theory (ROHF). As a first application we studied prototype atomic and molecular systems.

[1] T. L. Gilbert, Phys. Rev. B12, 2111 (1975).

[2] M. A. Buijse, E.J. Baerends, Mol. Phys. 100, 401 (2002); S. Goedecker, C. J. Umrigar, Phys. Rev. Lett. 81, 866 (1998).

[3] A. Shukla, M. Dolg, P. Fulde, H. Stoll, Phys. Rev. B60, 5211 (1999);
A. Shukla, M. Dolg, H. Stoll, Phys. Rev. B58, 4325 (1998);

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Oral contributions **C9**

A Time-Dependent DFT study of [Fe(CN)6]4- and ruthenium-polypyridyl complexes sensitization of TiO_2 nanoparticles

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A key process in the operation of dye sensitized photovoltaic solar cell devices is the charge injection from the dye molecule to the semi-conductor. For Ru(II)-polypyridyl dyes the generally accepted injection mechanism involves photoexcitation to a dye excited state, from which an electron is transferred to the semiconductor conduction band states.[1a] By contrast, a mechanism involving a direct photoexcitation from the dye to an empty state of the nanoparticle is believed to occur for $[Fe(CN)_6]^{4-}$ on TiO_2.[1b]
We present Car-Parrinello Density Functional Theory (DFT) and Time Dependent DFT calculations of the absorption spectrum of $[Ru(dcbpyH_2)_2(NCS)_2]$ and $[Fe(CN)_6]^{4-}$ adsorbed on a TiO_2 anatase nanoparticle model. We provide a detailed description of the electronic structure of these prototype systems and of the character of the states involved in the molecule → semiconductor charge transfer process. We show that a direct charge injection process from an occupied dye state to a nanoparticle excited state localized on a few Ti atoms, rather than to a delocalized conduction state, takes place in $[Fe(CN)_6]^{4-}$,[2a] at variance with the $[Ru(dcbpyH_2)_2(NCS)_2]$ where electron injection takes place via an indirect mechanism.[2b]

[1] a) B. O'Regan, M. Gratzel *Nature*, **1991**, *353*, 737; b) M. Yang, D.W. Thompson, G.J. Meyer. *Inorg. Chem.* **2002**, *41*, 1254.
[2] a) De Angelis, F.; Tilocca, A.; Selloni, A. *J. Am. Chem. Soc.* **2004**, *126*, 15024; b) M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, M. Grätzel, **2005**, *submitted.*

Oral contributions **C10**

Relativistic unrestricted two-component calculations of electronic g-tensors and hyperfine structure

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The first two-component relativistic DFT approach for the calculation of electronic g-tensors and hyperfine structure (HFS) is reported that includes spin polarization using non-collinear spin density functionals. The method is based on the relativistic Douglas-Kroll-Hess Hamiltonian and has been implemented into the ReSpect program package. Comparisons with ZORA and Dirac methods are presented. Using three SCF calculations with orthogonal orientations of total spin, the full g-matrix and HFS tensor are obtained. In contrast to previous spin-restricted two-component treatments, g-tensor results with the new approach agree excellently with spin-polarized one-component calculations for light-atom radicals. Additionally, however, the method reproduces also successfully the negative $\Delta g_{\parallel}$ values of heavy-atom $^2\Sigma$ radicals, and the negative $\Delta g_{\perp}$ components in cysteinyl. Further validation examples include a number of organic radicals, as well as transition metal complexes. The new method removes effectively the dilemma existing up to now, regarding the simultaneous inclusion of spin polarization and higher-order spin-orbit effects in calculations of g- and HFS tensors. Moreover, it is straightforwardly applicable to higher than doublet spin multiplicities.

Oral contributions **C11**

The tensorial magnetic shielding function in DFT background and applications

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The induced magnetic field (IMF) of molecules can be calculated from the tensorial nuclearmagnetic shielding function σ(r), which is readily available within modern densityfunctional theory [1]: $B_{ind}(r)= -\sigma(r)B_{ext}$. The magnetic field lines of aromatic and antiaromatic molecules show a particularly longranged response towards an external field Bext [2]. Indeed, the shielding function and IMF are molecular fields which can be used as descriptors of mobile delocalised electrons. Such descriptors are useful tools for the design of new molecules, as for example those containing planar tetracoordinate carbon (ptC) [3]. The longrange character of the shielding function has implications for the computation of NMR parameters, as the shielding tensor at a nucleus may be influenced by longrange contributions of the system. For vander-Waals crystals of aromatic molecules such as benzene or biphenyl the intermolecular contributions become increasingly important, and can account for up to 10% of the total shielding. This claim has been confirmed by a combined experimentaltheoretical study the ^1H NMR chemical shift tensors of biphenyl [4]. In this study, the intermolecular contribution to the shielding tensor is computed by a superposition of individual contributions of those molecules which are located within a sphere of 70 Å around the central molecule. The same methodology has been applied to calculate the shielding tensor of solid benzene [5].

[1] T. Heine et al., Chem. Rev., **2005**, submitted.
[2] G. Merino et al., *Chemistry Eur. J.*, **2004**, *10*, 4367.
[3] G. Merino et al., *J. Am. Chem. Soc.*, **2005**, *126*, 16160.
[4] F. Schönborn et al., *J. Magn. Res.*, **2005**, accepted.
[5] T. Heine et al., in preparation.

Oral contributions **C12**

Semi-empirical exchange-correlation functionals in Kohn-Sham Theory

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We review our previous [1,2] and recent attempts to develop improved semi-empirical GGA and hybrid exchange-correlation functionals. Particular attention is paid to (i) the introduction of terms designed specifically to increase HOMO-LUMO eigenvalue differences, which are important for ensuring high quality NMR shielding constants and related properties; and (ii) the inclusion of a diverse range of properties in the fitting data. Results from the new approximations are compared with those of popular functionals.

References

[1] T. W. Keal and D.J. Tozer, *J. Chem. Phys.*, **2003**, *119*, 3015.
[2] T. W. Keal and D.J. Tozer, *J. Chem. Phys.*, **2004**, *121*, 5654.

Oral contributions **C13**

4-component relativistic TD-DFT: Properties and excited states

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In order for any theoretical model chemistry to give a balanced description of *all* elements of the periodic table, some treatment of relativity is necessary. On the other hand the efficient treatment of electron correlation offered by DFT becomes particularly important for the heavy elements, where correlation effects can be even more important than relativistic effects. It is therefore perhaps somewhat surprising that most of the development and benchmarking of exchange–correlation functionals take place in the realm of the lighter elements; the heaviest element of the widely used G2 set of molecules is chlorine.

Recently 4-component relativistic DFT has been extended to the calculation of electric and molecular properties as well as excited states [1,2]. Static molecular properties can be defined as energy derivatives at zero perturbation strength. A generalization to time-dependent properties is possible with the introduction of the time-averaged quasienergy which also provides a general framework for time-dependent DFT. In the quasienergy formalism (Floquet theory) the initial state dependence of the Runge–Gross theorem is replaced by periodic boundary conditions.

In this contribution I will provide a brief introduction to theory and then discuss some recent applications of 4-component relativistic TD-DFT, including the calculation of the frequency-dependent diatom polarizability as well as lower excited states of the mercury dimer. All calculations have been performed with the DIRAC code (http://dirac.chem.sdu.dk).

[1] J. Gao, W. Liu, B. Song, and C. Liu, *J. Chem. Phys.*, **2004**, *121*, 6658.
[2] P. Salek, T. Helgaker and T. Saue, *Chem. Phys.*, **2005**, *311*, 187.

Oral contributions **C14**

An effective potential for the natural spinorbitals

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It is well know that in the Kohn-Sham (KS) formulation of the density functional theory the variational principle leads to one-electron equations for the KS orbitals with the effective local potential. Until now it has not been clear if an analogous effective potential exists for the natural spinorbitals and how to construct it explicitly. This problem is of great importance for the density matrix functional theory (DMFT), where the total energy is expressed in terms of the one-electron reduced density matrix (1-matrix).

It will be shown how to construct an effective nonlocal potential that, for a given set of the occupation numbers, produces the optimal natural spinorbitals. The problem of its nonuniqueness in the case of degenerate one-matrices will be discussed. The knowledge of the effective potential leads to the one-electron equations for the natural spinorbitals that may be of great value for efficient DMFT calculations. Although the eigenequations for the natural spinorbitals do not produce approximation to the ionization energies, it may be shown that there is a relation between the Lagrange equations for the natural orbitals and the extended Koopmans' theorem. Such a relation furnishes a straightforward way for calculating ionization energies in DMFT. Sample results will be presented for the recently proposed density matrix functionals [2].

[1] K. Pernal, *Phys. Rev. Lett.* (submitted).
[2] O. Gritsenko, K. Pernal, and E.J. Baerends, *J. Chem. Phys.*, (accepted).