Contents

Structure, Energetics, and Thermodynamics of Gold Clusters

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The three most stable isomers of Au$_N$ clusters with N between 2 and 150 have been determined by using a combination of the embeded-atom (EAM), the quasi-Newton, and our own[1–3] Aufbau/Abbau methods for calculation of the total energies, local and global minima, correspondingly. We have employed the Voter-Chen version[4] of the EAM method, which is also parameterised to the dimer properties.

Many structural and energetical descriptors are presented, such as stability and similarity functions, shape analysis, vibrational frequencies per mode, heat capacities, etc.

The Au$_{54}$ icosahedron without a central atom and the Au$_{146}$ decaheron are found to be more stable than the second and third Mackay icosahedra that could be obtained at $N = 55$ and 147, respectively. The three lowest-lying isomers of Au$_{55}$ and Au$_{147}$ are all low-symmetrical structures. Also the clusters with the highest heat capacities in this study are disordered. The radial distributions and the similarity function point to a disordered growth interrupted by the formation of a few islands with decahedral, tetrahedral, and icosahedral symmetry. The shape analysis reveals that most of the highly stable clusters prefer compact shapes, and that the larger clusters with more than 70 atoms have mostly cigar-like shapes. The 'magic' clusters have distinct vibrational peaks, however, the Au$_{19}$ cluster with D$_{5h}$ symmetry has the highest vibrational frequency that equals 315,2 K.

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Fast Non-Iterative Orbital Localization for Large Molecules

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We use the Cholesky decomposition of the AO density matrix to define a new set of occupied molecular orbital coefficients. Analysis of the resulting orbitals ("Cholesky MOs") demonstrates their localized character inherited from the sparsity of the AO density matrix. Comparison with the results of traditional iterative localization schemes[1] shows only minor differences with respect to a number of suitable measures of locality. The procedure devised here for generating orthonormal localized orbitals is non-iterative and may be made linear scaling. Our present implementation scales cubically with a very small prefactor. Nevertheless, the algorithm is much faster than any of the known localization schemes and produces for large molecules orbitals confined in space. Moreover, the σ or π nature of the orbitals is preserved. In addition, since this approach does not require the use of starting orbitals, we expect it to be very useful in local correlation treatments on top of diagonalization-free Hartree-Fock optimization algorithms. We present an application of the Cholesky MOs in screening techniques aimed at linear scaling evaluation of the Exchange Fock matrix using a Cholesky[2] or RI[3] representation of the two electron integrals. Similarly, a sparse density-like matrix can be obtained from the projected atomic orbitals of Saebø and Pulay.[4] As for the occupied space, we demonstrate that starting from this density-like matrix our procedure leads to a set of non-redundant localized orthonormal orbitals spanning the virtual space.

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Rydberg States with Quantum Monte Carlo

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Calculations on Rydberg states were performed for the first time using quantum Monte Carlo (QMC) methods.[1–4] The excitation energies and the appropriate singlet-triplet splittings have been calculated exemplarily for the carbon atom and for carbon monoxide. The considered atomic excitations are from the ^{3}P ground state into the ^{3}P and ^{1}P 2pns Rydberg states with n=3-6, the molecular ones are from the $^1\Sigma$ ground state into the $^1\Sigma$ and $^3\Sigma$ states with the electron configurations $5\sigma 6\sigma$ and $5\sigma 7\sigma$ respectively. Kohn-Sham Slater determinants constructed from open-shell localized Hartree-Fock (OSLHF) orbitals were used for the guide and trial functions.[5, 6]

The variational quantum Monte Carlo (VMC) method leads to accurate excitation energies and singlet-triplet splittings, if the VMC sampling is adapted to the properties of the Rydberg electron. The excitation energies calculated using fixed-node diffusion quantum Monte Carlo (FN-DMC) are close to experiment, but the singlet-triplet splittings have the wrong sign in the case of the carbon atom. A novel approach has been developed for excited state FN-DMC calculations that allows a right description of the singlet-triplet splittings.

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Magnetism and Electronic Structure of hcp Gd and the Gd(0001) Surface

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The localized $4f$ states of Gd represent a challenge for first-principle theory. Our calculations support previous findings that within the local density approximation (LDA) the itinerancy of the $4f$ states is overestimated[1]. In particular, the large density of states at the Fermi energy due to the minority $4f$ electrons is unphysical, and our results show that this is the origin of the incorrect prediction of the antiferromagnetic ground state for hcp Gd by many LDA and generalized gradient approximation (GGA) calculations. We show that different methods of removing these states from the region close to the Fermi energy, e.g. the treatment of the $4f$ electrons as localized core electrons or by using the LDA+U formalism, lead to the prediction of the correct ferromagnetic ground state for the bulk and a ferromagnetically coupled surface layer on the (0001) surface. With these methods ground-state properties like the magnetic moment, the equilibrium lattice constant and surface relaxations can be determined in good agreement with experiment. The energetic position of the surface states of the Gd(0001) surface are compared to experimental data.
Employing the full-potential linearized augmented plane wave (FLAPW) method in the framework of vector-spin density functional theory[2] we use non-collinear calculations to determine the exchange interactions in bulk Gd and on the (0001) surface[3]. Using the exchange constants obtained from these calculations we estimate the Curie temperature of the bulk in the mean field approximation[1,4]. To model the temperature dependence of the electronic structure of the Gd(0001) surface, we performed non-collinear spin-spiral calculations. We calculated the local density of states, which is probed by scanning tunneling spectroscopy (STS) experiments, as function of the spin-spiral q-vector. We find that the spin-splitting of the surface state vanishes but a finite local moment at the Gd surface atoms remains.

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DFT Study of Oligomers of IPR-Violating Fullerenes

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Small fullerenes C_n ($n < 60$) do not conform to the isolated pentagon rule (IPR) and their cage structures are characterised by several neighbouring five-membered rings. As a consequence, the molecules are highly strained and thus more reactive, particularly at the sites where two pentagons meet.

It has been shown through adsorption/desorption experiments, that the behaviour of C_{58} and C_{60} on a HOPG surface is quite different[1,2]. C_{60} forms rather compact islands in accordance with a van-der-Waals type interaction between the fullerene cages. In contrast, C_{58} layers reveal a fractal-like growth and higher thermal stability. This indicates a different aggregation mechanism and/or interaction with the substrate. Considering that HOPG is a very inert surface and that non-IPR fullerenes show high reactivity, it is natural to assume covalent binding of these molecules.

Hence, our goal is to study the reactivity of the fullerenes $C_{50}, C_{52}, \ldots, C_{60}$ using density functional theory. We are interested in the ability of these molecules to form dimers or larger aggregates, as well as the reaction pathways and the properties of the various reaction products. The results of a first approach which takes into account aggregation by means of [2+2] cycloaddition are shown on the poster[3]. In further studies, we investigate as well singly-bonded dimers and the capacity of the monomers to attach hydrogen.

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A Non-Adiabatic Hybrid QM/MM Approach for Studying Photoswitchable Polymers in the Condensed Phase

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Polymeric materials containing the azobenzene moiety are of increasing interest because of their photoswitchable macroscopic properties due to the light-induced E-Z isomerisation of the central nitrogen double bond[1].

Realistic models of such systems are typically too large to be treated by means of pure ab initio molecular dynamics (AIMD). Classical atomic force fields, on the other hand, are not parametrized to deal with photoexcitations. The challenge to theory is to embed microscopic quantum mechanical methods to investigate the photoinduced reaction in the excited electronic state into large scale atomic force field methods for studying polymers.

We combine the ROKS-DFT based Surface Hopping method[2] for non-adiabatic excited state AIMD with the hybrid quantum–classical QM/MM approach[3] implemented in the CPMD Package[4]. This extends the applicability of non-adiabatic AIMD to large condensed phase systems consisting of several thousands of atoms.

Based on purely *ab initio* ground state Car-Parrinello molecular dynamcis, a force field description of the fundamental azobenzene building block has been derived. As a first realistic test case, we study the photoisomerisation of a single azobenzene chromophore in bulk liquid azobenzene at 400 K.

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A Highly Accurate and Optimal Method to Calculate Long Range Interactions

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The calculation of Coulomb potentials is a very important task in molecular dynamics simulations of charged or polar systems. Due to the long ranged nature of the electrostatic potential the use of a cut-off radius to reduce the computational complexity may result in severe errors in the static structure and dynamics. A full summation over all interacting particles has a complexity of $\mathcal{O}(N^2)$, which is computationally too demanding.

For both open and periodic boundary conditions there exist algorithms that reduce the algorithmic complexity. There are both mesh-free approaches like the Fast Multipole Method (FMM)[4] as well as mesh-based algorithms like the Particle-Particle-Particle-Mesh (P3M) method[2] or the Particle Mesh Ewald (PME) method[1]. The mesh-based methods make use of the fact that calculating the potential of a given charge density is equivalent to solving Poisson's equation with this charge density on the right hand side of the PDE. So multigrid methods can be used for the calculation of the potential in a molecular dynamics simulation. This approach has been chosen for systems with periodic boundary conditions by Füllenbach[3]. There the P3M method is modified to use another splitting of the potential and multigrid is used for the solution of the PDE. A different approach has been chosen for the multigrid method for open boundaries by Sutmann and Steffen[5]: Here a discrete Green's function is being used to eliminate the influence of the particles in the near field to calculate the force and energy due to near particles using direct summation.

The present work presents ingredients for highly accurate multigrid-based, and thus optimal, methods for the calculation of long ranged interactions. The main contribution presented here is the use of body-centered B-spline densities for the splitting of the potential in a short and a long ranged part. In contrast to the widely used splitting-functions these densities avoid charge assignment to the grid and therefore strongly reduce discretization errors. The combination with high-order discretization of the PDE[6] yields in a novel method for the computation of the electrostatic force and energy. This method can be used with either periodic or open boundary conditions imposing Dirichlet boundary conditions calculated with e.g. a multipole expansion as in the work of Sutmann and Steffen[5].

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Transport in Nanowires with Noncollinear Magnetic Order

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Metal nanowires are very attractive systems to study the influence of low dimensionality on the magnetic properties. The results of recent experiments indicate the existence of noncollinear magnetic order in metallic nanowires[1,2]. However, for systems with a large number of magnetic degrees of freedom direct unambiguous measurements of the magnetic configuration without preliminary model considerations are impossible. In this respect the predictive role of first-principle calculations is of great importance. We extended the screened Korringa-Kohn-Rostoker (KKR) multiple scattering method based on density functional theory to noncollinear magnetic systems. Both the diagonal and off-diagonal elements of the spin density matrix are calculated to obtain the orientation of the local moments.

We present *ab initio* calculations of the transport properties of metallic atomic-sized nanowires. The nanowires consist of atomic Co chains suspended between two semi-infinite leads of the same material. We used the first principle screened KKR method to calculate the electronic properties of the systems, treating the leads and the atomic contact on the same footing without adjustable parameters. In addition, we calculate the conductance using the Landauer approach in the formulation of Baranger and Stone[3] generalized for noncollinear magnetic structures. It is shown that the noncollinear magnetic order has considerable effect on the transport properties of the nanowires.

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Effects of Substitution and Solvation on Excited State Tautomerism and Nonradiative Decay of Guanine

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Tautomerisation of guanine (G) in the first excited singlet state, S_1, has been investigated by means of Car-Parrinello molecular dynamics both in the gas phase and in aqueous solution. The excited state electronic structure problem were solved using the restricted open-shell Kohn-Sham method [1, 2]. In the gas phase, N7H-keto was found to be the most stable tautomer in the excited state [3]. Due to the stability of the investigated tautomers with respect to excited state proton transfer both in the gas phase and in aqueous solution during the time span of our simulation, we made use of a coordination constraint technique [4] in order to enforce deprotonation of the N7H-enol G hydroxy group, being the most acidic site of the molecule. At a specific O–H distance of this group, a change in character of the excited state occurred from $\pi \rightarrow \pi^*$ to $\pi \rightarrow \sigma^*$ type. The σ^* orbital was delocalised in the aqueous environment. After reprotonation of G at N1 position leading to the N7H-keto tautomer the excited state switched back to a $\pi \rightarrow \pi^*$ type localised at the solute. The results in aqueous solution were compared with calculations in the gas phase as well as in microsolvated environment. Nonradiative decay mechanisms and excited state lifetimes of different keto-G tautomers in the gas phase [5, 6] and in aqueous solution [7] have been investigated using a nonadiabatic Car-Parrinello surface hopping technique [8]. The biologically relevant N9-keto tautomers were observed to have, in general, shorter lifetimes compared to other G tautomers. The influence of different substituents, e.g. Me and F, at N9 with respect to structural and electronic properties in the S_1 excited state have been investigated.

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Parallel Implementation of the Recursive Green's Function Method

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A parallel algorithm for the implementation of the recursive Green's function technique[1], which is extensively applied in quantum transport formalism[2], will be presented. The algorithm goes beyond the (straightforward) parallelization with respect to the external parameters of the scattering problem, such as e.g. Fermi energy or magnetic field, and proceeds with the scatterer's domain decomposition in internal independent domains which are linked via interface blocks. The latter are reordered and collected in a virtual block and then a parallel Gaussian elimination is applied in order to calculate the Schur's complement block in the form of distributed blocks among the processors. If the method is applied recursively, thereby eliminating the processors cyclically, it is possible to arrive at a Schur's complement block of small size and compute the desired block of the Green's function matrix directly. The numerical complexity due to the longitudinal dimension of the scatterer scales linearly with the number of processors, though, the computational cost due to the processors' cyclic reduction, establishes a bottleneck to achieve efficiency 100%. The presented algorithm will be accompanied by a performance analysis at hand of one numerical benchmark, in which the dominant sources of computational load and parallel overhead as well as their competitive role in the efficiency of the algorithm will be demonstrated.

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Investigation of the Local Density Inhomogeneities and Dynamics in Neat Supercritical Fluids using MD Simulation Techniques: Comparison between Hydrogen- and Non Hydrogen-Bonded Fluids

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The local density inhomogeneities in neat Supercritical Fluids (SCFs) [1] were investigated via Canonical Molecular Dynamics (MD) simulations. The selected systems under investigation were a polar, hydrogen-bonded SC fluid (methanol) and a non-hydrogen bonded one (carbon dioxide). The *effective* local densities [2,3], as well as the local density augmentation and enhancement factors for both systems were calculated for several thermodynamic state points along an isotherm close to the critical temperature of each system. The results obtained, reveal a strong influence of the polarity and hydrogen bonds in the intensity of the calculated local density augmentation in each fluid. Furthermore, in both cases the values of the calculated local density augmentation are maximized in the region near 0.7 ρ_c (critical density), an observation that is in agreement with previous studies reported in the literature [1,3]. In addition, the local density dynamics of each fluid were investigated and the calculation of the appropriate time correlation functions reveals that the bulk-density dependence of the local density reorganization times is very sensitive to the size of the local region. The results obtained have been found to be in accordance with previous studies [4]. Finally, the single reorientational correlation times were also investigated. The corresponding reorientational correlation times are in good agreement with experiment [5] and their bulk-density dependence indicates a possible relation between the single-molecule and local environment dynamics.

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Molecular Dynamics Simulation of Liquid Crystalline Systems

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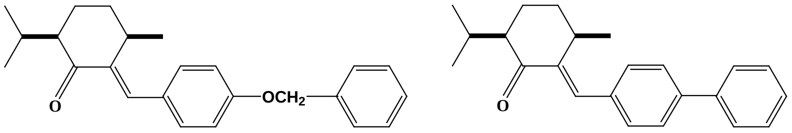
Liquid crystals (LC) are fascinating materials both from a fundamental and applied point of view. Despite its key importance for the synthesis of LC materials having optimal properties for specific technological applications, the relationship of macroscopic properties to molecular structure and microscopic organization was studied insufficiently up to now. The central aims of this work are to develop and validate the computational infrastructure for achieving realistic modeling of LC materials, and to investigate the mutual influence of LC environment and dopants in LC compositions on each other.

The liquid crystalline nematic phase - 4-n-pentyl-4'-cyanobiphenyl (5CB), and two different solutions of two chiral dopants (CDs) (see Fig. 1) with 2-arylidene-p-menthan-3-one skeleton in 5CB at low CD's concentrations - 1% of CD and 99% of 5CB are investigated. Chiral compounds of this series have been shown to induce strong helicity in achiral nematic systems[1]. The investigations are carried out using classical molecular dynamics (MD) technique. In order to obtain unknown parameters for MD simulation (Fourier coefficients for specified dihedral angles, partial charges) ab initio quantum chemistry electronic structure calculations are performed. Simulation of liquid crystalline systems is carried out using parallel version of MD program[2] on parallel computer cluster of Petrodvorets Telecommunication center of Saint-Petersburg State University.



CD1 **CD2**

Figure 1. Chemical structure of CDs

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Ab Initio Study of Magnesium Alanate $Mg(AlH_4)_2$

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Hydrogen, which is a great and clean energy carrier, promises to be tomorrow's fuel for vehicles and other mobile devices. Storing hydrogen in a safe and sufficiently dense form is one of the main problems. Using metals for hydrogen storage is an option since hydrogen dissolves in large quantities in atomic form inside the crystal lattice of many bulk metals. Light-weight alkali and alkaline earth aluminium hydrides are potential candidates as hydrogen storage materials. Magnesium alanate $Mg(AlH_4)_2$ has recently raised interest as a potential hydrogen storage material. We apply *ab initio* calculations to characterize structural, electronic and energetic properties of $Mg(AlH_4)_2$. Geometry optimization and energy calculations are done using density functional theory within the generalized gradient approximation (GGA) and electronic structure is studied using both DFT and quasi-particle calculations at the GW level. $Mg(AlH_4)_2$ has a fundamental band gap of 6.5eV and classified as a large band gap insulator. The hydrogen atoms are covalently bonded to Al atoms inside AlH_4 complexes, and their states dominate both the valence and the conduction bands. On the basis of total energies, the formation enthalpy of $Mg(AlH_4)_2$ is 0.17 eV/H_2 (at T = 0). The enthalpy of the dehydrogenation reaction that is responsible for the actual hydrogen production (Eq.1) is close to zero, which would indicate that magnesium alanate is not sufficiently stable at the conditions required for applications.

$$\mathrm{Mg(AlH_4)_2} \rightarrow \mathrm{MgH_2} + 2\mathrm{Al} + 3\mathrm{H_2}(g) \qquad (1)$$

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All-Electron *GW* Approximation in the Augmented Plane Wave Basis-Set Limit

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The *GW* approximation for the electronic self-energy is known to yield quasiparticle band structures in much better agreement with experimental measurements than the local density approximation (LDA) for a large class of materials. However, almost all actual implementations so far are based on the plane wave pseudopotential approach, which effectively restricts applications to simple metals and sp-bonded semiconductors. In order to overcome this limitation, we have developed an alternative implementation within the all-electron full-potential linearised augmented plane wave (FLAPW) method, which is also applicable to systems with localised electrons like transition metals or rare-earth elements. Additional simplifications, such as plasmon-pole models, are avoided.

While the FLAPW method treats the core electrons explicitly and does not suffer from the uncontrolled pseudisation of the wave functions, another source of errors resulting from the linearisation is frequently overlooked. This arises because the radial wave functions in the muffin-tin spheres are expanded around fixed reference energies. Irrelevant for the valence bands in density-functional theory, it cannot be ignored in the *GW* approximation, where unoccupied states more than 100 eV above the Fermi level must typically be included in the self-energy to guarantee converged results. To eliminate this error, we have improved the FLAPW basis set by including second and higher energy derivatives of solutions to the radial scalar-relativistic Dirac equation in the form of local orbitals. With this modification, we show that the eigenstates converge systematically towards the exact APW spectrum, which contains no linearisation errors.

This careful approach finally allows us to comment on the controversial apparent discrepancy between pseudopotential and all-electron *GW* results addressed in several recent studies.[1,2] For the example of silicon, we demonstrate that the inclusion of a much larger number of unoccupied states and the elimination of linearisation errors both contribute to an increase of the band gap. While a certain deviation from pseudopotential calculations remains, it is smaller than previously claimed, and both results lie in comparable proximity to the experimental value.

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Methane Chemisorption on Ni(111): Dissociation Energetics and Vibrational Analysis

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Steam reforming of methane (CH_4) is the most common method employed in hydrogen production[1]. To enhance its yield, theoretical understanding of the rate-limiting step (the dissociative chemisorption of methane into adsorbed CH_3 and H) and the effect of vibrational pre-excitation of the different vibrational modes of CH_4 on this step is necessary. It is the first time that nudged elastic band[2] method has been applied to find the reaction path and transition states for this reaction and allow the vibrational analysis of the methane. This analysis shows the involvement of vibrational coordinates as suggested by experiments[3,4]. A potential energy surface (PES) is being developed that depends on all fifteen degrees of freedom of CH_4. The PES is constructed based on the supercell approach of planewave-pseudopotential density functional theory at the generalized gradient approximation level of theory, using the RPBE functional[5]. The PES will be fitted with a modified Shepard interpolation scheme[6]. The PES will be used in classical dynamics calculations and quantum dynamics calculations using the multi-configuration time dependent Hartree[7] method to compute reaction probabilities.

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The Role of Water in the Initial Steps of Methanol Oxidation on Pt(211)

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In direct methanol fuel cells (DMFC) the hydrogen atoms are produced 'in situ' by dissociation of methanol on precious metal catalysts (Pt, Pt/Ru). Thereby the abstraction of the first hydrogen atom achieved via the cleavage of one CH-bond is generally considered to be the rate limiting step of dissociative methanol adsorption on the catalyst surface.
We present first results of quantum-mechanical density functional theory calculations of the initial steps of methanol oxidation in aqueous solution on the stepped (211) face of a platinum single crystal. Water turned out to play an important role in the reaction pathway as found from energy minimization calculations: A coadsorbed water molecule promotes the adsorption of a methanol molecule close to the surface by formation of a hydrogen bond (experimental findings of a concerted mechanism of methanol adsorption were reported elsewhere[1,2]). The methanol molecule is then adsorbed via a carbon-hydrogen atom preparing the scission of the CH-bond as the first reaction step. The decisive impulse for the cleavage stems from neighboring water molecules in the aqueous phase, establishing a hydrogen bond via the OH-group of methanol. These interactions entail an increase of the C-H bond length pointing towards the metal surface as well as a decrease of the platinum-hydrogen and the carbon-oxygen distance, hinting towards the scission of the corresponding carbon-hydrogen bond, which clearly differs from the reaction pathway in gas phase[3]. Employing a positively charged platinum surface enhances the above described effects. The reported findings are in line with a previously observed reaction mechanism of methanol on Pt(111) from *ab initio* molecular dynamics simulations[4].

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Conformational Analysis of 3-Aminomethylene-2,4-Pentandione and Its N-Methyl Derivatives

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The purpose of this work is the conformational study and interpretation of vibrational spectra of 3-aminomethylene-2,4-pentandione aits N-methyl derivatives. These compounds belong to the so-called push-pull olefines, which are often used as materials for numerous organic synthesis in pharmacy, in the branch of polymers, dyes etc. In spite of this wide utilization, no interpretation of vibrational spectra have been done, or it was restricted only on the description of vibrational peaks of some groups. This work contains quantum chemistry calculations on the one hand and vibrational and NMR spectra on the other hand. Theoretical calculations were realized at AM1, MP2 and B3LYP levels. Studies of similar aminodiesters show, that these compounds exist in solid state and in solution with polar solvent in EZ-conformation. In solution with nonpolar solvent, ZZ-conformer was observed too. Our task was to verify this statement or to disprove it.

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Ab Initio Investigation of Structural and Magnetic Properties of Nanosized Fe-Clusters

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We report the structural and magnetic properties of iron clusters of icosahedral, cuboctahedral and Bain-transformed[1] cuboctahedral shape with up to 309 atoms. The results are obtained within the framework of Density Functional Theory including full structural relaxation using the Vienna ab Initio Simulation Package (VASP)[2,3]. We find that from 147 atoms on the bcc-like structures have the lowest energy while there is an second minimum for a closed packed structure which is only slightly higher in energy. This structure appears to be shell-wise transformed along the Mackay[4] path with the inner shells being closer to the cuboctahedral structure and the outer shells being more icosahedral. For the bcc structures the moments agree well with experimental data[5], while in the other case the magnetic moment is reduced due to antiferromagnetic ordering. The structural properties are contrasted with the results of molecular dynamics simulations of Lennard-Jones particles of different sizes.

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Fully Relativistic Four-Component Dirac-Hartree-Fock Calculations of the Magnetic Properties of Xenon Dimer

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As an extension of our non-relativistic study of the magnetic properties of xenon dimer,[1] the nuclear shielding and nuclear quadrupole coupling tensors are treated within the fully relativistic four-component Dirac-Hartree-Fock (DHF) scheme, principally to estimate the remaining relativistic effect via binary chemical shift on the second virial coefficient of the nuclear shielding of xenon dimer. This is the experimentally best-characterized intermolecular interaction effect in nuclear magnetic resonance (NMR). Secondly, the properties, the binary chemical shift, the anisotropy of the shielding tensor and the nuclear quadrupole coupling, are calculated as a function of the internuclear distance. These properties can be parametrized and used in future studies concerning the pairwise additivity of the interaction effects on magnetic properties of gaseous xenon as well as a molecular dynamics approach to the spin-lattice relaxation in the NMR experiment.

The basis set used in the calculations is constructed from the dual family basis set of Fægri,[2] and expanded considerably by, firstly, adding a series tight and diffuse functions for each angular momentum quantum number l-based sets and, secondly, adding a whole set of diffuse functions simultaneously. Further techniques of basis set construction include the freezing of the small component basis set. Initial work shows that basis set demands, especially for the nuclear shielding tensor, are great, particularly in the diffuse area of basis functions. Preliminary results with DHF theory for the magnetic properties using a large, however not yet quite converged basis set, are illustrated in the poster.

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A Comprehensive DFT Study of the Nitric Oxide Assisted Nitrous Oxide Decomposition over Fe-ZSM-5

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Most catalytic systems active for nitrous oxide (N_2O) decomposition are inhibited by nitric oxide (NO). In contrast, for iron zeolite catalysts, it has been reported that nitric oxide significantly enhances the N_2O decomposition rate. The mechanism that causes this enhancement is yet unknown.

In the present work, the NO-assisted N_2O decomposition over iron zeolites was studied on a molecular level using density functional theory (DFT). For a reaction network consisting of about 100 elementary reactions the geometries and energies of potential energy minima as well as transition states were determined on different spin surfaces. Transition states were localized using a combination of interpolation[1] and local methods[2]. Transition state theory was then used to calculate all relevant reaction rate constants. Using this molecular information the mechanism of the NO-assisted N_2O decomposition was elucidated.

Former DFT-calculations for the N_2O decomposition on single iron sites in Fe-ZSM-5 in the absence of NO have shown that small amounts of water (in the ppb to ppm range) in the incoming gas stream poison active iron sites at low temperatures[3,4]. Therefore, in the absence of NO, N_2O can be decomposed only at temperatures above 700 K where water does not adsorb on active iron sites.

In the present work the influence of temperature and partial pressures of NO and N_2O on the steady state surface composition was investigated. It is demonstrated that NO reduces the amount of poisoned sites of type $Z^-[Fe(OH)_2]^+$ (Z represents the zeolite lattice) by forming $Z^-[FeOH]^+$ sites which are active for N_2O decomposition. At lower temperatures the $Z^-[FeOH]^+$ sites are formed faster and to a larger amount than the active iron oxide site $Z^-[FeO]^+$ responsible for N_2O decomposition in the absence of NO[3,4]. Active $Z^-[FeOH]^+$ species displace inactive $Z^-[Fe(OH)_2]^+$ sites at lower temperatures. This result explains the accelerating effect of NO on the N_2O decomposition rate. At a temperature of 600 K the decomposition rate is calculated to increase by a factor of 93 if NO is present. At higher temperatures water desorbs from $Z^-[Fe(OH)_2]^+$ sites such that the main active surface species are $Z^-[FeO]^+$ and $Z^-[FeO_2]^+$ leading to the previously reported reaction mechanism[3,4].

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The Role of Orbitals in $LaTiO_3$ and VO_2, Studied by X-Ray Absorption Spectroscopy and Cluster Calculations

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We have used x-ray absorption spectroscopy and full multiplet configuration interaction cluster calculations in order to obtain information about the orbital degrees of freedom in $LaTiO_3$ and the orbital occupation at the metal insulator transition of VO_2. X-ray absorption at the $L_{2,3}$ edge of transition metals ($2p$ to $3d$ transition) is a sensitive local probe. These spectra show, due to the large $2p$ - $3d$ Coulomb interaction many fine multiplets,[1,2] therefor cluster calculations are the ideal tool to interpretate these spectra.

For VO_2 we determined quantitatively the orbital polarizations and found direct experimental evidence for an orbital switching in the V $3d$ states across the metal-insulator transition. These results strongly suggest that, in going from the metallic to the insulating state, the orbital occupation changes in a manner that charge fluctuations and effective bandwidths are reduced, that the system becomes more one dimensional and more susceptible to a Peierls-like transition, and that the required massive orbital switching can only be made if the system is close to a Mott insulating regime.[3]

In $LaTiO_3$ we show that the orbital momentum is strongly reduced from its ionic value, both below and above the Néel temperature. By comparing Ti $L_{2,3}$ x-ray absorption spectra with cluster calculations including different *ab-inito* local non-cubic crystal fields, we found that the crystal-field splitting in the t_{2g} subshell is about 0.12-0.30 eV. This large splitting does not facilitate the formation of an orbital liquid.[4]

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Influence of the Monomer Excess on the Structure and Properties of Polyaniline Oligomers

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Polyaniline is among the most intensely investigated polymers due to its exceptional properties affording its current and potential applications[1,2]. The structure and energy spectra of isolated oligomers and infinite chains in different oxidation states and degrees of protonation have been discussed at length from experimental and theoretical perspective. The reaction environment effect, however, has received less attention and particularly the influence of monomer excess has been completely neglected in theoretical studies. Experimental measurements show that residual aniline is always detected in emeraldine samples obtained at low pH. Upon addition of oxidant to emeraldine PANI samples, post-polymerization due to the presence of excess monomers occurs. This is an indication for the formation of aniline-PANI complexes in the reaction medium. The presence of aniline monomers should affect the PANI chains arrangement and optical/conducting characteristics. Therefore, model clusters of aniline with neutral or singly protonated emeraldine tetramers in explicit water medium and periodic boundary conditions are addressed in this paper using a Monte Carlo/AMBER96/AM1 computational protocol to simulate the absorption spectra[3]. The monomer impact on the structure, energy characteristics and UV/VIS spectra of the polymer is discussed. Examination of the energy of the studied systems shows that the presence of aniline in the reaction medium will facilitate protonation of PANI in the emeraldine oxidation state. The interaction with aniline always leads to strong bathochromic shift of the longest-wavelength visible transition but it remains the most intensive one in the visible spectrum. In one of the structures studied, even an intermolecular CT transition from aniline to the tetramer emerges. The latter can be considered as a 'fingerprint' for the presence of aniline in partially protonated PANI samples.

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Applications of Orbital-Free Frozen-Density Embedding

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We present two different applications of the orbital-free frozen-density embedding scheme by Wesolowski and coworkers[1] within density-functional theory (DFT).

First, we apply the embedding scheme to the calculation of the induced dipole moments in the weakly interacting van der Waals-complexes $CO_2 \cdots X$ (X = He, Ne, Ar, Kr, Xe, Hg) to test its performance for a simple test case.[2] The accuracy of the embedding calculations is assessed by comparing to the results of supermolecular DFT calculations. It is found that in supermolecular DFT calculations, different common approximations to the exchange-correlation potential are not able to describe the induced dipole moments correctly and the reasons for this failure are analyzed. It is shown that the orbital-free embedding scheme is a useful tool for applying different approximations to the exchange-correlation potential in different subsystems and that a physically guided choice of approximations for the different subsystems improves the calculated dipole moments significantly.

As a second application,[3] we use the frozen-density embedding scheme for modeling solvent effects and compare it to purely electrostatic solvent models, namely the discrete reaction field model (DRF) — a QM/MM scheme using a polarizable force field — and the COSMO continuum solvation model. As a model system, a water molecule in a solvent shell consisting of 127 water molecules is investigated. The comparison is done for both ground-state properties (dipole and quadrupole moments) and response properties (electronic excitation energies and polarizabilities).

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First-Principles Study of Nano-Scale Molecular and Biological Systems

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An effective elongation method has been developed to study the electron transport in nanoelectronic devices at hybrid density functional theory level. It enables to study electronic structures and transportation properties of a 40 nm long self-assembled conjugated polymer junction, a 21 nm long single-walled carbon nanotubes (SWCNT), and a 60-base-pairs DNA molecule. This is for the first time that a finite system consisting of 10,000 electrons has been described at such a sophisticated level.

Our simulations for polymer, SWCNT and DNA devices are all in very good agreement with experimental results available[1–4]. This allows us to conclude that the electron transport in sub-20nm long SWCNT and short DNA molecules is dominated by the coherent scattering through the delocalized unoccupied states. The derived length dependence of coherent electron transport in these nanostuctured systems will be useful for the future experiments. Moreover, some unexpected behaviors of these devices have also been revealed.

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Low–Energy Defects on ZnO Surfaces and Their Characterization by STM Image Calculations

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Atomic defects on surfaces have been found in many cases as the active sites for chemical reactions. Identification of the dominant surface defects is therefore essential for microscopic understanding of the activity of a catalyst on its most common surfaces. Scanning tunneling microscopy (STM) technique is an ideal tool for this task, however the interpretation of STM experiments in terms of atomic structure and chemical identity if often difficult. Using density functional theory (DFT) in combination with a thermodynamic formalism we have calculated the formation energy for the most simple atomic defects on the ZnO($10\bar{1}0$) surface as a function of the redox properties of a surrounding gas phase. To give guidelines on how these defects may appear in an STM experiment we have calculated their STM images together with selected I(V)–profiles (scanning tunneling spectroscopy – STS) using our recent implementation of the Bardeens tunneling formula into the Car–Parrinello Molecular Dynamics (CPMD) code. We find significant differences in the tunneling properties between the ideal surface and O–, Zn–, and ZnO–vacancies, ranging from increases/decreases in the tunneling current by an order of magnitude to contrast reversal which may allow to identify these defects in STM measurements.

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Density Functional Study of Ion Hydration for the Alkali Metal Ions (Li^+,Na^+,K^+) and the Halide Ions (F^-,Br^-,Cl^-)

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We performed first principles Density Functional calculations to study the effect of monovalent ions M^+ (M=Li,Na,K) and A^- (A=F,Cl,Br) in water with the aim of characterizing the local molecular properties of hydration. For this reason, several ion-water clusters, up to five or six water molecules were considered; such structures were optimized and the Wannier analysis was then applied to determine the average molecular dipole moment of water. We found that with an increasing number of water molecules, the polarisation of the water molecules is determined by the water-water interaction rather than the water-ion interaction, as one would intuitively expect. These results are consistent with those obtained in previous Density Functional calculations and with other results obtained by employing classical polarizable water models. The main message of this work is that as one increases the number of water molecules the average dipole moment of all water molecules and of ones in the first shell tends to the same value as the average of a similar sized cluster. This implies that the use of non-polarisable classical models of water is valid.

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Orbital Functionals in Spin and Current Density Functional Theory

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In density functional theory (DFT), explicitly orbital-dependent approximations to the exchange-correlation energy can be treated with the Optimized Effective Potential (OEP) method.[1] Here we present two extensions of the OEP method to 1) non-collinear magnetizations in spin-DFT and 2) current-DFT which (unlike spin-DFT) also takes the coupling of magnetic fields to the orbital degrees of freedom into account.

In non-collinear spin-DFT, the exchange-correlation energy becomes a functional of two-component spinor orbitals. We derive the corresponding OEP equations for the exchange-correlation scalar potential and magnetic field.[2] The solution of these equations for a magnetically frustrated Cr monolayer shows how intra-atomic non-collinearity may be underestimated when using local functionals.

In current-DFT, in addition to the density and the magnetization density, the paramagnetic current also becomes a fundamental variable.[3,4] Electron-gas-based (LDA-type) functionals of current-DFT exhibit derivative discontinuities as a function of the magnetic field whenever a new Landau level is occupied which makes them difficult to use in practice. On the other hand, the appearance of Landau levels intrinsically is an orbital effect and therfore it is particularly appealing to use orbital-dependent functionals. We derive the OEP equations of current-DFT and present a numerically tractable scheme for their solution within a KLI-type approximation. Some preliminary numerical results, in exact exchange-only approximation, for open-shell atoms and quantum dots in magnetic fields will be discussed.

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Polarization Damping in Ion-Water Dimers

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The inclusion of polarization in classical Molecular Dynamics simulations seems indispensable to simulate heterogeneous environments[1,2]. We have developed new polarizable models which reproduce the ab initio results for the induced dipole moment of selected dimers[3,4]. They include a substantial nonlinear damping (at separations corresponding to the first hydration shell) due to electron cloud repulsion. These short range effects are tackled with a new implementation of the Thole damping method[5,6].

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Infrared Spectra of Protonated Water Clusters in Bacteriorhodopsin: Identifying the Release Group by QM/MM Molecular Dynamics

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The nature of the so called proton release group (RX) in the photo-driven proton pump Bacteriorhodopsin (BR) has been a long standing puzzle. Recent FTIR measurements[1] in combination with our findings[2] suggest that the excess proton, which is released from RX to the extracellular membrane surface during the photocycle, is stored within an internal water cluster. In particular, our computed FTIR spectra point toward a Zundel like proton solvation complex.

We present our latest investigations of this protonated water cluster in the BR ground state by QM/MM molecular dynamics simulations, as implemented in the CPMD/Gromos interface[3]. We address the question of hydrogen bonding dynamics and the role of a possible protonation of the nearby Glutamic acids E194 and E204, which have been formerly suggested to be candidates for RX.

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Strong Metal-Support Interaction in Cu/ZnO Catalysts: Insights from First-Principles Calculations

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Oxide surfaces and oxide supported metal particles are important catalysts for many industrial applications. In some cases, for example for Cu/ZnO, the oxides are not just carriers for the metal particles but strongly modify their chemical properties and catalytic activity. Experimental studies have provided evidence that this "strong metal–support interaction" is caused by reversible and dynamical changes in the structure and composition of the metal clusters in response to the redox properties of the surrounding gas phase: In an oxidizing atmosphere the metal clusters are more spherical-like whereas under reducing conditions the metal particles start to wet the surface and reduced oxide species are incorporated into the clusters.

The driving force for such dynamical changes in the morphology of the catalyst surfaces has been investigated for the specific example of Cu supported on ZnO by combining DFT calculations with a thermodynamic description of the Cu/ZnO interface. Assuming that the catalyst surfaces are in thermodynamic equilibrium with an ambient gas phase, low-energy structures of small Cu clusters on the ZnO surfaces with varying structure and composition have been determined as a function of the oxygen and hydrogen chemical potential. In particular for the polar ZnO surfaces it is found that the amount of adsorbed hydrogen and of oxygen vacancies strongly depends on the environment [1], which in turn significantly modifies the interaction of the surfaces with Cu [2]. Therefore, the polar ZnO surfaces allow for a wealth of different Cu/ZnO surface structures depending on parameters such as coverage, defects and coadsorbates, in agreement with the experimental observations.

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First-Principles DFT Calculations of Electron Transfer Rates in Azurin Dimers

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The modern research in electronic technology envisages exploiting the intrinsic functions of biological systems to realize nanoelectronic components. In particular, the blue copper protein azurin (Az) (see Fig. 1a), performing electron transfer in different biochemical processes, seems to be a good candidate for the implementation of biomolecular electronic devices. The increasing availability of both electron transfer kinetic data and powerful computational tools enabled a number of comparisons between theory and experiment[1].

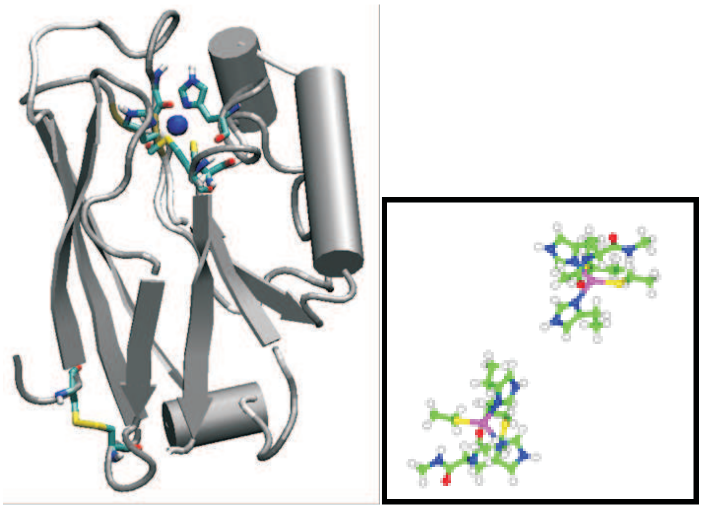

Figure 1. (a, left) Tertiary structure of Az. (b, right) Largest model of the Az dimer investigated in Ref. 3, in a ball-and-stick representation. The two molecules dock through their hydrophobic patches.

In particular, since electron transfer matrix elements (also called transfer integrals) play a key role in determining the rate constants of many biochemical redox processes, there have been considerable efforts to compute them through several quantum chemical methods[2]. In this context, we have conceived and implemented a new method to calculate transfer integrals between molecular sites, exploiting few quantities derived from DFT electronic structure computations[3]. The method uses a complete multi-electron scheme, thus including electronic relaxation effects. Moreover, it does not require the knowledge of the exact transition state coordinate and makes no use of empirical parameters. The computed electronic couplings can then be combined with estimates for the reorganization energy through mixed atomistic/continuum simulations, to evaluate the transfer rates (Marcus-Hush- Jortner theory) that are measured in kinetic experiments: the latter are the basis to interpret electrontransfer mechanisms.

We have applied our approach to the study of electron self-exchange processes in the encounter complex formed by one reduced and one oxidized Az. For our plane wave electronic structure calculations (realized through the PWSCF code[4]) we used the same geometry as in the crystal structure, after an accurate pruning of the Az proteins (Fig. 1b). The electron transfer rates obtained by the proposed method have been compared with the results of previously suggested computational techniques and with experiment-fitted models, showing a remarkable accordance with them. In addition, we have found the expected exponential decay of electron transfer rates with respect to the distance between the redox sites (Fig. 2). Thus, our method is a promising framework for the predictive investigation of charge transfer mechanisms in biochemical environments.

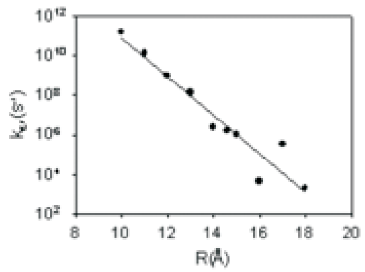

Figure 2. Dependence of the electron transfer rates on the copper-to-copper distances R. The regression line is superimposed to data-points.

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Computational DFT Study of the Non-Heme Iron Center of Photosystem II

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Photosystem II is large membrane-bound molecular complex[1] utilized by higher plants, algae and cyanobacteria for trapping the light energy by the means of rapid electron transfer (ET). The non-heme iron center is located between two quinone molecules: Q_a and the terminal electron acceptor, Q_b. However, its role in the electron transfer process remains unclear[2,3]. Experimental studies suggest that, unlike in bacterial reaction centers, in PS II the ET from Q_a to Q_b could be modulated by binding of various ligands to the iron cation[4].

We present a quantum chemical (Density functional theory) investigation for molecular models of the iron center. Some initial results for electronic structure of the iron center are discussed. Calculations on the small model system predict the high spin state to be the ground state.

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The Mechanism of the Gold(I) Catalyzed Rautenstrauch Rearrangement: A Center-to Helix-to Center Chirality Transfer

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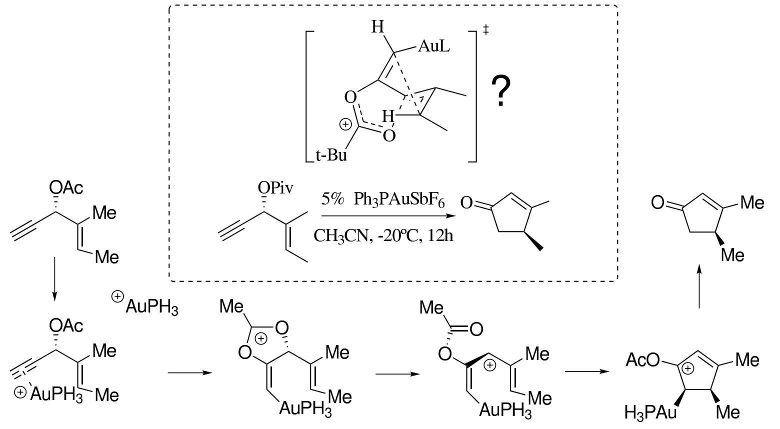
Recently, a gold(I) catalyzed variant[1] of the Rautenstrauch reaction[2] has been described, which displays a remarkable center-to-center chirality transfer.

In this work, we have used DFT (B3LYP/6-31G*, SDD for Au) to study the mechanism of the gold(I) catalyzed Rautenstrauch rearrangement of (*E*)-1-ethynyl-2-methyl-but-2-en-yl acetate to 3,4-dimethyl-cyclopent-2-enone, in order to determine the origin of the experimentally observed stereoselectivity.

Our results indicate that the C–C bond formation event follows the Au(I)-induced acetyl transfer to the vicinal C_{sp^2} atom and that the chiral information is preserved on the helicity of the pentadienyl cation intermediate.

For this center-to helix-to center chirality transfer to be efficient, both the helix interconversion and the pivaloyl rotation should be disfavored relative to cyclization, as calculations predict.



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Magnetic Order of *3d* Transition-Metal Adsorbates on W(001) Surface

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Recently systematic first-principle study by Ferriani[1] found that V, Cr and Mn monolayers on the W(001) surface exhibit a ferromagnetic ground state, while Fe and Co favor the antiferromagnetic state. This surprising trend in magnetic ordering of $3d$ transition-metal monolayers on W(100) is in contradiction to that what was observed for other substrates, e.g. Cu(100), Pd(100). We continue the theoretical investigation of above mentioned systems and concentrate our attention on the ground state for the submonolayer coverages and binary alloy monolayers.

We employ the tight-binding linear muffin-tin orbital method (TB-LMTO) combined with the surface Green function approach and the coherent potential approximation to study the random systems. The effects of dipole barrier are included in the present TB-LMTO formalism[2]. We investigated the stability of different magnetic configurations (FM, AFM, DLM) and estimated the concentrations at which a transition between two magnetic orders occurs. Full potential linearized augmented plane wave method (FLAPW) is applied to find the relaxed geometry of the surfaces and to check the results. We discuss in more details the role of disorder as well as the influence of top monolayer relaxations on the phase transitions.

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Cu(I) Sites in Faujasite and Their Interactions with CO Molecule - Theoretical Studies

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Copper exchanged zeolites have been the object of many studies since an unusually high activity of Cu(I)-ZSM-5 in NOx decomposition processes was reported by Iwamoto and al.[1] Apart from deNOx processes copper exchanged zeolites catalyses many organic reactions.

In our studies we focus on Cu(I) sites in faujasite (FAU), high alumina zeolite. We have investigated Cu(I) sites alone as well as their interactions with CO molecule, which is widely used as a probe molecule in infrared spectroscopy. We apply the combined quantum mechanic/interatomic potential functions method (QM-Pot),[2] which is particularly useful in investigations of the extended systems. Within this approach system is divided into the cluster, small enough to be easily described by advanced methods of the quantum mechanic (QM) Density Functional Theory in our case, and the periodic environment, treated at lower computationally expensive methods of the molecular mechanic (MM). Calculations are performed using QMPOT program, coupling the Turbomole package in QM part with the GULP program in MM part. QM-Pot gives more reliable results than simple cluster models and is less computationally expensive than periodic QM calculations.

Our calculations shows that stable positions of Cu(I) are sites I and II (with threefold coordination), while site III (with twofold coordination) are much less stable. CO binding is the stronger the weaker is Cu(I) binding. Reliable CO frequencies can be obtained using semiempirical scaling based on the CO bond lengths.[3] CO frequencies in FAU are site specific, as well as they depend on the number of Al atoms in the nearest neighborhood of the adsorbed molecule. All results are in well agreement with experimental data.

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Computational Study of Water on Cu(110) Surface

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Adsorption geometry, energetics and vibrational properties of water on Cu(110) surface was computationally modelled.

The vibrational potential energy surface of the adsorbed molecule was calculated and represented as an analytical function. The kinetic energy operator used was the exact kinetic energy operator for the isolated water molecule. The resulting Hamiltonian was then used to calculate variationally the wavenumbers of vibrational transitions of the adsorbed molecule. The similar method applied to ammonia on Ni(111) surface is explained in[2].

All electronic structure calculations were performed using Vienna *ab initio* simulation package, Vasp[1]. The code is based on density functional theory with generalized gradient approximation (GGA), plane wave basis set, pseudopotentials and periodic boundary conditions.

According to the premilinary results, there are many energetically almost equivalent adsorption geometries for water on Cu(110). It is common for these structures that the adsorption site is atop and the adsorption geometry is tilted with respect to the surface. These results are in good agreement with experimental results. Calculated adsorption energy is $0.3 - 0.4$ eV suggesting physisorption mechanism for adsorption. In good agreement with experimental results, calculated vibrational wavenumbers for stretches are lower than corresponding gas phase values.

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Role of the Conduction Electrons in Mediating Exchange Interactions in Heusler Alloys

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Because of the large separation of the Mn atoms in Heusler alloys ($d_{Mn-Mn} > 4$ Å) the Mn 3*d* states can be treated as well localized. Therefore the 3*d* states belonging to different atoms do not overlap considerably. The available inelastic neutron scattering experiments support this point of view. The ferromagnetism of the Mn moments in these systems is thought to arise from an indirect exchange interaction mediated by the conduction electrons. To reveal the nature of the ferromagnetism of various Mn-based semi- and full-Heusler alloys we perform a systematic first-principles study of the exchange interactions in these materials. The calculation of the exchange parameters is based on the frozen-magnon approach. The Curie temperature, T_C, is calculated within the mean-field approximation. We use the *s*-*d* model of Anderson[1][2][3] to interpret the results obtained. Our calculations show that magnetism in these systems strongly depends on the number of conduction electrons, their spin polarization and the position of the unoccupied Mn 3*d* states with respect to Fermi level. Various magnetic orderings have been obtained depending on these characteristics such as ferromagnetism, antiferromagnetism and non-collinear behavior. In the case of large conduction electron spin polarization and unoccupied Mn 3*d* states far from the Fermi level an RKKY-like ferromagnetic interaction is dominating while antiferromagnetic superexchange becomes important in the case of large peaks of unoccupied Mn 3*d* states close to the Fermi level. The calculational results are in very good correlation with the conclusions made on the basis of the Anderson *s*-*d* model and with available experimental data.

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Searching for the Properties of the Nodes of Many-Body Wave Functions

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The fixed node DMC method, FN-DMC, bases on the so called guidance functions which approximates the real wave function of the investigated system. These guidance functions are obtained from ab initio or DFT calculations. The quality of the functions depends on the used basis sets and on the calculation method.
One challenge in the calculation of the guidance function is to enhance the approximation of its nodes to these of the real wave function. Because, if one has the exact nodes of the real wave function in the guidance function FN-DMC calculations deliver exact results within the statistical error.
We examine the properties of given guidance function's nodes considering as example the carbon atom. We investigate the symmetry properties as well as the local and global properties of the nodes, like how the position of single electrons or the positions of some electrons relativ to each other influence the nodal hypersurface. The observed effects are interpreted physically or related to the approximation of the guidance function (the so called nodes artefacts).

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The Isotope Effect in the Ferroelectric Phase Transition of KDP Using *Ab Initio* Path Intergal Simulations

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We perform *ab initio* path integral simulations on protonated and deuterated KDP at different temperatures and lattice constants in order to probe the origin of the isotope effect of the ferroelectric phase transition in this material. By taking into account the quantum nature of the proton/deuteron our simulations are capable of distinguishing the direct effects of a pure mass change versus the indirect structural effect in the hydrogen bonding geometry upon deuteration. In reality, the direct and indirect effects amplify each other in a self-consistent manner, leading to the huge isotope effect on the transition temperature. With our calculation we can selectively investigate the manisfestation of the two phenomena. We characterize the ferro and paraelectric phases with the help of a recent modification of the path integral implementation in the CPMD package which enables us to compute momentum distributions of the proton/deuteron both above and below the transition temperature in order to characterize the extent of proton/deuteron delocalization in both phases.

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Magneto-Mechanical Interplay in Spin-Polarized Point Contacts

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In atomic-sized ferromagnetic systems under external bias the net electron flow, which transfers both charge and spin, is expected to produce a concurrent effect upon both the spatial and magnetic degrees of freedom of the current-carrying structure. Thus the modeling of such systems requires the combined description of the electron transport together with a description of the local magnetization and structural dynamics at the atomic level.

We have developed a common-framework computational approach to investigate the interplay between magnetic and structural dynamics in ferromagnetic atomic point contacts under bias. It is based on the non-equilibrium Green's function (NEGF) solution to the steady-state transport problem in a tight-binding Hamiltonian implementation and a description of the magnetization dynamics in terms of quasistatic transitions between stationary magnetic configurations[1].

This method is applied to investigate the effect of the atomic relaxation on the energy barrier for magnetic domain wall migration and, reversely, the effect of the magnetic state on the mechanical forces and structural relaxation. We observe changes of the barrier height due to the atomic relaxation up to 200%, suggesting a very strong coupling between the structural and the magnetic degrees of freedom[2]. The reverse interplay is weak, i.e. the magnetic state has little effect on the structural relaxation at equilibrium or under non-equilibrium, current-carrying conditions.

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Wavelet Based Summation of Long Range Interactions in Molecular Systems

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Long range interactions often play a crucial role in determining structure and dynamics of charged and polar systems. Due to the inherent complexity of $O(N^2)$ a direct calculation of electrostatic interactions imposes a computational burden which makes large systems intractable for this method. Therefore, reducing the computational complexity of eletrostatic calculations is still a field of active research and different methods were proposed with complexity $O(N \log N)$ (P^{3}M[1], tree methods[2]) or $O(N)$ (multipole[3] and multigrid methods[4,5]).
In the present work, a fast method of order $O(N)$ is proposed for the summation of Coulomb interactions. The main idea is to formulate the calculation of the potential energy ,Φ, as matrix-vector operation, where the entries of the matrix, A, consist of fixed distances between mesh points in a discretized space and the vector, Q, consists of time-dependent charge weights on these mesh points. A thresholded Wavelet-transform is applied to the matrix in order to make it sparse. Compression of matrix entries of more than 90% is achieved in that way. During the simulation, fast Wavelet transforms are applied to the time dependent charge-vector and the product $\tilde{\Phi} = \tilde{A}\tilde{Q}$ is evaluated, where $\tilde{A} = WAW^T$, $\tilde{Q} = WQ$ and W is a Wavelet-transform (in the present case Daubechies type[6]). Backtransformation of $\tilde{\Phi}$ then gives the potential energy on the grid points. In order to take into account short range interactions, self energies and contributions from near grid points are subtracted and particle-particle interactions are taken into account explicitly. Forces onto individual particles are calculated by high-order finite difference schemes. Results for timings and errors indicate that the method has indeed complexity $O(N)$.

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The Equilibrium Constant of Dimerisation of Carbon Dioxide

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Theoretical and experimental investigations of weakly bound molecular complexes are of fundamental importance for understanding of molecular interactions responsible for properties of condensed phases. Carbon dioxide has been a subject of many papers in recent years. Some deal with its role in the biosphere, mainly the greenhouse effect. Others have mainly studied the structure of the dimer. The carbon dioxide dimer was first detected in 1966 by Leckenby et al.[1]. Its structure is slipped-parallel(C_{2h} - geometry) which was shown as a result of quantum-chemical calculations[2] and experiments (high-resolution infrared and Raman studies[3–6]). The dimerisation equilibrium constant was evaluated from Slanina[7] using partition function and second virial coefficient. We have calculated the dimerisation constant from partition function, second virial coefficient and molecular dynamics simulations. The dimerisation constant from partition function has been calculated with different basis sets in the Møller-Plesset 2nd order perturbation approximation and the coupled-cluster method with and without counterpoise correction. The geometries were optimized and the frequencies were calculated with the program package $Gaussian98$[8]. The values obtained with these three methods do not differ from each other more than an order of magnitude and change approximately in the same way with temperature.

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Theoretical Modeling of Hydrides

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Hydrogen (H) is a clean energy carrier for the future, utilizing in principle only water as raw material for its preparation. Our research efforts on theoretical modeling have focused on metal and complex hydride materials for storage purposes. In many metal hydrides, H can be removed easily below 100^oC, but such hydrides have a relatively low weight percentage of stored H (1.5 to 2.5 wt.%). On the other hand, complex hydrides can store more H (up to 18.2 wt.%), but here the problem is high operating temperatures and slow absorption/desorption kinetics. One main aim of our research activities has been to identify materials that pack the H efficiently in the matrices. We have, inter alia been searching for metal hydrides with short H-H separations and tried to clarify the reasons for such short separations. We believe we have explained this feature for a series of hydrides and theoretically designed new hydrides with potentially very short H-H separations.[1] A challenging problem for the experimentalists who do not have access to neutron diffraction tools, is to establish the correct H position(s) in hydrides because H is small in size and has low atomic number. We have demonstrated different site occupation patterns in a large family of hydrides with the basis in the ZrNiAl-type structure. For these we have proposed a new empirical rule named the "site preference rule" to identify likely H positions in metal matrices by the use of theoretically calculated electron localization function.[2]

However, our basic challenge has all the time been to design new potential H storage materials and to get insight in the stability of various classes of hydrides. We have studied the structural stability of more than 50 different hydrides and their crystal structures have been predicted/verified. For example the crystal structure of $KAlH_4$ was first predicted by theory[3] and subsequent confirmed experimentally.[4] For MgH_2 several pressure-induced structural transitions have been predicted,[5] which in turn has been confirmed experimentally. We have also explored the stability of predicted phases and in some cases pointed out possible synthesis routes.

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Surface & Interface Calculations: GaAs on Ge, $SrTiO_3$ on $LaAlO_3$ & Pt on Ge

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Using VASP we calculated the potential, charge density and local density of states for a layered (001) Ge-GaAs system. We compare our results of GGA and LDA calculations. The two types of polar interfaces give rise to new energy states in the gap, depending on the type of interface. These states are caused by the valence discontinuity of the interfaces. We show that these states are localised at the interface. Understanding this simple system will help us understand the similar but more complex hetero-interface system $SrTiO_3$-$LaAlO_3$, which also has a valence discontinuity, and the interface of Pt nanowires on Ge, in which there exist 1D surface states pinned down between the Pt nanowires.

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Ab Initio Description of Electron Tunnelling in Magnetic Tunnel Junctions: Fe/MgO/Fe

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The tunnel-magneto resistance (TMR) effect is one of the fundamental discoveries in the field of spin-dependent electron transport and has been extensively studied in the last couple of years. Due to the complicated and mostly unknown atomic arrangement of the interfaces in tunnel junctions using amorphous barriers like aluminiumoxide, the theoretical description has often been restricted to simplified models. These models put typically the focus on the density of states of the magnetic material. Such descriptions, like the Julliere model, offer no clear framework to include neither the effect of the barriers nor of the interfaces.

We present an ab initio method which allows one to calculate the conductances of tunnel junctions using a Green function formalism. In our single particle treatment of electronic transport we focus here on the effects of localized states on the conductance. We discuss the different physical nature of sequential tunnelling in which localized states are involved and of the frequently discussed coherent tunnelling described by the Landauer equation. As model systems we use Fe/MgO/Fe[1–3] and Fe/vacuum/Fe.

We use an embedded Green function formalism[4] to treat the problem of an electron tunnelling through a barrier between two semi-infinite leads within the theoretical framework of the density functional theory. Our method allows an accurate and realistic description of the electronic structure of the tunnel junctions on all-electron level and is particularly suited for the treatment of magnetic systems involving transition metals. We have reformulated different schemes of elastic single electron tunnelling like the Landauer equation of coherent transport and Bardeen's transfer Hamiltonian approach within our Green function framework. The similarities and the fundamental differences of these schemes are discussed and demonstrated for model setups.

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