

**Abstracts of Invited
and Contributed Talks, Sep. 4**

Computational modeling of methyl transfer reactions catalyzed by cobalamin-dependent methionine synthase enzyme

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The cobalamin-dependent methionine synthase enzyme (MetH) catalyzes the transfer of the methyl group from methyltetrahydrofolate (CH₃-H₄folate) to homocysteine (Hcy) thus forming methionine (Met). The key step in the catalytic cycle involves displacement of the methyl group from the methylcobalamin cofactor (MeCbl) to Hcy in which the cobalamin cofactor serves as an intermediate cycling between hexa-coordinated methyl-cob(III)alamin and tetra-coordinated cob(I)alamin complexes. It is generally believed that the enzyme operates via an S_N2-type nucleophilic displacement. However, a related mechanism, referred to as *reductive cleavage* has been also suggested [1]. According to this mechanism, the cofactor is initially reduced by transfer of an electron from the deprotonated Hcy, forming a π-corrin based radical, followed by Co-C bond cleavage.

The transfer of the methyl group from the MeCbl cofactor to the Hcy substrate results in the formation of the cob(I)alamin intermediate which exhibits a complex electronic structure, between Co(I) and Co(II)-radical corrin states. It was found that the correlated ground state wave function consists of a closed-shell Co(I) (d⁸) configuration and a diradical contribution, which can be described as a Co(II) (d⁷)-radical corrin (π*)¹ configuration. Moreover, the contribution of the two configurations depends on the Co-N(His₇₅₉) distance [2].

Once every ~2000 turnovers, the MetH-bound cobalamin cofactor (Co¹⁺Cbx) is converted to the inactive cob(II)alamin (Co²⁺Cbx) form, from which Co¹⁺Cbx has to be recovered in order to ensure efficient catalysis. The Co²⁺/Co¹⁺ is a thermodynamically challenging reaction because the midpoint reduction potentials of the physiological reducing agents are considerably more positive than that of the Co²⁺Cbx cofactor. Based on spectroscopic and X-ray structure studies the generation of tetra-coordinated Co¹⁺Cbx has been invoked to be the key molecular determinant of the enzyme-mediated redox tuning of Co²⁺/Co¹⁺ process. However an alternative catalytic strategy for driving Co²⁺/Co¹⁺ reduction can be envisioned if one takes into account the formation of a biologically relevant Co¹⁺--H bond [3].

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Good Vibrations in Enzymatic H-Tunnelling: the Effect of Pressure on Barrier Compression and Isotope Effects

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The shape of the reaction barrier is crucial for enzymatic hydrogen tunnelling reactions, and therefore the concept of barrier compression is of fundamental importance. Promoting vibrations are rapid, sub-picosecond donor-acceptor compressive modes that transiently compress the barrier, enhancing the rate of H-transfer. For reactions dominated by H-tunnelling, such vibrations can be inferred from the kinetic isotope effect (KIE) and its temperature-dependence ($\Delta\Delta H^\ddagger$). However, promoting vibrations cannot be directly observed experimentally, and their role in H-tunnelling reactions remains contentious. For the rate-limiting H-transfer in the reductive half-reaction of morphinone reductase (MR), significant barrier compression has been inferred from both the strong temperature-dependence of the KIE and its counter-intuitive pressure-dependence, which has been explained by invoking an *ad-hoc* increase in the force constant for a low-frequency promoting vibration [1].

We present MM and QM/MM studies on the effect of pressure on donor-acceptor compression, barrier shape and the KIE in MR. Using spectral density analysis and digital filtering we identify the promoting vibration for this H-transfer (Figure 1) and confirm the hypothesis that the force constant increases with pressure. Using a vibronic (wavefunction overlap) formalism we show how pressure affects the KIE, $\Delta\Delta H^\ddagger$ and the rate constant, demonstrating that changes in experimental observations are directly coupled to the promoting vibration. Finally, QM/MM calculations reveal how the increase in force constant affects the relationship between barrier width and height and how this relates to the tunnelling parameters. [2]

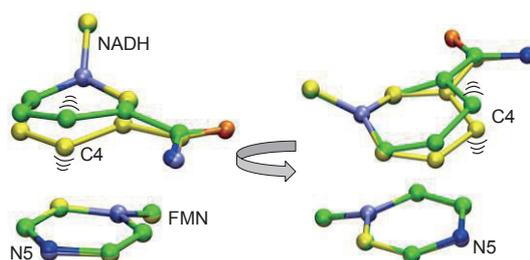


Figure 1. Promoting vibration for the H-transfer in MR at 1 bar.

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MD Simulations of Micelles Formation in $C_{12}E_x$ Solutions

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Since the dawn of polymeric micelles application as drug delivery systems in the late 1980s [1], numerous polymer self-assemblies have been extensively investigated, designated to deliver various substances including: low-molecular-weight anticancer drugs, contrast/imaging agents, proteins, etc. Promising building blocks of drug delivery containers are deemed nonionic surfactants of the poly(ethylene glycol) alkyl ethers C_nE_m .

One of the purposes of the present study is to derive from first principles calculations and test molecular mechanics parameters for such ethers to be used in subsequent all-atom simulations. Monomers and dimers with two different types of periphery, which are short-chain prototypes of the amphiphilic surfactant $C_{12}E_x$, were used as model systems. The geometry of low-energy conformers is optimised (PBE and MP2) in vacuum and in implicit solvent. Validation of the derived parameters provided the comparison between the thermodynamic parameters obtained from MD simulations (Amber99/NPT/300 K) of diethyl ether and the existing experimental data.

On the other hand, the stability of the pre-aggregates is determined, which are supposed to exist in aqueous solution before the actual micelles assembly, and to assess the aptitude to their formation. All-atom and coarse-grained molecular dynamic simulations (NPT/293 K) of two molecules of each species in explicit water (TIP4P) with PBC applied were carried out to estimate the mutual orientation and the interaction between the surfactants in the dimers. The derived force field parameters for the ether groups were used for this aim. The structural aspects of the amphiphilic organization in aqueous medium from the simulation data with the MARTINI CG force field for surfactant concentrations are discussed.

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4D-QSAR Analysis for the Cytotoxicity of Lamellarins Against Human Hormone-Dependent T47D Breast Cancer Cells

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4D-QSAR models were built and investigated for the cytotoxicity of a set of 26 lamellarins against human hormone dependent T47D breast cancer cells. 4D-QSAR models were first constructed from the exploration of eight possible receptor binding alignments for the entire training set. Since the training set is small (25 compounds), the generality of the 4D-QSAR paradigm was then exploited to devise a strategy to maximize the extraction of binding information from the training set, and to also permit virtual screening of diverse lamellarin chemistry. 4D-QSAR models were sought for only six of the most potent lamellarins of the training set as well as another subset composed of lamellarins with constrained ranges in molecular weight and lipophilicity. This overall modeling strategy has permitted maximizing 3D-pharmacophore information from this small set of structurally complex lamellarins that can be used to drive future analog synthesis and the selection of alternate scaffolds. Overall, it was found that formation of an intermolecular hydrogen bond and hydrophobic interactions for substituents on the E ring most modulate the cytotoxicity against T47D breast cancer cells. Hydrophobic substitutions on the F-ring can also enhance cytotoxic potency. The optimized 4D-QSAR model has a LOO cross-correlation value of $xv-r^2 = 0.947$. This work reveals that it is possible to develop significant QSAR, 3D-pharmacophore models for a small set of lamellarins showing cytotoxic behavior in breast cancer screens that can guide future drug development based upon lamellarins.

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Open-boundary cluster model for electronic excited states of adsorbate-surface systems

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I. Introduction The importance of photo-excited interface has recently been growing [1]. It is relevant to a broad range of practical applications including dye-sensitized solar cells and photo-catalysts. To investigate photo-excited interfacial systems, it is crucial to calculate both of the potential energy curves and lifetimes of the excited states. We have recently developed the open-boundary cluster model (OCM) [2], a generalized cluster model by introducing the outgoing-wave boundary condition at the edge of a model cluster mimicking an adsorbate-surface system. In the present contribution, we report the formulation of the first-principles approach based on OCM and its application to a Cs/Cu(111) system.

II. Application to a Cs/Cu(111) system The OCM Kohn-Sham (KS) equation is constructed by adding the absorbing potential to the KS equation for a model cluster. The ground-state energies of CsCu_n ($n = 1 - 31$) were calculated and it has been found that the cluster-size convergence of the interaction energy of Cs-Cu_n is remarkably improved by the OCM procedure. This is because the artificial edges inherent in a conventional cluster model are removed by introducing the outgoing-wave boundary condition. In the framework of OCM, the excited states are determined by the linear-response of the ground state. Figures 1 and 2 show the potential energy curves and the electronic lifetimes, respectively, for low-lying states for CuCs, the minimal model for Cs/Cu(111). The lowest excitation is $\text{Cu } 4s \rightarrow \text{Cs } 6s\sigma$. The excitation energy (2.4 eV) and lifetime (50 fs) are in reasonable agreement with experimental observations, and thus the first-principles OCM approach is considered to be promising for investigating photo-excited interfacial systems.

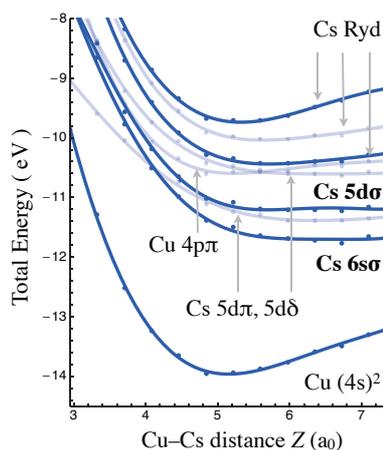


Fig.1 Potential energy curves for low-lying states of Cs/Cu(111)

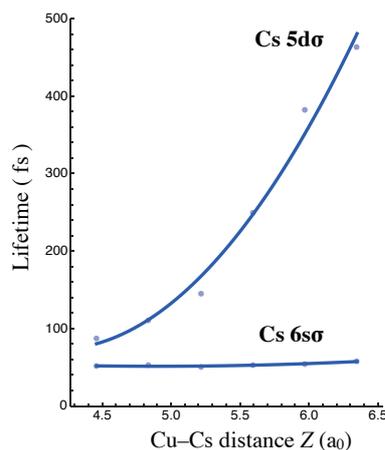


Fig.2 Electronic lifetime of Cs $6s\sigma$, $5d\sigma$ excited states

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Excited-State Nuclear Forces on the Adiabatic Potential Energy Surfaces by Time-Dependent Density Functional Theory

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Photoinduced processes are fundamental to physical, chemical, and biological phenomena. Owing to the recent developments in laser technology, the dynamical reactions including structural deformation, dissociation, isomerization, etc., have been investigated experimentally. To understand these excited-state dynamics theoretically, the accurate and efficient quantum simulation is required.

The simulation of photoinduced excited-state dynamics needs two ingredients. One is the nonadiabatic coupling terms (NACs) between the adiabatic states, and the other is the nuclear forces acting on atoms or ions on the adiabatic potential energy surfaces (APES) [1]. Recently, Hu *et al.* developed the efficient methods for calculating NACs using time-dependent density functional response theory [2]. However, the force calculation is still computationally expensive. In order to find a computationally reasonable force calculation method, we develop the excited-state force calculation method using the Casida ansatz [3]. This formulation is very simple, and the computational cost for the excited-state forces is almost the same as that of the NAC calculation.

First, we calculate the two APES for excited states of $^1\Sigma_u^-$ and $^1\Pi_g$ using adiabatic local density approximation for N_2 molecule. Comparing with the experimental value, the bond lengths of each state are well described within 0.03\AA . Next, we calculate the excited-state forces using the Casida-ansatz formulation and compare it with the finite-difference numerical derivative of each energy curves. The Casida-ansatz force well reproduces the equilibrium bond length for $^1\Pi_g$ state, but overestimates that of $^1\Sigma_u^-$ by 0.1\AA . Thus, we consider that the forces on the APES with lower excited energies are well approximated by the Casida-ansatz force.

In the presentation, we discuss the difference in the force calculation method between the Casida-ansatz formulation and previous studies[4,5]. We further discuss the Casida-ansatz forces for various kinds of molecules and show the simulation results of the excited-state dynamics.

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Role of the interface in the chemical reactivity of ultrathin oxide film

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Ultrathin oxide films grown on metal substrate are of great interest not only as supporting materials for chemically active nanoparticles but also as catalysts in the field of heterogeneous catalysis [1]. Using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations, we have demonstrated that the chemical reactivity for water dissociation on an ultrathin MgO film grown on Ag(100) substrate depends greatly on film thickness and is enhanced as compared to that achieved with their bulk counterpart [2]. The change of chemical reactivity of ultrathin MgO film depending on the film thickness can be explained by the strengthening of the interaction between the oxide and metal interface layers. This result implies that the artificial manipulation of the local structure at the oxide-metal interface is expected to play a pivotal role in controlling the catalytic activity of oxide film. Therefore, water dissociation on three model systems with defects at the oxide-metal interface of the 2-ML MgO/Ag(100) – an O vacancy (Fig. 1a), an Mg impurity, or an O impurity – has been examined and compared with the case of a MgO film without defects using periodic DFT calculations [3]. Our results clearly show that such structural imperfections at the interface can improve the chemical reactivity of ultrathin MgO film supported by Ag(100) substrate. This is closely correlated with the accompanying change of charge distribution of the oxide surface due to the accumulation of transferred charge density at the interface (Fig. 1b). In addition, the chemical reactions on the ultrathin oxide film surface can be tuned by interface defects regardless of the charging of adsorbates. Our study about water dissociation on MgO/Ag(100) not only reveals the potential of an ultrathin oxide film as a catalyst but also opens new vistas for the development of techniques to control and measure the interface structure of oxide film deposited on a metal substrate.

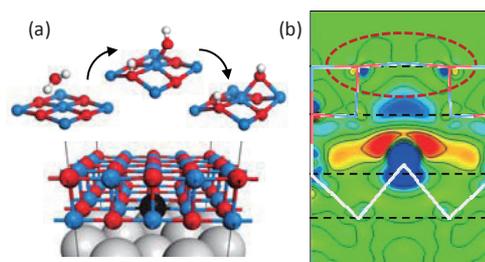


Figure 1. (a) Water dissociation on MgO/Ag(100) with interface O vacancy and (b) charge density difference map.

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Comparison of QM cluster calculations and QM/MM calculations for reactions in proteins

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During the latest decades, quantum mechanical (QM) calculations have become an important complement to experiments for the study of the structure and function of proteins. However, there is still no consensus on how such calculations should be performed. Instead, two schools have emerged: In the first, a small model (50–200 atoms) of the active site is cut out from the protein and is studied in isolation by QM methods. In the second approach, the entire protein, including some surrounding water molecules are explicitly studied by the combined QM and molecular mechanics (QM/MM) approach, in which the active site (again 50–200 atoms) is studied by QM methods, whereas the rest is modelled at the MM level.

We have studied the convergence of the QM cluster approach with respect to the size of the QM system and compared various methods to select atoms to include in the calculations [1]. For our test system, a simple proton-transfer reaction in [Ni,Fe] hydrogenase, various approaches to add groups to the QM system converge after ~15 groups have been added and the effect of the continuum solvent becomes unimportant at the same size. Unfortunately, different approaches to add groups converge to different results that differ by up to ~60 kJ/mol.

Likewise, we have studied the accuracy of QM/MM calculations, compared to pure QM calculations on a 446-atom model of [Ni,Fe] hydrogenase, again systematically increasing the size of the QM system [2]. We have tested several variants of both mechanical and electrostatic embedding. The results show that the junctions introduce inaccuracies that are hard to correct if they are too close to the reactive centre. However, QM/MM methods converge faster than QM-only methods. We will discuss how the two approaches may be combined to obtain the most reliable results.

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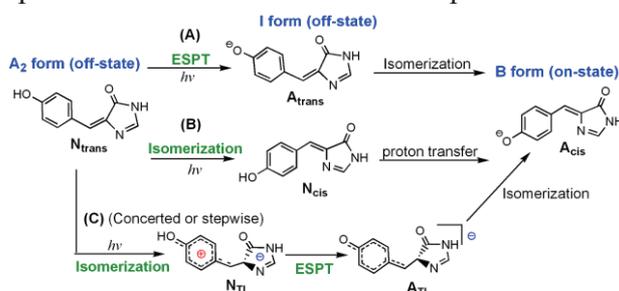
Reaction Mechanisms of Novel Fluorescent Proteins

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Wild-type green fluorescent proteins (GFP) and its variants play an important role in biological imaging and analysis. Recently, a new class of fluorescent proteins, (such as reversible photoswitching fluorescent proteins [1], irreversible photoconversion fluorescent proteins [2] and photoactivatable fluorescent proteins [3]) has become available and advanced our fluorescent protein technology. However, the reaction mechanisms of new photophysical and photochemical processes in these novel fluorescent proteins remain unclear.

We investigated possible reaction mechanisms for these novel fluorescent proteins by high-level QM and ONIOM(QM:MM) methods. New mechanistic pathways (e.g. photoisomerization coupled with excited-state proton transfer for Dronpa and competitive E1 and E1cb pathways for Kaede) were found [4-6]. In addition, we employed our developed non-adiabatic ONIOM(QM/MM) MD simulations [5] to elucidate primary events of photodynamics of the GFP chromophore in different environments. Significant effects of the environment on photodynamics were found and will be discussed. We also plan to add some additional results of our recent progress.

Scheme 1. Proposed mechanisms for reversible photoswitching in Fluorescent Proteins



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Structural and Energetic Analysis of Mutant K103N HIV-1 Reverse Transcriptase/Efavirenz Complex using ONIOM Calculations

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The most frequently observed mutation on the NNRTIs resistant is the K103N residue. Interestingly, there are still not clearly explained why this mutation encodes resistance to a wide range of NNRTIs, especially Efavirenz (EFV) inhibitor. Consequently, it is rather difficult to test and investigate experimentally. Therefore, a two-layered ONIOM calculation was performed in order to compare the binding interactions of EFV inhibitor and the HIV-1 RT binding pocket of both wild type (WT) and K103N mutant type, using a combination of different methods of calculation [B3LYP/6-31G(d,p), HF/6-31G(d,p), and PM3]. Additionally, the K103N mutation reduces the binding affinity and stability of the inhibitor by approximately 5.81 kcal/mol as obtained from ONIOM2B (B3LYP/6-31G(d,p):PM3) method. These indicate that the small loss of binding energy to K103N mutant can be attributed to a slightly weakened attractive interaction between the drug and residues surrounding the binding pocket due to the adaptation of HIV-1 RT against drug-resistance, which observed from the deformation energy. This energy comes from the binding pocket of K103N RT that requires more energy for the structural rearrangements than the WT by approximately 4.0 kcal/mol based on the ONIOM2B calculations. Moreover, it is confirmed that the non-bonded interaction of EFV to both wild type and K103N mutation HIV-1 RT are also slightly changes. The substitution of the linear side chain of K by the branched of N at 103 position appears to greatly affect the chemical environment in the K103N mutation, bring to the differences in interatomic distances, hydrogen bonding, electrostatic and hydrophobic interactions. Therefore, the knowledge based of the main contribution, non-bonded interactions and also the binding energy of EFV to WT and K103N RT complexes provide insight into the better understanding for improving a new drug resistance mutation.

Key words: Efavirenz, HIV-1 RT, K103N mutation, ONIOM, non-bonded, hydrogen bonding, hydrophobic, electrostatic and binding pocket

A coarse grained QM/MM approach for the description of hole transfer in DNA

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Charge transfer in DNA has received much attention in the last years due to its role in oxidative damage and repair in DNA, but also due to possible applications of DNA in nano-electronics. Despite intense experimental and theoretical efforts, the mechanism underlying long range hole transport is still unresolved. This is in particular due to the fact, that charge transfer sensitively depends on the complex structure and dynamics of DNA and the interaction with the solvent environment, which could not be addressed adequately in the modeling approaches up to now. We present a new computational strategy to evaluate the charge-transfer (CT) parameters for hole transfer in DNA. Based on a fragment orbital approach, site energies and coupling integrals for a coarse grained tight binding description of the electronic structure of DNA can be rapidly calculated using the approximate Density Functional method SCC-DFTB (1,2). Environmental effects are captured using a combined quantum mechanics/molecular mechanics (QM/MM) coupling scheme and dynamical effects are included by evaluating these CT parameters along extensive classical molecular dynamics (MD) simulations. This methodology allows to analyze in detail several factors responsible for CT in DNA. The fluctuations of the counterions, strongly counterbalanced by the surrounding water, leads to large fluctuations of the site energies, which govern the hole propagation along the DNA strand, while the electronic couplings depend strongly on DNA conformation and are not affected by the solvent (2). Using this methodology, the time course of the hole can be followed by propagating the hole wave function using the time dependent Schrödinger equation for the coarse grained Hamiltonian (5,6).

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Biomimetic design of Charged Brush-like Nanopores: Simulation studies

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Ion channels and porins are nanopores that in many cases, display high levels of solute specificity. Their selectivity has been exploited in new technologies: for instance synthetic functional nanopores have been fabricated based on the permeation properties of biological channels. One of anion-selective channels, phosphate (Pi)-selective outer membrane protein P (OprP) shows great ability for Pi selectivity over chloride ion. The previous simulation study indicates a crucial role of basic pore-lining residues which provide a 'charged brush' in determining Pi selectivity. In this study, OprP is used as a template for designing a series of computational models of synthetic nanopores that exhibit both OprP's anion-vs-cation selectivity and a preference for Pi over common chloride ion. The potential of mean force (PMF) has been used to investigate the energetic properties of modelled pores in comparison with that of OprP. The PMF of modelled nanopores shows similar profile to that of OprP. The K_d values of the modelled pore computed from the PMFs are 0.45 nM for Pi and 0.17 μM for Chloride corresponding to ~400-fold stronger binding of Pi than Chloride ion. Importantly, the results show that the high selective properties of biological channels can be transferred when their functional architecture and pore geometry are duplicated.

Solvent and Salt Effects on Structural Stability of Human Telomere

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I. Introduction

Human telomere DNA is of intense interest because of its role in the biology of both cancer and aging. The single-stranded telomere terminus can adopt the structure of a G-quadruplex, which is of particular importance for anticancer drug discovery, and various G-quadruplex structure have been reported. However the structure of human telomeric DNA has been controversial: the solution structure in the presence of Na⁺ has been reported to be antiparallel basket-type G-quadruplex by NMR, while the crystal structure in the presence of K⁺ has been reported to be parallel propeller-type. The solution structure in the presence of K⁺ has drawn intense interest, as the intracellular K⁺ concentration is higher than that of Na⁺, but the structure is still open to address.

II. Method

The 3D-RISM theory is a statistical mechanics theory of molecular liquids. This theory can provide the solvation free energy and the force from solvent without sampling. We combined a structure optimization method (the Quasi-Newton method) with the 3D-RISM theory, and performed the optimization of the telomere structure in aqueous solution of electrolytes to investigate the stability of various structures.

III. Results and Discussion

In pure water, the chair-type conformation was found to be the most stable structure, which is followed by basket-, hybrid-, and propeller-type structures in the order. It is clarified that the order of the stability is determined essentially by the solvation free energy, not by the conformational energy.

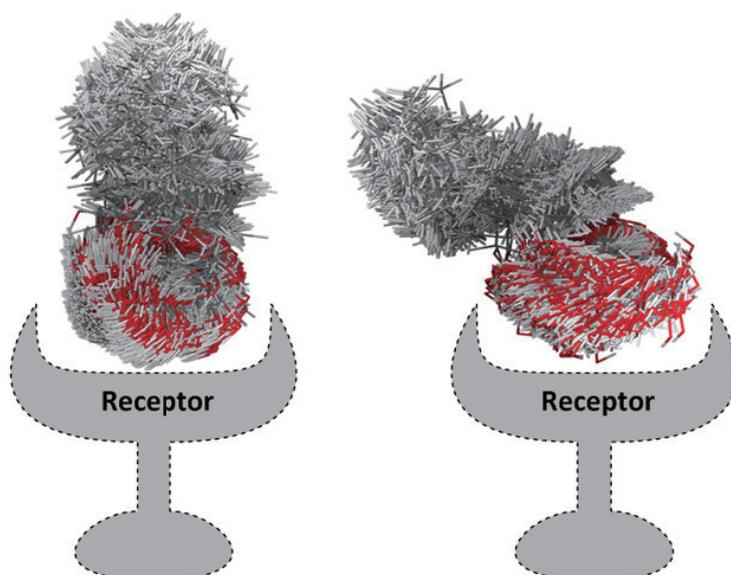
The order of the stability changes in 0.1 M NaCl solutions from that in pure water. The basket-type structure becomes the most stable one in the electrolyte solution. The theoretical finding is consistent with the experimental observation due to NMR. The reversed order of the conformational stability was attributed to the salt effect, especially, to that from the Na⁺ ions bound at inter-strand spaces of DNA.

Concerning the conformational stability in KCl solutions, our results predict that the order is not changed from that in pure water, that is, the chair-type is the most stable one. The finding suggests that the effect of the potassium ion upon the structure is not so strong as the sodium ion to change the order of the stability determined in pure water. The result is consistent with our finding for RDFs of the ions bound at the inter-strand spaces in DNA, which indicates clearly that the affinity of K⁺ to the binding site is weaker than that of Na⁺.

Complexity in Molecular Recognition

Jörg Grunenberg¹¹ Department of Life Science, Hagenring 30, 38106 Braunschweig, Germany**Abstract**

The anomer selectivity of artificial carbohydrate receptors was studied using in silico methods in order to shed light on the thermodynamic driving forces at work during molecular recognition in general. The contributions of relevant intermolecular hydrogen bonds were investigated by means of generalized compliance constants in order to dissect important from less important non-covalent interactions. Even at this moderately low rung on the ladder of complexity essential aspects of molecular recognition are not explainable in terms of additive intermolecular interactions. Though molecular recognition seems to be complex an emergent property, a rationale for the diastereoselectivity of carbohydrate receptors was obtained by a combination of experimental data, free energy simulations and ab initio calculations.[1-3]



Superimposed structures of the 500 low energy conformers of the β -octyl-glucoside (left) and the α -anomer (right). Due to a pronounced anomeric effect the α -anomer is stabilized by 15 kJ/mol

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A general view on hydrophobicity

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Solubility of hydrophobes in water is very low. There are, however, many other combinations of solutes and solvents that give low solubility. For example, argon dissolves very little in hydrazine. What grants a special interest to hydrophobes in water is the following observation: transfer of a hydrophobic solute in water is in fact energetically favorable, that is, the transfer is entropically so unfavorable that the net solvation free energy is large and positive [1]. This is thermodynamically equivalent to that the solubility of hydrophobes in water becomes even lower as the temperature is raised. This temperature dependence of solubility is well known for noble gases and many hydrocarbons in water.

Above arguments implicitly assume the process of solvation or the process of temperature change is carried out at fixed pressures. The constant-pressure condition is a natural choice for most experiments; the constant-volume condition is another possible choice, often employed in theoretical calculations. If the original phase from which a solute is transferred is an ideal gas and the final phase is some condensed phase β , difference between solvation entropy ΔS_p^* for a constant-pressure condition and ΔS_V^* for a constant-volume condition, or equivalently difference between solvation enthalpy ΔH_p for a constant-pressure process and solvation energy ΔU_V for a constant-volume process, is given by

$$\frac{\Delta S_p^*}{k} - \frac{\Delta S_V^*}{k} = \frac{\Delta H_p}{kT} - \frac{\Delta U_V}{kT} = \frac{\epsilon^\beta \overline{V}_A^\beta}{k\chi_\beta} - 1$$

where ϵ^β is the coefficient of thermal expansion, χ_β the isothermal compressibility, and \overline{V}_A^β the molar volume of solute, all defined in the β phase. For infinitely dilute Lennard-Jones (LJ) solutions [2], these solvation thermodynamic quantities are calculated as functions of ϵ and σ , the solute-solvent LJ energy and size parameters. It was found that the solvation analogous to the hydrophobic hydration is realized for a wide range of the LJ parameters if the constant-volume process is assumed. If the constant-pressure is assumed the range of the parameters in which the “hydrophobic hydration” is realized still exists but is very small. We will compare what we found for the LJ solution with those in a realistic model solvent of water.

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Computational Investigations of Complex Aqueous Solutions and Heterogeneous Ice Nucleation

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This talk is divided into two parts. In the first part, we will discuss recent results for complex aqueous solutions such as mixtures of water and 2-butoxyethanol. These solutions are complex because the solutes tend to associate even at very low concentrations, giving structures on mesoscopic length scales. We will discuss the nature and origin of such structures in light of molecular dynamics simulations on very large systems (up to 32,000 molecules), that are necessary to explore mesoscopic behavior. Results for different systems and models will be described, and where possible comparisons will be made with experimental data.

The second part of the talk will describe surface induced ice nucleation. Heterogeneous ice nucleation is very important in many physical situations, being particularly important for cloud formation in the upper atmosphere. We will show that some particular surface-fields that extend only a short distance ($\sim 10\text{\AA}$) from the surface can effectively cause ice to nucleate and grow in undercooled water.

Hund's rule and conjugate Fermi hole in two-electron atomic systems

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Hund's rules initially derived empirically in atomic spectroscopy of pre-quantum-mechanics era consist of three rules that predict the ordering of the energy levels possessing different spin and orbital angular momentum quantum numbers. These three rules, particularly the first one concerning the spin multiplicity, proved to be almost universally valid not only for atomic systems, but for molecules and *artificial atoms* [1]. Concerning the origin of this first rule, a traditional interpretation given by Slater has been often quoted, which says that a higher spin state has a smaller electron repulsion energy [2]. However, actual quantum chemical computations for singly-excited states of the helium atom, performed initially by Davidson [3], have showed that the triplet state with the higher spin multiplicity has a larger electron repulsion energy than does the corresponding singlet state possessing the lower spin. This indicates that the reason for a lower energy of the triplet state relative to the corresponding singlet cannot be due to a decrease in the electron repulsion potential, but must be ascribed to a more compact electron density distribution of the triplet state, which then results in a much larger energy decrease due to the nuclear attraction potential. Nonetheless, there still exists an ambiguity concerning the reason why the triplet state has a more compact electron-density distribution than the corresponding singlet state. In our previous study [1], the origin of the Hund's multiplicity rule in two-electron artificial atoms was studied and the mechanism for a more compact electron density distribution in the triplet state than that of the corresponding singlet state was clarified by examining the nodal pattern of the wave functions in the internal space. Motivated by this earlier analysis the present study examines the internal wave functions of the helium and He-like two-electron atomic ions in order to provide a deeper understanding into the workings of the first Hund's rule.

The internal part of the full configuration interaction wave functions for low-lying singlet-triplet pairs of states has been extracted and visualized in the three-dimensional internal space (r_1, r_2, ϕ_-) . The electron-electron repulsion potential has been also visualized in the internal space. It manifests itself by three striking poles, penetrating exactly into the spatial region defined by the Fermi hole. Because of the existence of these strong potential poles in the vicinity of the Fermi hole, a major part of the singlet probability has to escape from this region. In contrast, the corresponding triplet wave function is less affected by these poles thanks to the presence of the Fermi hole. The evading singlet probability was shown to migrate far away from the original region close to the origin to the region where either r_1 or r_2 are large. This results in a more diffuse electron density distribution of the singlet state than the corresponding triplet state. The mechanism of the evolution of the singlet probability towards the large r_i ($i = 1, 2$) region in the presence of the electron repulsion potential has been rationalized on the basis of a new concept of the so-called *conjugate Fermi hole* [4].

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First-principles modelling of dynamic, dielectric and catalytic properties of various materials for the production and storage of energy

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Many of materials based on alkaline-earth or transition metals have a wide range of applications (fuel cell, storage of energy, catalysts, photovoltaic, thermoelectricity...) due to their peculiar properties (high-dielectric constants, ferroelectricity, thermoelectricity...). The knowledge of their bulk and surface properties is essential in designing targeted devices with high performance. For instance, ABO_3 perovskites are peculiarly interesting for their atomic structural flexibility (for instance, allowing high number of atoms substitutions) which gives them specific chemical and electrical properties compared to the pure compounds. In this context, first-principles calculations can be useful to understand the structural and electronic properties of these materials. This contribution will focus on the use of the first-principles methods in various fields of materials sciences and applications, such as phase transitions, catalysis, storage of energy, thermoelectricity

Further examples of applications of quantum mechanical approaches of the oxides and inter-metals properties will be described: among them: the study of the pressure driven phase transitions and their influences on the ABO_3 high-dielectric response, the study of CO_2 tolerance and/or the protons diffusion in perovskites. The studies of the properties of novel thermoelectric materials based on inter-metallic compounds will be also presented. All the studied phenomena are analysed in terms of evolutions of the atomic and electronic structures, of the spontaneous polarization, electronic structure, phonon and defects effects. It will be shown that a good agreement between calculated, and, other theoretical and experimental various properties can be obtained. This contribution will also illustrate the complementarity between the theoretical approaches and the experimental methods used to characterize the various properties of materials (IR, Raman, EXAFS, ...), and, the link between the calculated observables and the physical data of interest (phonons, thermoelectric properties, ...).

Density functional theory study on charge-transfer and local excitation states of Pentacene/C₆₀ model complex

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I. Introduction

The reliability of the calculation methods is investigated for the excited states on the pentacene/C₆₀ model complex as the minimal structural unit of the donor-acceptor heterojunction in pentacene/C₆₀ organic cells. We have focused on the lowest excitation energies for the local excited state of pentacene (LXP) and the charge-transfer excited states (CTX), as well as their difference (CTX-LXP), which are the key factors for the charge separation process in the pentacene/C₆₀ organic cells. In this study, we clarify the applicability of the long-range corrected density functional theory (LC-BLYP) method together with a tuning scheme of its range separating parameter to the reproduction of the excitation energies of the pentacene/C₆₀ model.

II. Results

The geometries are optimized at the B3LYP/6-31G** level of approximation for the isolated monomers. The range separating parameter (μ) of the LC-BLYP method is optimized so as to meet the many-electron self-interaction free (ME-SIF) condition [1] both for the pentacene and C₆₀, and thus we found the optimized parameter $\mu = 0.20$.

Table 1 lists the excitation energies of the pentacene/C₆₀ model (see Fig. 1). The reference values are estimated from experimental data. All of the calculations [CIS, B3LYP, LC-BLYP ($\mu = 0.00, 0.10, 0.20, 0.33, \text{ and } 0.47$)] are performed with the 6-31G* basis sets under the frozen core approximations. We found that the LC-BLYP ($\mu = 0.20$) method under the ME-SIF condition semi-quantitatively reproduces the reference values all for LXP, CTX, and CTX-LXP, though the excitation energies are sensitive to the calculation methods.

III. Reference

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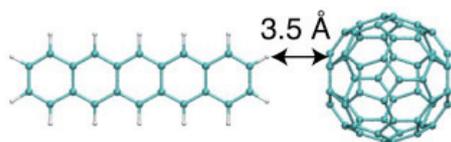


Figure 1. Pentacene/C₆₀ model

Table 1. Excitation energies in the pentacene/C₆₀ model [eV] (calculated by the 6-31G* basis sets)

Method	μ	LXP	CTX	CTX-LXP
Estimate	---	2.312	2.746	0.438
CIS	---	2.899	4.190	1.291
TD-B3LYP	---	1.947	1.085	-0.862
TD-LC-BLYP	0.47	2.605	3.995	1.390
	0.33	2.501	3.666	1.165
	0.20	2.259	2.948	0.689
	0.10	1.904	1.722	-0.182
	0.00	1.663	0.387	-1.276

Second hyperpolarizabilities of open-shell singlet metal–metal multiple bonded systems

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I. Introduction

We have theoretically investigated open-shell singlet molecules as a novel class of nonlinear optical (NLO) systems, and have revealed their structure–property relationship: singlet diradical systems with intermediate diradical characters (y) tend to exhibit larger second hyperpolarizabilities (γ) than pure diradical and closed-shell systems [1,2]. Many polynuclear metal complexes are expected to show singlet multi-radical nature due to the unpaired electrons in the d-orbitals of metal atoms. In particular, metal–metal multiple bonded complexes are good NLO candidates because they could present singlet multi-radical characters originating from interactions between the d-orbitals, which can create $d\sigma$, $d\pi$ and $d\delta$ bonds as shown in Figure 1. In the present study, we theoretically investigate the diradical characters of $d\sigma$, $d\pi$ and $d\delta$ orbitals [$y(dX)$, where $X = \sigma, \pi$ or δ] and γ values of several dimetal systems with multiple bond. We also analyze the contributions of these orbitals to γ [$\gamma(dX)$, where $X = \sigma, \pi$ or δ] in order to reveal a relationship among the orbital symmetry, diradical character and γ value.

II. Results

Figure 2 shows the bond length (R) dependences of γ and $\gamma(dX)$ as well as those of $y(dX)$ for the dichromium system [Cr(II)–Cr(II)] calculated by the UCCSD and UHF methods. It is found that the $d\sigma$ orbital dominantly contributes to γ , while the contributions of the $d\pi$ and $d\delta$ orbitals are negligible. The $\gamma(d\sigma)$ value is found to be enhanced in the intermediate $y(d\sigma)$ region. The same results are observed for other dimetal systems. We also discuss the effects of the charge on the γ values and on the diradical characters.

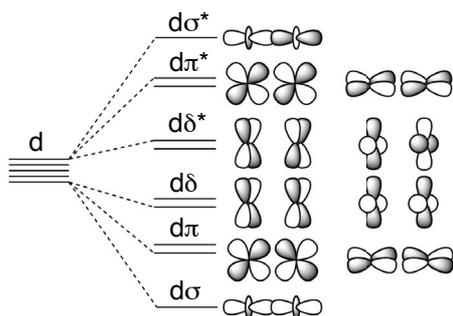


Figure 1. Molecular orbital diagram of d–d interaction.

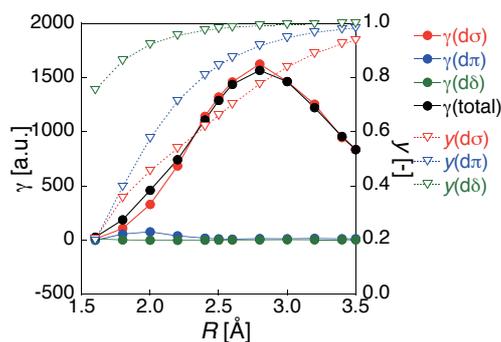


Figure 2. Variation of γ and y with bond length (R) for Cr(II)–Cr(II).

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Universal product angular-momentum distributions in photodissociation and reaction collisions

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The talk reviews recent results on the full quantum mechanical treatment of the spin and orbital angular momentum recoil angle distributions of the products of *chemical* and *photochemical reactions* in diatomic and polyatomic molecules. The distributions obtained are presented in the body frame and in the molecular frame using the spherical tensor formalism. The main result is that the recoil angle distribution can be written *irrespective of the reaction mechanism* in a universal form in terms of the anisotropy transforming coefficients \mathbf{c}_{K,q_i}^K which contain all information regarding the reaction dynamics and can be either directly determined from experiment, or calculated from theory.

The coefficients are scalar values which depend on the photofragment state multipole rank (K), on the initial reagent spherical tensor rank (K_i), and on component q_i of the ranks K and K_i projected onto the recoil direction \mathbf{k} . An important new conservation rule is revealed through the analysis, namely that the component q_i is preserved in any scattering, or photolysis reaction. The coefficients \mathbf{c}_{K,q_i}^K act as transformation coefficients between the angular momentum anisotropy of the reactants and that of the product. The results obtained are generalized to the case where the reaction reagents possess spin, or orbital electronic angular momentum polarization.

General expressions for the anisotropy-transforming coefficients beyond the axial recoil limit contain scattering S -matrix elements and take into account all possible types of nonadiabatic interactions in the reaction complex, as well as the full range of possible coherence effects. Several important particular cases of these expressions are discussed. These are: (a) the role of the Coriolis interactions in the photolysis of linear molecules which result is the molecular helicity non-conservation; (b) quasiclassical approximation of the molecular scattering function in the high- J limit.

The talk also reviews recent experimental results on photodissociation of a number of polyatomic molecules and shows how the investigation of the determined values of the speed-dependent parameter β and higher rank anisotropy parameters supported the interpretation of the photodissociation dynamics.

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4B3-3I

Studies of solvent mediated long-range electron transfer $\text{IBr}^{-*}\dots\text{CO}_2$ and excited state dynamics of ICN^{-*}

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In this talk, I will discuss two recent studies in which understanding the spectroscopy and dynamics of relatively small systems: $\text{IBr}^{-}\text{CO}_2$ and ICN^{-} has led to insights into much broader questions. Specifically, when IBr^{-} is promoted to electronically excited states that correlate to a $\pi \leftarrow \sigma$ or a $\sigma^* \leftarrow \sigma$ transition it will dissociate to form $\text{I}^{-}+\text{Br}$ or $\text{I}+\text{Br}^{-}$, respectively. The introduction of a single CO_2 molecule is sufficient to open the charge transfer channel. Interestingly in the first case (the $\pi \leftarrow \sigma$ excitation) this transfer occurs at a 7 Å I-Br separation. Investigating the origins of this observation provides insights into the mechanism for such a long-range charge transfer. In the second part of the talk, I will turn my attention to how the of vibrational and rotational structure to one of the photofragments affects the resulting dynamics upon electronic excitation and electron detachment, and focus on recent studies on the photoexcitation dynamics of ICN^{-} . In spite of the extensive literature on the electronic structure and dissociation dynamics of ICN , much less is known about ICN^{-} , and this work seeks to shed light on some surprising aspects of the excited state dynamics and photoelectron spectrum of this anion.

The performance of Density Functional Theory for Hydrogen Bonded Systems: Shortcomings and Solutions

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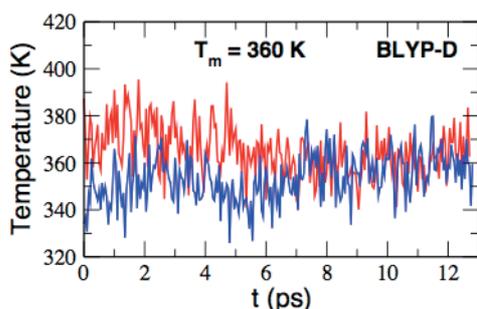
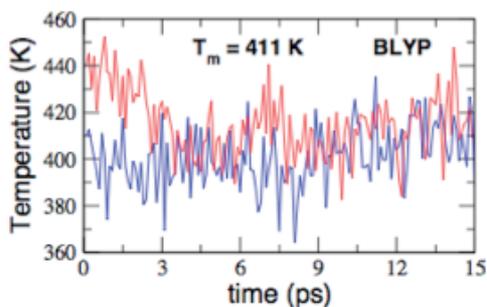
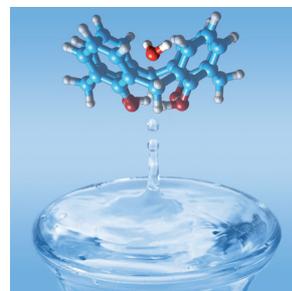
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We will present an assessment of the accuracy of various density functionals in describing non-covalent interactions between guest molecules (H_2 , H_2O , NH_3 , CH_4 , C_2H_2) and host functional molecules (calixarenes) (1) and the coordination of hydroxide ions in water clusters (2). The results of high-level electronic structure calculations at the

CCSD(T) level are used as benchmarks to assess the importance of dispersion in recently developed density functionals.

We subsequently evaluate the performance of functionals with and without dispersion corrections in describing the melting temperature of liquid water (3, 4). Based on these results we rely on a relative-to-the-melting (T_m) rather than an absolute temperature scale for comparing results obtained with various models with experiment. Preliminary results on that relative scale include the 2-D infrared (IR) spectra (5) and the anisotropy of liquid water (6).



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Ab initio fragment molecular orbital-molecular dynamics (FMO-MD) study of solvation differences between *cis*- and *trans*-platins in water

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Since *cis*-platin ($[\text{Pt}^{\text{II}}\text{Cl}_2(\text{NH}_3)_2]$) is recognized as an anticancer substance, a lot of studies have been devoted to the bio-chemical functions of its derivatives [1]. The anticancer functions of *cis*- and *trans*-platins are completely different, namely *cis*-platin is highly effective in treating various cancers while *trans*-platin has less anti-tumor activity, on the basis of their distinct spatial arrangement of ligands to DNA. Despite the extensive research on *cis*- and *trans*-platins and their derivatives, understanding of the biochemical activities of these compounds still needs to be developed. It is well known that the final step of the antitumor treatment is the combination between *cis*-platin and DNA, further leading to the physical and chemical modifications to the DNA structure. On the other hand, it is believed that some preliminary steps, such as solvation process before reaching the final target, are also important to the efficacy of drugs. To reveal the different nature on the medical application between *cis*- and *trans*-platins, their solvation in water, as the first step of biophysical chemistry processes in living system, deserves to be investigated.

In this study, water solvation structures of *cis/trans*-platin were studied using relativistic FMO-MD (fragment molecular orbital method based molecular dynamics) simulations [2]. Time evolutions of natural charges in hydrated *cis/trans*-platin are shown in Figure 1. The widths of charge fluctuations are larger for Cl and Pt than for NH_3 . Further, the charge fluctuations of Cl and Pt show good correlation with each other, suggesting that there are charge transfer interactions between them. The frequency of the charge fluctuation is predicted to be 334 cm^{-1} . The frequency is well assigned to the H_2O -platin intermolecular vibrational modes ($311\text{-}321\text{ cm}^{-1}$) shown in Figure 2. This means that the Cl-Pt bond stretching motion couples with those of hydration waters. Comparing the two isomers, we could observe much more intense Cl/Pt charge fluctuation for *cis*-platin. The difference of hydration between *cis/trans*-platins and further quantum insights of the solvation dynamics will be discussed.

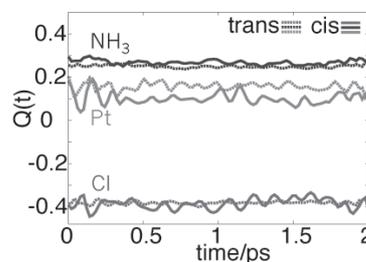


Figure 1: Time evolution of net charge obtained by FMO(3)-MP2/MCPdzp. [3,4]

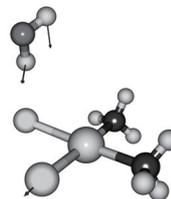


Figure 2: Intermolecular vibrational mode between *cis*-platin and H_2O .

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Multi component molecular theory for hydrogen bonded systems and positronic compounds

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Recently, we have developed some first-principles approaches for multi-component systems including both electrons and nuclei (or positron) quantum-mechanically: (I) Multi-component molecular orbital (MC_MO) [1,2], DFT (MC_DFT) [3], quantum Monte Carlo (MC_QMC) [4], and (II) *ab initio* path integral molecular dynamics (PIMD) [5,6,7] methods.

First, we would like to show some application to positronic compounds of some nitrile (-CN functional group) species. Recently, we have demonstrated that HCN, as the simplest nitrile molecule, can bind a positron by the QMC approach [4]. We have also found that the positron affinity (PA) value of acetonitrile with electronic 6-31++G(2df,2pd) and positronic [15s15p3d2f1g] basis set with the CI scheme of MC_MO method is calculated as 4.96 mhartree [2], which agrees to within 25% with the recent experimental value of 6.6 mhartree by Danielson et al. [8]. Our PA values of acrylonitrile and propionitrile (5.70 and 6.04 mhartree) are largest among these species, which is consistent with the relatively large dipole moments.

Next, we will show some results for nuclear quantum effect on some hydrogen bonded systems by using path integral simulation with 2nd and 4th order Trotter expansion. We have elucidated the H/D isotope effect on deprotonated water dimer anion H_3O_2^- [5, 6] and fluoride ion-water cluster [7], particularly focusing on the geometrical isotope effect.

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Anions Dramatically Enhance Proton Transfer across Water Interfaces

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Many fundamental processes in chemistry and biology are driven by proton transfer (PT) across water interfaces with hydrophobic media. However, what distinguishes PT ‘on water’ at the interface from conventional PT ‘in water’ in the bulk remains unclear. Here we show that PT from gaseous nitric acid to liquid water is dramatically accelerated by non-specific anions. We found experimentally that HNO₃(g) fails to dissociate on pure water surfaces but is fully deprotonated at the surface for 1 mM NaCl and other electrolytes. Quantum mechanical (QM) calculations confirm that HNO₃(g) dissociation on the surface of pure water is unfavorable despite its strong acidity in the bulk liquid. QM also shows that chloride polarizes and pre-organizes interfacial water, thereby enhancing HNO₃(g) adsorption and setting the stage for adiabatic PT. Our findings in this prototype system provide direct evidence of the critical role electrostatic pre-organization plays in catalyzing proton transfers across water-hydrophobe interfaces, such as those involved in cloud acidification and enzymatic events.

Strong correlation of electrons in molecules and solids

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I will discuss our work to treat electronic structure far away from mean-field in both molecules and solids, using one or more of the following approaches: (i) generalized correlator-Pfaffian wavefunctions, (ii) density matrix renormalization group and related techniques, and (iii) density matrix embedding theory.

The existence of thermodynamic limit and size-consistent design

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Why is energy extensive and is an application of statistical thermodynamics to chemistry valid? It has taken 40 years for mathematicians to complete the proof of the extensivity of energy or, equivalently, the existence of thermodynamic (infinite-volume) limit of energy density. I will offer an alternative, more accessible proof of the extensivity of energy for electrically neutral, metallic and nonmetallic crystals by establishing the same for its individual energy components, namely, the kinetic, Coulomb, exchange, and correlation energies. On this basis, I will address size-consistent design of electronic and vibrational many-body methods. Our findings are summarized as follows: The significance of the distinct use of the intermediate and standard normalization for extensive and intensive operator amplitudes, respectively; The extensive and intensive diagram theorems, which serve as the foolproof criteria for determining size consistency of a method for extensive and intensive quantities; The extensive-intensive operator consistency theorem, which stipulates the precise balance between the determinant spaces reached by extensive and intensive operators in a size-consistent excited-state method.

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Generalization of Constrained Unrestricted Mean-Field Methods for Controlling Spin-Contamination: Application to Singlet-Triplet Splittings

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We have recently shown that unrestricted Hartree-Fock (UHF) variationally reduces to high-spin restricted open-shell Hartree-Fock when constraints are imposed on the eigenvalues of the spin density matrix[1]. This scheme, called constrained UHF (CUHF), however, always reduces to restricted Hartree-Fock (RHF) for singlet systems even though they may exhibit an open-shell singlet electronic structure, where a single reference wave function of RHF is well known to be inadequate. In this talk, we extend the ideas behind CUHF and propose to control spin-contamination in UHF by releasing the constraints in an active space while imposing elsewhere. If the active space is properly chosen, our generalized CUHF method greatly benefits from a controlled broken-symmetry effect while avoiding the massive spin contamination arising in the traditional UHF[2]. We show a simple generalization of Møller-Plesset perturbation theory in CUHF to include weak correlation, and also apply Löwdin's projection operator to CUHF and obtain multireference wave functions with moderate computational cost. We report results on singlet-triplet energy gaps to show that our constrained scheme outperforms fully unrestricted methods. This constrained approach can be readily used in Kohn-Sham (KS) density functional theory with similar favorable effects, provided that spin-contamination is given by the KS orbitals as in UHF.

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Novel Basis-Set Free Approaches to Solving the Electronic Schrödinger Equation

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Few electronic structure methods are able to obtain the accuracy required to predict experiments (less than a milliHartree error). The most obvious method for reliably achieving this accuracy is the full-configuration interaction (Full-CI) method. However, Full-CI is very computationally expensive (exponential scaling) and as such is rarely useful other than for benchmarking calculations. Full-CI is a method that would work for arbitrary Hamiltonians. Thus, Full-CI does not take advantage of the inherent smoothness associated with the solutions to the electronic Hamiltonian. In the molecular electronic structure problem simplicity arises from every electron being identical, and that the electronic-Hamiltonian only contains one- and two-body symmetric operators. This modern grid-based approach takes into account these advantages neglected in the Full-CI approach. Grid-based methods, often termed “basis-set free” methods, have been seen as anathemas resulting from their reputation of exponential scaling. However, recent results from Griebel and others in the mathematics literature show how one may construct accurate grids for performing cubature (multidimensional quadrature) with only polynomial scaling when there is sufficient smoothness. Utilising these efficient grids for electronic structure provides grid-based methods that scale polynomially while maintaining Full-CI accuracy. In this presentation the formalism of the approach will be explained and recent results will be demonstrated.

Orbital-Dependent Energy Expressions for Kohn–Sham Potentials

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Suppose we are given an exchange–correlation Kohn–Sham potential $v_{\text{xc}}([\rho]; \mathbf{r})$ whose parent functional is unknown. One can obtain the energy corresponding to this potential by integrating $v_{\text{xc}}([\rho_t]; \mathbf{r})$ along a path of suitably parametrized densities $\rho_t(\mathbf{r})$. If the parent functional exists, then every path yields the same result; otherwise, the energy is path-dependent. For potentials that are not functional derivatives (i.e., for most *model* Kohn–Sham potentials), the path of uniformly scaled densities, $\rho_t(\mathbf{r}) = t^3 \rho(t\mathbf{r})$, usually gives the most sensible results. We explore a distinctly different path in which intermediate densities are constructed by filling Kohn–Sham orbitals with fractions of an electron in accordance with the *Aufbau* principle,

$$\rho_t^J(\mathbf{r}) = \sum_{i=1}^{J-1} |\phi_i(\mathbf{r})|^2 + t |\phi_J(\mathbf{r})|^2, \quad \begin{array}{l} J = 1, 2, \dots, N \\ 0 \leq t \leq 1 \end{array}$$

Here N is the total number of electrons in the system and $\phi_i(\mathbf{r})$ is the spatial part of the i th spin-orbital. Two versions of this method are examined: (i) one in which the orbitals are found once by solving the N -electron Kohn–Sham equations with $v_{\text{xc}}([\rho]; \mathbf{r})$ and then kept frozen along the entire path; (ii) using relaxed and fully self-consistent Kohn–Sham orbitals at each point of the path. The frozen-orbital *Aufbau* path leads to the following orbital-dependent energy expression

$$E_{\text{xc}}[\rho] = \int d\mathbf{r} \sum_{J=1}^N \int_0^1 v_{\text{xc}}([\rho_t^J]; \mathbf{r}) |\phi_J(\mathbf{r})|^2 dt.$$

The relaxed-orbital path is shown to give the same result as the Janak theorem,

$$E[\rho] = \sum_{J=1}^N \int_0^1 \epsilon_{\text{HOMO}}(J-t) dt,$$

where E is the total energy and $\epsilon_{\text{HOMO}}(J-t)$ is the highest occupied Kohn–Sham orbital of the $(J-t)$ -electron system. Possible applications of *Aufbau* paths are discussed and numerical results for several model potentials are presented.

TDDFT study on quantization behaviors of nonadiabatic couplings in polyatomic systems

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Nonadiabatic couplings (NACs) play a central role in nonadiabatic quantum simulations. For the efficient computation of NACs, time-dependent density functional theory (TDDFT) methods have been developed in recent years [1-2], which eliminate the necessity of constructing many-body wave functions. It was demonstrated that the TDDFT approach well reproduced the quantization behaviors of NACs near Jahn-Teller or Renner-Teller intersections, and gave results in an accuracy comparable to wave-function based methods. However, preceding studies in the literature are mostly limited to small three- or four-atom molecules, due to the computational cost. Therefore, it is necessary to utilize the efficiency of TDDFT to study the quantization behaviors of larger systems. This is particularly important for Jahn-Teller and Renner-Teller systems, as the corresponding models are just based on the two-level hypothesis without further considerations on the different symmetries of intersections.

In the present paper we present extensive calculations on polyatomic Jahn-Teller and Renner-Teller systems by examining the angular NACs between the ground state and the first excited state, using the TDDFT scheme in Ref. [2]. Taking the sodium clusters (Na_n , $n \leq 11$) as the example (which are well known for the Jahn-Teller distortions in equilibrium geometries), we show that the angular NACs show different quantization behaviors as the symmetry of conical intersections changes with respect to the atomic number n . The angular NACs in Na_3 (C_{3v} symmetry) converge to the quantized value of 0.5 when the contour radius q around the intersection point is decreased, while results of other sodium clusters show significant oscillating behaviors, no matter how small the contour radius q is. In spite of the above differences, the same “geometric phase” with a value of π can be obtained, by performing the integral of the angular NACs with respect to the angles on the whole contour. This is consistent with the prediction of the Jahn-Teller model. On the other hand, calculation examples on the HC_nS ($n \leq 9$) systems show that the angular NACs in the polyatomic Renner-Teller systems are always 1.0, showing no dependence on the atomic number n , as understood from the fact that the symmetry of the linear atomic chain does not change when n is increased.

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Embedding as a new perspective on electronic structure theory

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The concept of embedding is at the heart of electronic structure theory: even Hartree-Fock theory works by considering the quantum mechanics of a single electron embedded in an effective potential that approximately describes interactions with the environment. Embedding has been used very widely in theoretical chemistry, and common examples of embedding of one kind or another include QM/MM calculations, polarisable continuum and use of effective core potentials. Here I will discuss the use of embedding for high-accuracy description of condensed matter, and, more generally as a framework for developing new electronic structure methods.

The work on condensed-matter systems concentrates on various ways to incorporate many-body effects into truncated many-body expansions, and can be used, for example, in the study of organic crystals.

In more general terms, embedding will be explored as an alternative to inter-pair coupling (which led from the independent-electron pair approximation to coupled-cluster theory) and to higher excitation levels.

Towards an accurate WFT-in-DFT subsystem approach to computational chemistry

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In the conventional approach to electronic structure theory a system is viewed as an unstructured collection of nuclei and electrons, requiring only the specification of nuclear positions and charges and the total number of electrons to start a calculation. This truly *ab initio* approach is very appealing and can for small molecules lead to results that rival high-resolution spectroscopic techniques, thereby providing a numerical laboratory to study electronic properties and reactivity. One realization of this approach is relativistic coupled-cluster method¹ in which electron correlation and relativity are treated on equal footing. I will show some examples of applications² done with the implementation available in the Dirac programme suite³ to illustrate its capabilities. While the application of large-scale supermolecular calculations is still gaining popularity, due to the ever-increasing computational power, such an uncompromising approach also has its disadvantages, however. For complex systems one would ultimately like to understand trends observed upon substitution of functional groups in terms of familiar concepts like chemical bond strength, steric hindrance, atomic or molecular charges, etc. Rather than just obtaining these concepts in an a posteriori analysis, one would ideally like to utilize chemical knowledge concerning the distinction between metal and ligands, solvent molecules, functional groups already in the setup of the calculations. In the flexible subsystem scheme⁴ implemented in the Amsterdam Density Functional⁵ (ADF) code this is made possible. The theoretical framework for this technique is the frozen-density embedding method, that was first formulated by Wesolowski and Warshel⁶, and defines the total electron density of a supermolecular system as a sum of densities obtained in individual calculations of chemically well-defined subsystems. We have extended this theory to include also magnetic interactions⁷ and introduced a capping approach⁸ to treat connections between strongly coupled systems. We are now working on the improvement of currently available kinetic energy functionals by studying the properties of accurate reference potentials⁹. I will give an overview of our experiences¹⁰ with this subsystem formulation of density functional theory and discuss perspectives for its further development as a WFT-in-DFT subsystem method¹¹.

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Large-scale electronic structure calculation with ELSESES and its application to conjugated polymer

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A simulation code ‘ELSESES’, Extra-Large-Scale Electronic Structure calculation code, was developed and realizes large-scale calculations with 10^3 - 10^7 atoms. [1] Novel linear-algebraic theories, such as multiple Krylov subspace theory, were constructed for ‘order- N ’ algorithms in standard or generalized eigen-value equations. Tight-binding form Hamiltonians are used. Application studies of metallic and insulating systems were carried out for nanostructured solid, nanowire and liquid.

The present paper focuses on poly-(9,9 dioctyl-fluorene), known as a conjugated polymer and a promising material for future light-emitting devices. A previous theory paper [2] drove us to the present large-scale calculations. A molecular dynamics simulation was carried out and is shown in Fig. 1 (a)-(c). In results, the relation is discussed between the non-ideal nanostructures with bending and twisting and the localized π wavefunctions of the highest occupied (HO) and lowest unoccupied (LU) levels, shown in Fig.1 (d)(e). The above discussion is general and will construct a systematic understanding of related conjugated polymers.

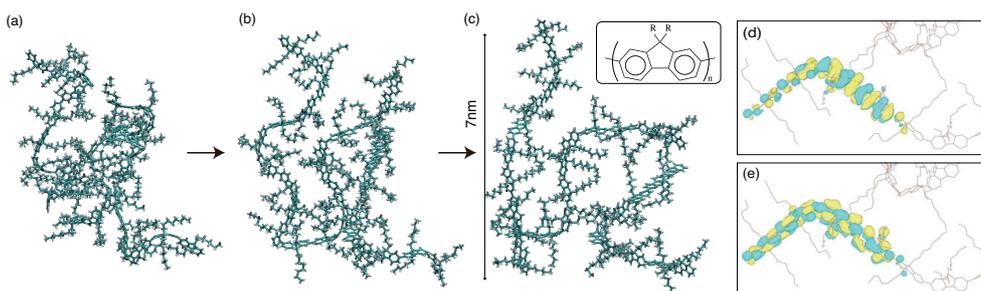


Figure 1: (a)(b)(c) Molecular dynamics simulation of poly-(9,9 dioctyl-fluorene). The monomer unit is drawn in the inset of (c). (d)(e) A close-up of the resultant structure with the HO and LU wavefunctions, respectively.

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Kinetic energy and chemical binding

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The H_2^+ molecule, containing only one electron, is an ideal system for understanding what happens when a chemical bond forms. The three important factors in forming this bond, namely the sharing of that electron, the polarization of atomic orbitals, and the contraction of the atomic orbitals are not complicated by many-body electron correlations.

Revisiting our old analysis[1] using converged basis sets[2,3] confirms its correctness. The changes from a hypothetical system "H plus a proton located at the correct H_2^+ bond distance" to the exact wavefunction of H_2^+ will be analyzed in terms of these three changes. The analysis uses the variational principle, and also the virial theorem, since the true H_2^+ function must minimize the total energy $E=T+V$ and the ratio $|V/T|$ must be 2. The results emphasize the importance of *kinetic energy* changes in causing bond formation. The conventional wisdom that increased electron density at the center of a bond causes a lowering of *potential energy* is demonstrably false; rather, the ultimate origin of H_2^+ 's lower potential energy is contraction towards both nuclei.

The insight gained from the study of H_2^+ will be shown to apply to other diatomics. Consideration of H_2 introduces e-e repulsions. New results will be presented for cases such as Be_2 , B_2 , C_2 , N_2 , O_2 , and F_2 , which add the complication of inner shells, as well as multiple bonds, non-singlet states, avoided crossings, or prominent dispersion interactions.

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Quantum Chemistry Beyond Atomic Orbitals and Slater Determinants

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Atomic orbitals and Slater determinants have supported the development of accurate quantum chemical theory since 1930s. They both are the pillars of the well-established "technology" of quantum chemistry that is used to rationalize and guide many experimental studies of today. However, augmenting and/or dismantling both of these concepts may be necessary for truly predictive electronic structure methods.

First, I will describe our work on the explicitly correlated (R12) electronic structure methods that go beyond purely orbital approximation and describe the correlation of pairs of electrons directly in terms of the interelectronic distances. The R12 methods attain higher precision (smaller basis set error) than the standard wave function methods by the virtue of a more efficient description of the Coulomb correlation at short interelectronic distances. Our focus will be primarily on the development of R12 methods for modeling multiple electronic states.

In the second part I will discuss methods that do not use atomic orbitals. Atomic basis sets are ubiquitous in electronic structure studies of molecules and are becoming popular for solids. In search for more universal and robust numerical representations we are exploring adaptive spectral-element basis sets that in principle allow to compute wave functions with guaranteed high precision. Our focus will be on computing two-electron correlated wave functions in such bases. To make such computations feasible it is essential to use low-rank (separated) representations for both operators and functions. We will present pilot MP2 computations with such an approach.

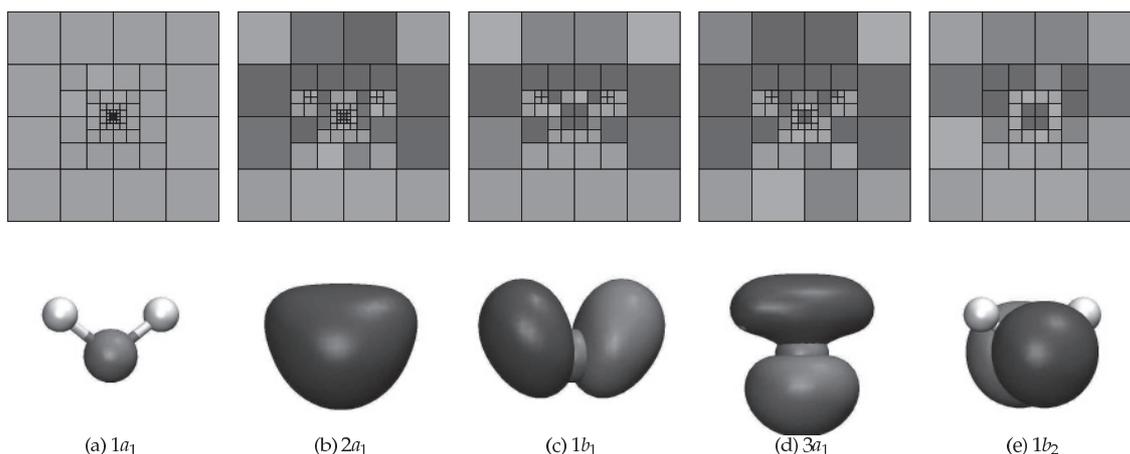


Figure 1: Multiresolution structure of the orbitals of the water molecule. The darkest volume elements have the highest separation ranks.

Why sp^2 Nanosilicons Should Not Form: Insight From Quantum Chemistry

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Quantum chemistry theory concerns a common essence joining topics that seem absolutely different at first glance. If radicals are well accepted characteristics for the molecular chemistry, dangling bonds and magnetic electrons are typical terms for the surface science and magnetism. However, actually, all the features are of the same origin and are connected with *odd electrons* of atoms that form either molecules or surfaces and magnetic solids. The term stands from the difference between the number of atom valence electrons and that of chemical bonds formed by the atom. The very fact of the odd electron availability is absolutely necessary for an atomic system to be peculiar, while not enough. The peculiarity implementation is directly dependent on the odd electron behavior, mainly, on their coupling. The latter is particularly evident when comparing basic regularities that govern nanoscience of carbon and silicon. Thus, in the case of carbonaceous substances such as ethylene or benzene and to some degree other aromatic molecules, odd electrons are covalently bonded while silicoethylene as well as siliceous aromatic molecules do not exist at all. The bare carbon surfaces are nonconductive and nonmagnetic while silicon surfaces are conductive and magnetic. sp^2 Nanocarbons are both chemical and physical reality while sp^2 nanosilicons do not exist, and so forth.

A unified theoretical and/or computational quantum chemical odd-electron approach has been suggested [1] making a unified consideration of different nanomaterials on the same conceptual basis as well as on the same computational footing. The current paper presents the approach application to the nanoscience of silicon involving electronic structure and magnetic properties of siliceous sp^2 analogues of carbon, such as fullerenes, nanotubes, and graphene, thus proving the impossibility of their existence [2-4].

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