

Modeling dimer structure for efficient singlet fission

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Using the simple model of singlet fission¹ we analyze the matrix elements contributing to the singlet fission rate, either in direct or in mediated mode in case of ethylene dimer. From the calculations of the matrix elements (using 6-311+G* basis set) we conclude that the direct mechanism is negligible comparing to the mediated mechanism in all studied geometries, which include parallel stack-slip structures, structures with one molecule rotated around the C=C bond and around the axis perpendicular to the molecular plane. The SF rate can be significantly enhanced by the stabilization of the ionic states. The model can be farther simplified by taking into account only the one-electron Fock integrals (or their empirical approximations), which dominate over the two-electron contributions.

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Complex Chemical Reaction Pathways Explored by Automatic Search Strategy

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A chemical reaction takes place on a potential energy surface (PES) representing the ground electronic state or cascades through several potential energy surfaces representing electronic excited states as well as the ground state. Potential energy surfaces are high-dimensional ($f=3N-6$) hypersurfaces in nuclear coordinates, where N is the number of atoms in the system considered. Minima (MINs) on a PES correspond to structures of reactants, products and intermediate species. First-order saddle points, often called transition states (TSs), on a PES are critical points for chemical reactions; their relative energies determine the rate of reaction. Finding TS as well as MIN structures is one of the most important tasks in the theoretical study of chemical reaction mechanisms. The seam of crossing between two PESs forms conical intersection (CI) hypersurface, and the minimum energy point on CI, called MECI, represents a critical point at which nonadiabatic transition between two PESs is most likely to take place. The Global Reaction Route Mapping (GRRM) strategy consists of two search methods, ADDF (anharmonic downward distortion following) and AFIR (artificial force induced reaction) methods, and allows automatic and unbiased determination of the critical structures on multidimensional potential energy hypersurfaces as well as on crossing hypersurfaces between two electronic states. ADDF starts from a MIN and walk up the PES to reach a TS, from which a minimum energy path leads to the next MIN. All the upward paths from a MIN are followed, and this is repeated for all MINs that are found. This method is efficient for automatic search of *intramolecular* reaction pathways. AFIR pushes two (or more) reacting molecules together and very efficiently finds approximate TS and MIN structures, from which true TS and MIN are optimized without force. Taking all random orientations of the reacting molecules, all the reaction paths are found automatically without prejudice. AFIR was originally intended for *intermolecular* reactions $A + B \rightarrow X (+ Y)$, but has been extended to cover *intramolecular* reactions.

Several examples of application of the GRRM strategy for complex chemical reaction systems will be presented.

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Toward understanding the bonding character and electric properties of coinage metals - lone pair ligands complexes.

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I. Interaction energies

We present CCSD(T) interaction energies and the bonding analysis for complexes of Cu, Ag, and Au with the lone-pair ligands, H₂O, OF₂, OMe₂, NH₃, NF₃, NMe₃, H₂S, SF₂, SMe₂, PH₃, PF₃, PCl₃, PMe₃ (ML complexes) [1-3]. We also study several π -donor complexes, like MC₂H₄, MC₂H₂ and their fluorinated and methylated analogs. Both, electron correlation and relativistic effects, are crucial in the bonding of all complexes. AuPH₃, AuPF₃ and AuPCl₃ complexes exhibit particularly large relativistic effects, 30 – 46 kJ/mol. Highest binding energies are computed for complexes with Au, followed by Cu and Ag. For all coinage metals the strongest interactions are computed for PX₃ ligands followed by SX₂, NX₃ and OX₂ ligands. Upon methylation the interaction energy rises significantly. Complexes with open shell ligands, like metal–thiol AuSCH₃ and AuCH₂ complexes form a separate class of exceptionally stable species. High stability of gold complexes is due to large relativistic enhancement of the electron affinity of Au. Along with the electron affinity of a metal we link the pattern of interaction energies in ML complexes with ionization potentials (IPs) of ligands. Strong interaction with P containing ligands is attributed to their lower IP and the lone pair \rightarrow metal electron donation accompanied with the back-donation. Energy data are accompanied with the Natural Bond Orbital (NBO) analysis. Computationally less demanding DFT method with the PBE0 functional provides correct pattern of interaction energies when compared with benchmark CCSD(T) results. We also provide similar analysis of metal clusters interacting with lone pair and π -donor ligands (M_nL complexes). It appears that the picture remains the same as with ML complexes.

II. Non-additivities of dipole polarizabilities in ML complexes

For a series of ML ligands we observe significant enhancement of parallel and to lesser extend perpendicular polarizabilities in comparison with the sum of polarizabilities of separated species. We link this enhancement with the mechanism of the interaction within ML complexes.

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Gas Absorption and Spin Transition of the Hofmann-type Metal Organic Framework: Theoretical Study

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Metal organic framework (MOF) or porous coordination polymer (PCP) is one of the most attractive materials in the modern chemistry. As well known, MOF is very useful for gas absorption and gas separation. Recently, its applications to catalyst and functional material also draw a lot of interests. Their functions are deeply related to their electronic structure. One of the good examples is the spin transition of the Hofmann type PCP induced by gas absorption.¹ When CS₂ is absorbed in this MOF, the spin state changes from high-spin to low-spin state. On the other hand, the similar CO₂ molecule does not induce any spin transition. In general, the gas absorption induces small changes in MOF but such small changes by the CS₂ absorption induce the spin transition interestingly.

To elucidate the reason why the gas absorption induces the spin transition, we need to evaluate how much strongly gas molecule interacts with the PCP, to clarify where gas molecule exists in the MOF, and also to evaluate the entropy change by the spin transition; remember that the spin transition occurs with entropy change.

One of the most important changes by CS₂ absorption is observed in the rotation of the organic ligand (pyrazine); it freely rotates in the high spin state without CS₂ but the rotation is suppressed by CS₂ absorption. This means that the rotational entropy decreases by the CS₂ absorption. We theoretically evaluated how much the entropy decreases by the CS₂ absorption and also how much the spin transition temperature changes by the entropy change.² Based on our computational results, we elucidated the mechanism of the spin transition.

The next question is why CS₂ can suppress the rotation of organic ligand but CO₂ cannot. To understand it, we need to evaluate the binding energies of these gas molecules with the MOF and the binding position. We successfully evaluated the binding energies of CS₂ and CO₂ with our new computational procedure.³ Our calculations clearly indicate that the CS₂ binding energy is much larger than the CO₂ one and the absorption position is different between them, as shown in Figure 1. The reason of these differences is understood in terms of difference in interaction.⁴

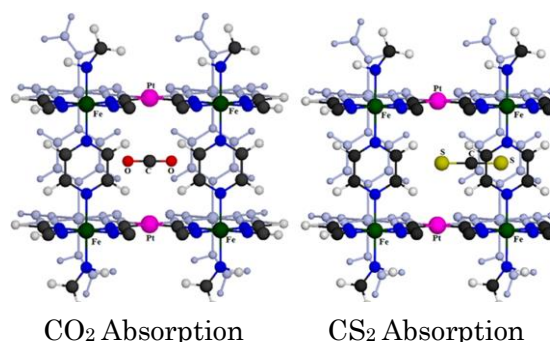


Fig. 1 CO₂ and CS₂ absorptions to the Hofmann type PCP.

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Ob-1

Computational Modeling of Inclusion Compounds Containing Dipolar Molecular Rotors

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We describe the use of computational modeling for optimizing the structure of dipolar rotors designed to form regular arrays with collective behavior. A computational investigation of rod-shaped dipolar molecular rotors inserted into the channels of hexagonal tri-*o*-phenylenedioxytricyclopophosphazene (TPP) has permitted a prediction of their supramolecular structures and their rotational barriers. The results for barriers in a series of 3,6-disubstituted pyridazines have been compared with values obtained by dielectric spectroscopy, the lowest of which are mere ~1.4 kcal/mol. The substituents serve the function of anchoring the rotor molecule firmly inside the channel. In some cases, more than one favored location of the rotor molecule in the channel exists and each is characterized by a different barrier size (Figure 1). The lowest barriers increase as the rotor molecule becomes longer. This correlation is believed to be due to the rotor's arc-like shape, which causes it to rub the interior walls of the TPP channel as it turns.

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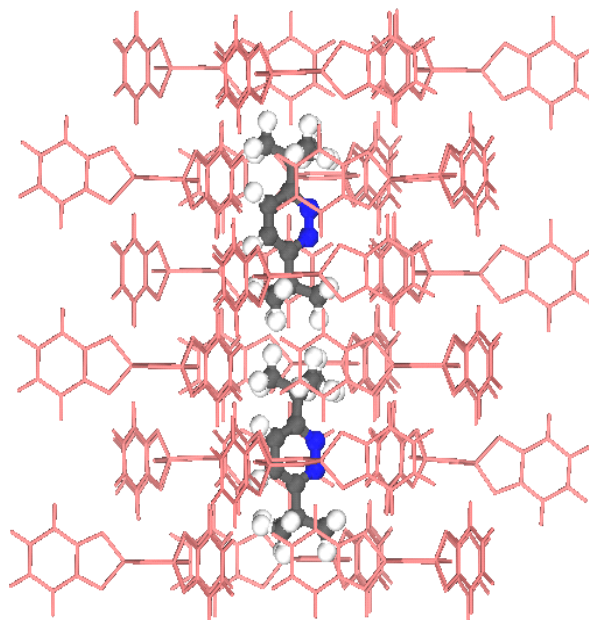


Figure 1. 3,6-Di-*t*-butylpyridazine included in two sites of a hexagonal TPP channel.

Analytic Second Derivatives in the Fragment Molecular Orbital Method

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I. Introduction

We developed the analytic second derivatives of the energy for the fragment molecular orbital (FMO) method. The accuracy of the Hessian is demonstrated in comparison to *ab initio* results for several molecular systems. By using the two residues per fragment division, we achieved the accuracy of 3 cm⁻¹ in the reduced mean square deviation of vibrational frequencies from *ab initio*.

II. Analytic second derivative in FMO

The total energy of two-body FMO (FMO2) is given by,

$$E = \sum_I^N E'_I + \sum_{I>J}^N (E'_{IJ} - E'_I - E'_J) + \sum_{I>J}^N \text{Tr}(\Delta \mathbf{D}^{IJ} \mathbf{V}^{IJ}) \quad (1)$$

where E'_X is the internal energy of fragment X ($X=I$ or IJ) and N is the number of fragments. The difference density matrix $\Delta \mathbf{D}_{IJ}$ is defined by,

$$\Delta \mathbf{D}^{IJ} = \mathbf{D}^{IJ} - (\mathbf{D}^I \oplus \mathbf{D}^J) \quad (2)$$

and \mathbf{V}_{IJ} is the environment electrostatic potential for dimer IJ . The second derivatives of FMO total energy (Eq.(1)) with respect to nuclear coordinates a and b is derived. We have developed program for the second derivatives with several FMO approximations and implemented it in a development version of GAMESS.

The accuracy is demonstrated in comparison of IR spectra of polyalanine with *ab initio* results (Table 1.) The FMO with two residues per fragment division, we achieved the accuracy of 3 cm⁻¹ in the reduced mean square deviations.

III. Conclusion

We have demonstrated that FMO hessian allows us to accurately simulate IR spectra and FMO hessian should be a useful tool for future studies of large molecular systems.

Table 1. Calculated IR spectra of alanine 10-mer at the RHF/6-31G(d) level. All frequencies are scaled by 0.8953.

isomer	AmideI C=O	AmideII N-H, C-N	Amide III N-H
FMO (two residues per fragment)			
α	1711.1	1557.6	1273.6
β	1696.3	1533.6	1209.6
e	1714.6	1500.8	1205.4
<i>ab initio</i>			
α	1711.3	1557.2	1272.1
β	1696.3	1532.8	1211.5
e	1715.7	1500.2	1205.11

α : α -helix, β : β -sheet, and e: extended conformer.

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Theoretical Approach to Nanomechanics of Modular Proteins

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Theoretical chemistry always has been used in solving practical problems. Atomic Force Microscopy (AFM) is mature experimental technique allowing for investigation of single molecules. Nanomechanical unfolding of individual biopolymers may be followed with piconewton resolution. In this presentation we will show how theoretical methods, such as all-atoms (AA) and coarse grained (CG) Steered Molecular Dynamics (SMD) simulations [1,2] contribute to understanding AFM force spectra of selected modular, adhesive proteins such as contactin CNTN4 [3,4] or neurexin NRX [4,5]. These proteins are present at the surface of neurons and contribute to the stability of the synaptic junction which in turn warrants proper functioning of brain. Some protein pairs linking pre- and post-synaptic neurons., for example neuroligins (NLG)-neurexins (NRX) present in the cleft, contribute to stability and signaling. Contactins (CNTN), present at Ranvier nodes, affect formation of a neuronal network. Genetic studies indicate that mutations in genes coding NRX or CNT protein lead to severe diseases such as autism. We hope that better understanding mechanical properties of synaptic junction proteins will help to find a remedy for some neurological disorders. In our lab we have combined single molecule AFM, and novel theoretical protocols to unfold CNTN4 [3,4], NRX [4,5], DNA helicase and cancer related protein gankyrin. We will discuss how such computer simulations of mechanical unfolding, despite the known problems with experimental timescale mismatch, provide information on intra-molecular interactions critical for protein functionality. Results of SMD unfolding of the whole CNTN4 protein (100 ns timescale, 10 modules, 100 katoms) and enforced dissociation of a NRX-NLG pair with Ca^{2+} ions will be presented. Theoretical approaches, together with AFM single molecule studies, provide new insights on the role of these medically important proteins.

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First-Principles Calculations on Switching Mechanism of a Molecule on Metal Surfaces

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I. Switching Mechanism of STM-controlled melamine on Cu(001) [1]

The origin of the selective switching of STM-controlled melamine on Cu(001) is investigated by using first-principles calculations. We evaluate the conformation dependent transport properties, the reaction path and the bias dependent energy barrier from first-principles by using the non-equilibrium Green's function formalism combined with density functional theory. Furthermore we calculate the inelastic tunneling spectroscopy (IETS) signal to identify the modes promoting the conformational changes of the molecule. The IETS signal also reveals why high-energy molecular conformations do not relax back to the lowest energy state even for large applied bias voltage. We then formulate a vibrational heating model to describe the STM-induced switching in this system, where the switching rates and their dependence on the voltage and current are estimated by using parameters extracted from our first principles results. We find that the different switching behavior for positive and negative bias originates from the different electronic properties of the empty and filled states of melamine on Cu, combined with changes of barrier height with the applied bias.

II. Switching Mechanism of C₆₀ sandwiched by Ag(100) electrodes [2]

Single molecule electronic devices, which consist of single molecule and metal electrodes, fascinate great interests for the potential of development of nanotechnology. As one of such molecular devices, single C₆₀ molecule trapped in a nano gap between silver electrodes is remarked as the switching of the conductance varying with the bias. The mechanism of the switching is investigated by using first-principles calculations. We find that the C₆₀ adsorbed structures on the Ag(100) surface have a different conductance depending on the orientation due to the shape of LUMO of C₆₀: lower conductance is shown facing two hexagons on the Ag surface and higher is shown facing one pentagon and hexagon. Assuming that the transition between the two states is triggered by the current-induced heating, the hysteresis in the switching processes is reproduced well. This plausible explanation of the switching mechanism shows a potential of designing new functional molecular devices.

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Oc-1

Evaluation of exchange integrals by Fourier transform of the $1/r$ operator and its numerical quadrature (Prospects for treatments of large molecules by methods giving results more accurate than the present DFT)

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Evaluation of exchange integrals persists to be a bottleneck in quantum chemistry. The purpose of this presentation is to show how this problem can be solved. It deals with the use of the old idea to replace the $1/r_{12}$ operator by the Fourier transform. If numerical quadrature is applied instead of derivation of formulas for analytical calculation, we obtain

$$\int f_1(\mathbf{r}_1) \frac{1}{r_{12}} f_2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{2\pi^2} \sum_p^{radial} \sum_j^{angular} \omega_p \omega_j (f_1(\mathbf{r}_1) \exp(-\mathbf{k}_{p,j} \mathbf{r}_1) (f_2(\mathbf{r}_2) \exp(\mathbf{k}_{p,j} \mathbf{r}_2),$$

where ω_p and ω_j are weights of roots of the numerical quadrature and expressions in parentheses are overlap integrals for functions f and plane-wave functions. The stimulus for this study arose from a need to evaluate efficiently exchange integrals of the type $(g_1(1)k_1(1)|g_2(2)k_2(2))$, where g 's and k 's, respectively, are gaussians and plane-wave functions. Evaluation of these integrals is still a bottleneck in *ab initio* calculations on electron scattering by polyatomic molecules. The objective of this contribution is to show that this way of evaluation of exchange integrals may be also beneficial for the mainstream quantum chemistry. For securing a needed accuracy of integrals the expansion of $1/r$ in plane-wave functions must be very large, but the formulas for overlap (gk) integrals and their analytical derivatives are simple and their evaluation is very fast. It will be shown that in spite of their large number considerable computer time saving may be achieved by making use of graphical cards. Evaluation of $(gk|gk)$ integrals is reduced to a plain multiplication $(gk)(gk)$ which is an ideal task for the use of gpu. This opens a way to treatments of electron scattering by larger molecules than it was possible so far. Possibly time saving may also be obtained in this way for the exchange energy in a pure Gaussian basis.

Entangled quantum electronic wavefunctions of the Mn_4CaO_5 cluster in photosystem II

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It is a long-standing goal to understand the reaction mechanisms of catalytic metalloenzymes at an entangled many-electron level, but this is hampered by the exponential complexity of quantum mechanics. Here, by exploiting the special structure of quantum states and using the density matrix renormalization group, we compute near-exact many-electron wavefunctions of the Mn_4CaO_5 cluster of photosystem II, with more than 10^{18} quantum degrees of freedom. Our calculations support recent modifications to the X-ray crystal structure. We further identify multiple low-lying energy surfaces, highlighting multistate reactivity in the chemistry of the cluster. Mn spin-projections for current candidates were determined directly from our wavefunctions

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DMRG-CASPT2 and DFT Studies on Reactive Intermediates in Non-Heme Diiron Enzymes

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Following our earlier computational study on spectroscopic properties of selected intermediates of the non-heme diiron Δ^9 -desaturase which allowed us to lock in the structure of the so-called **P** intermediate,[1] the results of the density matrix renormalization group (DMRG) complete active space (CASSCF) and second-order perturbational theory (CASPT2) calculations [2] are presented here. Model complexes representing the active site of non-heme diiron Δ^9 desaturase (Δ^9 D) at various stages of the catalytic cycle (including various transition state structures and reaction pathways) are used. Fairly large active spaces (up to 35 electrons in 26 orbitals) allow for the correlation treatment of most of the chemically important valence space. While the presented DMRG-CASPT2 calculations represent one of very few attempts to use the DMRG method in bioinorganic chemistry (for related work, see Ref. [3]), it is still not the method of practical use for production calculations on complex systems, such as the non-heme diiron sites. Therefore, we used the computed DMRG-CASPT2 data as the reference to benchmark the performance of popular DFT functionals for these computationally challenging systems. It is demonstrated that TPSS and TPSSH functionals may reproduce the activation barriers best and can be recommended as the sufficiently accurate functionals for studies of the reaction mechanism of Δ^9 D and related enzymes, such as methane monooxygenase (MMO) or ribonucleotide reductase (RNR).[4,5] Finally, we argue that DMRG-CASPT2 can be an important method in the accurate quantum chemical calculations of complex bioinorganic systems, such as the highly open-shell non-heme diiron sites.

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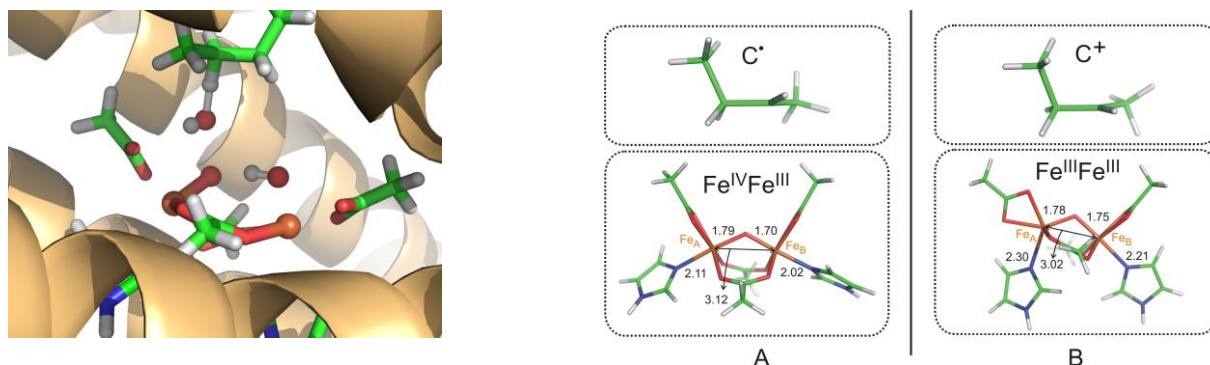


Figure: The active site of Δ^9 desaturase in the arrangement corresponding to the first transition state (C^\bullet -H hydrogen abstraction) and the schematic representation of the radical vs. cationic mechanisms. The electronic structure of these intermediates poses a great challenge for contemporary quantum chemical methods.

Towards Quantitative Analysis and Prediction of Protein-Protein Interactions

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To analyze and predict protein-protein complex structures, we have so far worked with the bioinformatics approach using empirical scores to perform rigid-body docking with a successive refinement procedure to allow molecular flexibility. We developed our own docking method, *surFit* (<http://sysimm.ifrec.osaka-u.ac.jp/surFit/>) [1-4], which semi-automatically docks a pair of protein molecular surfaces. The protocol successfully built many acceptable predicted complex structures with high qualities for the recent CAPRI targets [5]. However, there are several limitations by those bioinformatics approaches, in particular for revealing the quantitative features in protein-protein interactions.

To overcome the above problem, we have made an alternative approach by molecular simulation with *ab-initio* force field to draw free energy landscapes using all-atom protein models with explicit solvent models. For that purpose, we have developed the multicanonical molecular dynamics (McMD) method for enhanced structural sampling to draw free energy landscapes of the protein systems [6]. Using the McMD method, we have successfully obtained the free energy landscapes of the complex and free structures of intrinsically disordered proteins (IDPs) with and without their partner receptor proteins, respectively, for the NRSF-Sin3 [7] and pKID-KIX [8] systems. Very recently, the McMD method was applied to docking simulation of the engineered endothelin-1, successfully providing the free energy landscape for formation of the homo-dimer [9].

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Molecular Science for Liquid Interfaces

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Heterogeneous phenomena related to liquid interfaces are relevant to many fields of chemistry and physics, including bubbles, aerosols, electrochemical reactions, membranes, separation, mass transfer, etc. However, microscopic understandings of these heterogeneous phenomena have been quite limited so far. This is mainly due to scarcity of proper experimental probe techniques applicable to these liquid interfaces, which should have acute sensitivity and selectivity to the liquid interfacial species. Most of the experimental techniques to probe the molecules in bulk liquids or on solid surfaces are not suitable to the liquid interfaces. Therefore, molecular simulation has played important roles to investigate the liquid interfaces in molecular details.

Among the experimental probes of liquid interfaces, the vibrational sum frequency generation (SFG) spectroscopy is a general and powerful means, since it can selectively reveal the vibrational spectra of molecules at the liquid interfaces. Though the SFG spectroscopy is quite sensitive to the interfacial species, the observed spectra are often hard to be interpreted. Thus reliable theoretical analysis methods have been strongly desirable to fully extract the experimental information from the surface-sensitive spectroscopy. We have proposed and developed the theory and computational methods of SFG spectroscopy in combination of *ab initio* molecular modeling and molecular dynamics simulation for the first time. This talk will briefly summarize our recent efforts toward microscopic understandings of liquid interfacial phenomena in collaboration of surface-sensitive spectroscopy and molecular simulation.

Molecular Excited States in Proteins and Solutions

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Solvatochromism and fluorescent solvatochromism are well-known phenomena, and there are rich accumulations in experimental publications [1]. Color tuning in biological systems could also be solvatochromism but with a specific environment where anisotropic molecular interactions play important roles. In visual pigments and fluorescent proteins, controlling photo-absorption/emission energy of chromophore is the essential to furnish a protein with the photo-functionality. Depending on the molecular interactions with protein environment, these chromophores show a variety of photo-absorption/emission energies.

We have studied biological color tuning with the SAC-CI/MM calculations [2] in which MM description was adopted for the environmental effect. This classical scheme works very well for explaining the spectral tuning mechanism in photobiology, human color vision, firefly luciferin, and fluorescent proteins [2].

On the other hand, environmental electronic structure effect becomes important in some cases. To figure out the origin of the QM effect, we adopted a MO localization scheme [3] that can transform MOs into predefined shapes and regions. With the LMO representation, the role of the environmental electronic effect was interpreted in terms of amino acids' contributions such as local excitations and charge-transfers between chromophore and amino acids. In addition, the analysis also suggests the structure of the excited-state wave function for including the environmental electronic effect [3]. We examined numerical performance of this fragment-based and interaction-based truncated CIS wave function and showed a reasonable accuracy of this chemical-intuitive wave function [4].

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Fragment Molecular Orbital Study for Biomolecular Systems

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Since the ab initio fragment molecular orbital (FMO) method has been originally introduced by Kitaura in 1999, many contributors have developed FMO-based methodology and applied them for electronic structure calculation of bio-macromolecules [1,2]. We have developed our original FMO software, ABINIT-MP and its dedicated GUI program BioStation Viewer [3], and applied them for molecular interaction analysis by evaluating inter-fragment interaction energy (IFIE). One promising target of FMO calculation is receptor-ligand interaction analysis in a rational drug design [4]. Based on the four-body expansion of FMO method with an appropriate fragmentation, a quantitative estimation of interaction energy is possible between each functional group in a pharmacophore [5,6], which can be applied to structure-based drug design (SBDD). In addition, partial geometry optimization [7,8] of protein–ligand complex was performed at the MP2/6-31G* level. The protonation states and tautomer of Histidine (HIE, HID, HIP) were also considered for the calculations. In this talk, we introduce several applications of FMO method for receptor-ligand interactions, such as estrogen receptor (ER) and Influenza virus neuraminidase (NA), in the context of SBDD.

Acknowledgements

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Computer-chemistry understandings on worldwide anxious chemical reactions

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I. Introduction

The influences of trace of radioactive tritium in the ecosystem and how to improve the stability of largely produced silicon solar cell modules were studied using density functional theory. As for the tritium issue, the reactions of hydroxyl radical are simulated whether it reacts with DNA. As for the silicone cell issues, the contribution of photo-activated oxygen is simulated to react gradually with the organic materials used on silver grid faces in the modules.

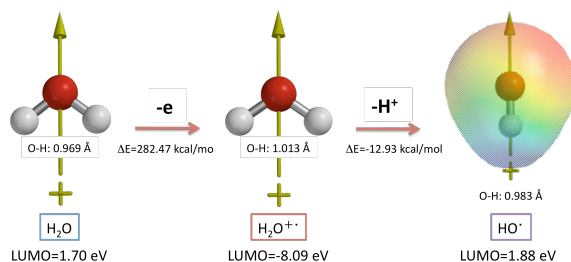
II. Results. (1) *Carcinogenic hydroxyl radical formation:* Tritium continuously releases the electromagnetic wave energy (18keV, 450 times stronger than UV light of 4eV), ejecting electron from water molecules, and the one-electron oxidation of water gives hydroxyl radical (Scheme 1). To know the anxious effect of hydroxyl radical on the ecosystem as internal exposure, the interactions of key parts of DNA with hydroxyl radical was simulated (Scheme 2). It is clear that hydroxyl radical strongly interacts with cytosine and thymine groups in DNA, which facts rationalize gradual damage of gene systems.

(2) *Oxidative degradation of organic materials facing the silver grid in the silicone cell modules:*

The energy structures of activated oxygen ($^1\text{O}_2$) are compared with ground state oxygen ($^3\text{O}_2$) and ozone on the basis of DFT (Table 1). $^1\text{O}_2$ has the LUMO potential comparable to that of ozone, and the oxidative reaction with EVA fragment is successfully simulated to give acetic acid, explaining the degradation as due to corrosion of the silver grid to AgO.

Acknowledgements; Mr. N. Uchida and M. Takahashi of Wavefunction Inc., Tokyo office.

Scheme 1. Simulation of one-electron oxidation of water to hydroxyl radical under irradiance of strong electromagnetic wave of tritium (β -ray:18keV).



Scheme 2. Simulation for the interaction of DNA key parts with OH radical.

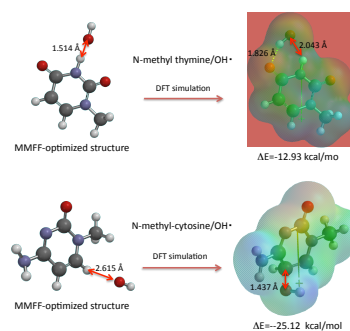


Table 1. Comparison of DFT-based energy structures of oxygen and ozone

Name	E (kcal/mol)	E LUMO (eV)	E HOMO (eV)	O-O distance (Å)
Ground state $\text{O}_2(^3\text{O}_2)$	-94327.33	5.35	-8.39	1.215
Activated $\text{O}_2(^1\text{O}_2)$	-94288.04	-4.88	-6.81	1.216
Ozone (O_3)	-141444.78	-5.02	-9.12	1.264

How accurate are "gold standard" CCSD(T)/CBS interaction energies?

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The CCSD(T) method stands out among various coupled-cluster (CC) approximations as the “golden standard” in computational chemistry and is widely and successfully used in the realm of covalent and noncovalent interactions. The CCSD(T) method provides reliable interaction energies, but their surprising accuracy is believed to arise partially from an error compensation. The convergence of the CC expansion has been investigated up to fully iterative pentuple excitations (CCSDTQP); for the smallest eight electron complexes the full CI calculations have also been performed. We conclude that the convergence of interaction energy at noncovalent accuracy (0.01 kcal/mol) for the complexes studied is reached already at CCSDTQ or CCSDT(Q) levels. When even higher accuracy (spectroscopic accuracy 1 cm^{-1} - 3 cal/mol) is required, then the non-iterative CCSDTQ(P) method could be used.

Helmholtz Energy Change between Neutral and Zwitterionic Forms of Glycine in Aqueous Solution

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Glycine is a molecule that can form an intramolecular hydrogen bond, and may convert from a neutral (N) form to a zwitterionic (Z) form in aqueous solution. Since the conversion between N form and Z form of glycine can be considered as a prototype of the tautomerization of amino acid, the process and the energy profile of the N-Z conversion have been extensively studied from both of theoretical and experimental points of view. Experimentally, the free energy of Z form has been estimated to be 7.27 kcal/mol lower than that of N form.

Solvation effect cannot be elucidated simply by taking account of only a few solvent molecules in a few selected configurations of the solvent, even if high level of theory is used. It is necessary to treat many solvent molecules and many solvent configurations explicitly. This is why several methods such as QM/MM-MC method have been adopted.

Here, the following three points are addressed to evaluate quantitatively the free energy change of glycine tautomerization in aqueous solution. The first is how to obtain a solute structure in aqueous solution which may be largely different from that in the gas phase. The second is how to include close surrounding water molecules in QM subsystem in free energy calculations. The last is how to treat the solute with higher level QM in the free energy evaluation. Thus, we present the multistage evaluation of Helmholtz energy change.

In aqueous solution, our computational Helmholtz free energy of the Z form of glycine is lower than that of the N form by 7.25 kcal/mol, and it compares well with the experimental value. The multistage strategy, which we present here, is a practical and promising way to evaluate the Helmholtz free energy change in solution quantitatively; enough solvent configurations are generated at MM level, a stable solute geometry is optimized fully in aqueous solution, solvation free energy is evaluated from selected configurations treating the solute with directly solvating water molecules at HF level, and the solute energy change is evaluated at higher level of theory.

Organic Open-Shell Systems as Models for Molecular Spin Quantum Computers and Spin Manipulation by Pulsed ESR Technology

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Considerable research on quantum computing and quantum information processing (QC/QIP) has been conducted from the theoretical side for the last decades. Among physically realized qubits, molecular electron spin-qubits have been the latest arrival, although electron spins have naturally been anticipated as typical matter spin-qubits. In this talk, we present electronic structures of molecular spin qubit systems for QC/QIP and pulsed Electron Magnetic Resonance-QC experiments for manipulating the molecular spin-qubits from the experimental side[1-4], emphasizing that we afford the bi- and tri-partite molecular-spin manipulation of electron and nuclear spin-qubits and the implementation of the phase-driven inter-conversion of the quantum states which consists of the electron-nuclear spin qubits.

Cw/pulsed ESR and Electron-Nuclear DOuble Resonance (ENDOR) spectroscopy has been applied to X-ray irradiated malonic acid and partially substituted diphenylnitroxide (DPNO) in single crystals in order to characterize and manipulate both electron and nuclear spins. Magnetic parameters of both the molecular systems were precisely determined, providing a testing ground of quantum chemical calculations. A time proportional phase increment (TPPI) technique was effectively exploited to evaluate the electron and nuclear spin state. The TPPI technique in pulsed ENDOR spectroscopy is known for the separation of multiple quantum coherences[5]. The phase interferogram signals of electron and nuclear spins in both the generated malonyl radical and DPNO systems were observed by using the TPPI technique. The observation of the interconversion enables us to directly prove 4π periodicity due to the spinor property of electron or nuclear spin-1/2. The spinor of the electron spin has been observed for the first time[2]. We have also manipulated a biradical system by ELDOR(ELctron-electron DOuble Resonance)-based spin technology, which is the smallest model for genuine molecular spin quantum computers. It is indicated that the ELDOR technique is available for the implementation of quantum gates.

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Four-Component Relativistic DFT Calculations of NMR Shielding Tensors for Paramagnetic Systems

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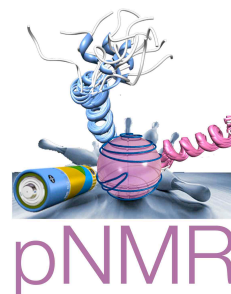
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I. Abstract

When going down the periodical table, EPR and NMR parameters become much earlier affected by relativistic effects than the geometry of molecules. While some problems can be safely treated by approximate relativistic approaches, there is still a need for fully relativistic calculations of magnetic resonance parameters. With this in view a new four-component relativistic method for the calculation of NMR shielding constants of paramagnetic systems has been developed and implemented. The method uses Kramer unrestricted non-collinear formulation of density functional theory (DFT). It provides the best DFT framework for property calculations of open-shell doublet species. Within this approach evaluation of paramagnetic NMR tensors (pNMR) reduces to the calculation of the electronic g-tensors, hyperfine coupling tensors and NMR shielding tensors for open-shell system. The use of both restricted kinetically and magnetically balanced basis sets along with gauge-including atomic orbitals ensures rapid basis set convergence. Developed approach is exact in the framework of the Dirac-Coulomb Hamiltonian, thus providing useful reference data for more approximate methods. Pilot benchmark calculations on Ru(III) complexes demonstrate a good performance of the method in reproducing experimental data and also its applicability to chemically relevant medium-sized systems [1].

II. Acknowledgement

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Recent progress in relativistic four-component calculations in NMR indirect nuclear spin-spin coupling constants

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I. Abstract

A new efficient approach for calculating indirect nuclear spin-spin coupling tensors at the four-component level will be presented.[1] The method has been developed and implemented in the context of the matrix Dirac-Kohn-Sham formulation. This approach makes use of the idea of Laikov [2], who proposed to employ fitted total and spin electron densities in the evaluation of matrix elements of the exchange-correlation potential. Performance of the newly developed method has been thoroughly tested by comparison with a reference method with evaluating the matrix elements of exchange-correlation kernel by numerical integration. The benchmark calculations were carried on a number of chemical species ranging from small molecules like the XH₄ (X = C, Si, Ge, Sn and Pb) to halogenated mercury compounds. The new method was found to yield results highly consistent with their counterparts obtained by the reference method and available experimental data. At the same time the new approach exhibited significant speedup of the computations.

II. Acknowledgment.

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Divide-and-conquer method for linear-scaling electronic structure calculations

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I. Introduction

For treating large systems in quantum chemistry, a number of linear-scaling computational methods have been proposed to date. A simple method to achieve linear-scaling computation is fragmentation of the system under consideration. Since 2009, we have distributed a fragmentation-based linear-scaling quantum chemical calculation program based on the divide-and-conquer (DC) method [1] as a part of GAMESS package [2]. Unlike the other fragmentation methods, this program is capable of treating large delocalized systems. Recently, this program was rewritten for efficient computation with K supercomputer. In this presentation, we will show our recent extensions of this program, which include the computation of dynamic hyperpolarizability [3] and the evaluation of the energy gradient at the level of MP2 [4].

II. Dynamic hyperpolarizability

We have developed the dynamic hyperpolarizability calculation scheme based on the DC method. This scheme also achieves the linear-scaling computation with respect to the system size. Fig. 1 shows the calculated macroscopic second-harmonic generation (SHG) coefficient, d_{22} , of polyvinylidene fluoride (PVDF), $\text{H}-(\text{CH}_2-\text{CF}_2)_n-\text{H}$, at wavelength $\lambda = 1060$ nm. The DC results accurately agree with the conventional ones for small systems. The linear extrapolation to $1/n \rightarrow 0$ yields $d_{22} = 0.209$ pm/V, which exhibits good agreement with the experimental report of 0.22 pm/V. Since the dynamic optical properties implicitly include the information of excited states, it is possible to evaluate excitation energies by finding poles of an optical property with respect to the wavelength of light.

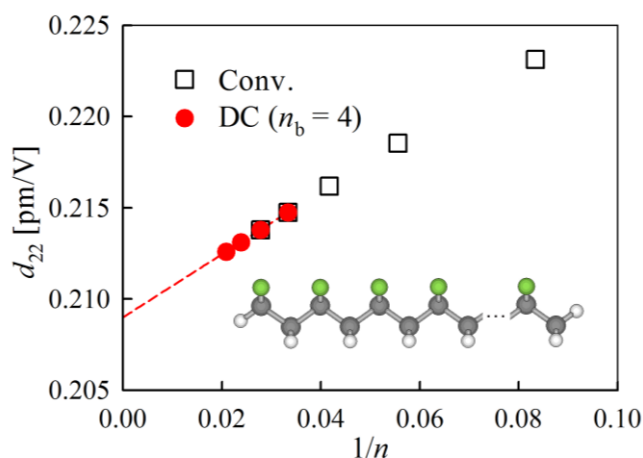


Fig. 1. System-size dependence of d_{22} of PVDF evaluated from $\beta(-2\omega; \omega, \omega)$ by (DC-)LC-BOP/6-31G** [3].

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Theoretical Study of Reactions of Nitriles with Organotransition Metal Complexes

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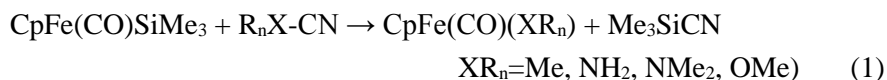
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The results of theoretical calculations for two types of reactions of nitrile molecules with organotransition metal complexes, the cleavage of X–CN σ bonds by an Fe silyl complex and the formation of pyridines from nitriles with cobaltacyclopentadiene.

Cleavage of inert bonds such as C–H, C–C, C–N, and C–O bonds could provide new species that are useful in organic synthesis, and a number of experimental and theoretical studies focusing on cleaving the inert bonds in the presence of transition metal complexes have been published. The cleavage of X–CN σ bonds is one of them. The results on the reaction mechanisms for Me–CN, R₂N–CN (R = H, Me) and MeO–CN bonds cleaved by an unsaturated iron(II) silyl complex, CpFe(CO)SiMe₃ are presented.[1]



The B3LYP calculations showed that, triggered by the silyl group migration to the nitrile N atom, the cleavage of these σ bonds can proceed easily. Analysis of the electronic process occurring in the reactions shows that these bonds are efficiently cleaved by its interaction with the vacant coordination site of the Fe atom or ring strain in three-membered ring produced during the reactions.

The reactions of nitriles and alkynes with cobaltacyclopentadiene, CpCo(C₄R₄), are an important step in the formation of aromatic compounds such as pyridine and benzene. There are some possible reaction pathways for these reactions, because organic molecules would insert into the Co–C _{α} bond or conduct [4+2] cycloaddition. On the other hand, cobaltacyclopentadiene is coordinatively unsaturated and it is more stable in the triplet state than in the singlet state, whereas the insertion and cycloaddition take place more easily in the singlet state. Accordingly, a change in the spin state may be involved during the courses of the reactions. Our calculations clarified that the mechanism shows two-state reactivity. We also found that an electro-positive molecule favors [4 + 2] cycloaddition and an electro-negative molecule favors insertion into the Co–C _{α} bond.

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Relativistic effects in the topology of electron density and properties of 2-component spin densities

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Abstract

Relativistic effects in the topology of electron density will be considered. Electron density and Laplacian maps of Ruthenium and Osmium complexes as well as bond critical point characteristics will be considered [1]. In addition, a concept for obtaining the weighted effective density for the Gaussian nucleus model will be presented [2], including the chemical shifts of Cu⁺, Ag⁺ and Au⁺ atoms and HgF₂ relative to neutral atoms. All relativistic calculations are performed at the Infinite Order Two Component level of theory (IOTC) [3]. This is why the electron density, Laplacians and the effective density have to be corrected for picture change error [4].

Second topic is the spin density at the 2-component level of theory, including Hamiltonians which account for spin-orbit effects. Besides spin contamination, different spin density models will be presented for several model systems [1,5-9], e.g. H₂O⁺, HCl⁺, phenoxy radical and/or [OsCl₅(Hpyr)]⁻.

Acknowledgements

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Theoretical Study on the Optical Properties of Open-Shell Singlet Molecular Systems

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Recently, the structure–property relationships in open-shell singlet molecular systems like polycyclic aromatic hydrocarbons (PAHs) have attracted a great deal of attention in materials science and engineering [1]. Several unique optical and magnetic properties of these systems are predicted to originate in the open-shell singlet ground states, which are characterized by small energy gap between the HOMO and LUMO and/or small singlet–triplet energy gap. As a hot topic of this issue, we have theoretically proposed a novel class of nonlinear optical (NLO) systems based on open-shell singlet molecules [2], which exhibit larger second hyperpolarizabilities γ (the third-order NLO properties at the molecular scale) than closed-shell and pure diradical molecules. This prediction was substantiated by adopting ab initio molecular orbital and density functional theory (DFT) calculations on several real and model diradical molecular systems [2] (see Fig 1 for example). These theoretical results have been supported by recent experiments on the two-photon absorption of several compounds [3]. In this talk, we briefly introduce the relationship between the diradical character (y) and excitation energies/properties based on the valence configuration interaction two-site diradical model [2] and then provide the diradical character dependence of γ . We also introduce a recent extension of our theory to asymmetric open-shell singlet systems, which have a possibility of further

enhancing the NLO properties as compared to the symmetric open-shell singlet systems [4]. In addition, the diradical character based molecular design guidelines are found to be applicable to not only the highly efficient NLO materials but also to the excitation energy conversion systems such as singlet fission molecules [5] because the diradical characters govern the relative excitation energies and properties of different spin states of electron-correlated molecular systems, and they are also related to conventional chemical concepts like aromaticity and resonance structures in the ground state.

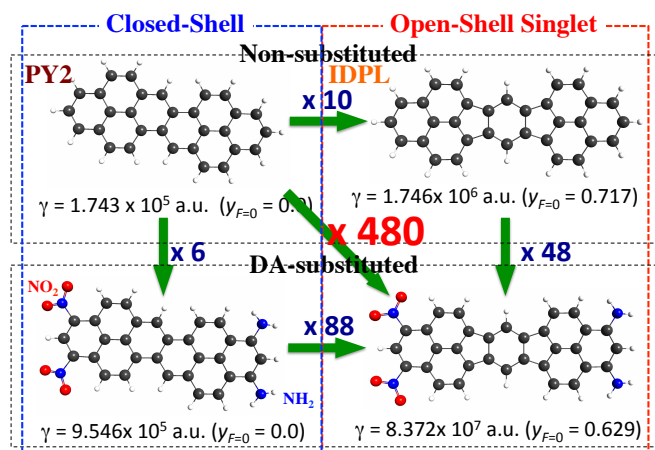


Fig. 1. γ and y values for symmetric/asymmetric closed-/open-shell singlet systems

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Systematic Exploration of Transition State Structures for Organic Reactions by the Artificial Force Induced Reaction (AFIR) Method

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I. Introduction

Finding transition states (TSs) is a highly important task in theoretical studies on the mechanism of chemical reactions. By locating a TS for a reaction, the structure of the TS can be visualized. The intrinsic reaction coordinate (IRC) can be calculated as the corresponding reaction path from the TS, and one can understand the movements of atoms along the IRC path. Its reaction barrier can also be estimated from the energy profile along the IRC path. Hence, numerous reaction mechanisms have been elucidated by calculations of TSs.

On the other hand, finding TSs is one of the most difficult tasks. This is because a good initial guess is required to locate a TS by a standard geometry optimization method. Although geometry optimizations have been successful in many previous studies on reaction mechanisms, it is a hard task to locate all relevant TSs in complex mechanisms involving many reaction steps and/or flexible parts controlling selectivity. In this talk, the artificial force induce reaction (AFIR) method is introduced as a powerful and efficient tool for finding TSs automatically [1]. Representative applications to some difficult cases to which standard geometry optimizations may not be readily applicable will also be presented [2-4].

II. Method

In the AFIR method, two or more reactants are pushed together by applying artificial force [1]. It uses a special function, called AFIR function, and this function controls the direction of artificial force. Starting from random orientations and directions among given reactants, TSs for their associative reactions can be found automatically. By considering a sufficient number of initial orientations and directions, all required TSs can be obtained.

III. Results

The following three examples are presented: (1) Eu^{3+} -catalyzed Mukaiyama-Aldol reaction in water [2], (2) Vinylogous Mannich-type reaction activated by a water molecule [3], and (3) H-H bond activation catalyzed by small gold clusters [4]. In all these cases, exhaustive TS searches were essential in correct understanding.

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Molecular dynamics with non-adiabatic and spin-orbit effects

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Molecular dynamics (MD) represents an important tool for modeling of the behavior of molecular systems in time. When applied to problems from photochemistry, a treatment of excited states and crossings between different potential energy surfaces has to be incorporated in the MD scheme.

We present efficient techniques which allow to approximately compute the non-adiabatic couplings and perform non-adiabatic (surface hopping) MD with CASSCF, MRCI, TDDFT, and ADC(2) methods, and assess this approach on the examples of photoisomerization of azobenzene and internal conversion of excited adenine.

Most recently, we have implemented in the Newton-X MD code the surface hopping on potential energy surfaces resulting from spin-orbit splitting, which allows to treat also

Ab Initio SemiClassical Molecular Dynamics (AI-SCMD) of nonadiabatic photochemical reaction

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The modern technology and the advent of the controllable synthesis of complicated molecules open exciting perspectives for the use of the quantum effect. In response to the modern chemistry, we really need new theoretical ideas to deal with the multi-dimensional system or large systems. One of the solutions is a SemiClassical Initial Value Representation (SCIVR) given by Miller [1] and also Herman-Kluk proposed (HK) frozen Gaussian wavepacket time-evolution [2] as one of the SCIVR approaches; which is employed in this paper.

On the other hand, Trajectory Surface Hopping method (TSH) can satisfy our need for describing the nonadiabatic reaction composed of many degrees of freedom. The HK method can give us a phase-information, while the TSH approach is more convenient than the HK method. Furthermore, Zhu-Nakamura theory is the exact formula to describe nonadiabatic transition. In this paper, we introduce our recent result using these approaches; (i) *ab initio* SCMD with including the nonadiabatic phase-information computed by the R-matrix expansion around the pseudo-crossing, and (ii) *ab initio* SCMD with ZN-TSH method [3]. Our idea would be discussed with photolysis reaction of H₂S and so on.

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Ab initio Molecular Dynamics Approach to Tunneling Splitting Calculations

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In an ab initio molecular dynamics (AIMD) approach, nuclear motion is treated by classical mechanics, so some additional treatment is required to take into account nuclear quantum effects such as tunneling. Makri and Miller developed a semiclassical method to evaluate quantities related to tunneling in molecular dynamics simulations [1]. Thompson and coworkers [2] applied the Makri-Miller method to explore tunneling dynamics for polyatomic molecules with simple potential functions of full dimensionality. In order to examine the effects of accuracy of potential energy surfaces on dynamics, we performed the semiclassical trajectory simulations for malonaldehyde, using global potential energy surfaces with full dimensionality generated by the interpolation of ab initio data [3]. It was shown later that the semiclassical instanton method with highly accurate ab initio electronic structure calculations can reproduce the tunneling splitting in malonaldehyde very accurately [4].

Recently we have implemented the Makri-Miller method to our AIMD code to develop a practical way for investigation of tunneling effects in chemical reactions [5]. Each time the turning point for tunneling is detected along the AIMD trajectory, the tunneling amplitude is evaluated on-the-fly through ab initio electronic structure calculation. The method was applied to umbrella inversion of ammonia and intramolecular hydrogen transfer in malonaldehyde in the electronic ground state, and also applied to intramolecular hydrogen transfer in tropolone in the electronic excited state. In applications to malonaldehyde and tropolone, effects of multi-dimensionality were examined by assigning quantum zero-point vibrational energies only to significant vibrational modes and changing the amount of energy given to other degrees of freedom. The detailed analyses will be discussed in the presentation.

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An all-atomistic molecular dynamics calculation study of virus using K-computer

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For over a half century, supercomputers have been making progress steadily in their performances. For example, the K-computer in Kobe, composed of 82,944 compute nodes, has a performance of 10 PFlops. Using this kind of high-performance supercomputers, MD calculation is extending its field to very large molecular systems, the number of atoms being in the order of ten million. In the present talk, our recent MD calculations for very large systems of viruses are presented.

A very highly parallelized general purpose MD simulation program MODYLAS[1] has been developed for the K-Computer. The MODYLAS may use 2^{16} (65,536) nodes simultaneously, i.e. totally 2^{19} (524,288) cores, or more. It is equipped by the fast multipole method (FMM) to evaluate the long-ranged forces, avoiding FFT needed in the conventional PME. Our benchmark test using 2^{16} (65,536) nodes showed that the parallelization efficiency is excellent even in the case of this very highly parallelized MD calculation. It can complete one MD step for a system composed of ten million atoms in 5 ms.

Polio virus capsid is composed of 240 proteins. The diameter is about 30 nm. The system may be constructed in computer by about 6.5-10 million atoms including solvent water. The K-computer is capable of executing MD calculation of this very large system. The calculations have been performed focusing our attention on the stability of the capsid and the initial process of infection, i.e. recognition by a receptor. Here, we show a sophisticated molecular setup of the viral capsid that stabilizes itself in solution. The findings must be a key to understanding molecular mechanism of self-assembling and uncoating processes of the viral capsids containing single-stranded RNA where extra chemical energy is not needed. Further, based on the present information, we discuss about possible molecular designs for a stable empty capsid of practical use as ideal vaccine and highly selective DDS carrier. We also found equilibrium very rapid spontaneous exchanges of water molecules between the inside and outside of the capsid. In spite of the exchanges of water molecules, the capsid does not allow the ions to pass through, indicating that the capsid works as a semi-permeable membrane. These explain the tolerance of poliovirus to very high pressures and environmental solutions such as fresh water and even sewage and, at the same time, we can understand its deactivation by exsiccation in terms of evaporating water.

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Structure of Analytical Wave Function of Helium Atom

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Schrödinger equation for the helium atom is one of the simplest problems in quantum mechanics (QM). The problem was formulated [1] soon after the discovery of QM. Highly accurate numerical estimates of the ground state energy and the ground state wave function are available [2] but the details of the analytical structure of the wave function have not been explicated until today despite of substantial effort in this direction. [3, 4, 5, 6, 7] The current talk is supposed to review the situation in the field and suggest a possible line of further development using the concept of homogeneity and inversion of the kinetic energy operator. Note that discovering a compact analytical ansatz for the helium wave function may have far-reaching consequences for whole field of quantum chemistry, because the many-electron wave functions of atoms and molecules may have much simpler structure in the helium-like geminals rather than in the hydrogen-like orbitals.

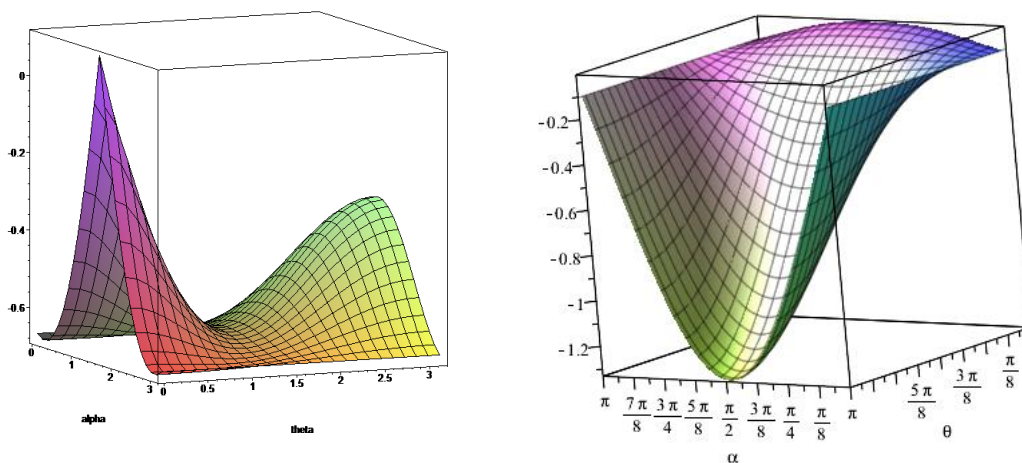


Fig. 1. Two components of the analytical wave function of the helium atom with homogeneity 2.

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Improved Density Dependent Correction for the description of London Dispersion Forces

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The Tkatchenko–Scheffler (TS) method [1] for calculating dispersion correction to standard density-functional theory has proven to be successful in number of practical applications including structural optimizations of molecular crystals and layered materials [2]. Unfortunately, this method fails to describe the structure and the energetics of ionic solids. Although van der Waals interactions are usually not considered as important for this class of materials, one should bear in mind that there are mixed systems, like molecular adsorbates on the surface of ionic solids, where it is indispensable to include dispersion corrections in a single generic procedure valid for all bonding situations. In this contribution, we will analyze the reasons for the above-mentioned failure of the TS method and suggest solution that extends applicability of the method to ionic materials. The performance of the improved TS method [3] will be demonstrated on selected real-world problems such as adsorption of small molecules in zeolites and structure and energetics of Li-intercalated graphites.

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Characterization of Multielectron Dynamics in Molecules: A Multiconfiguration Time-dependent Hartree-Fock Picture

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We have theoretically investigated the dynamics of molecules in intense laser fields. Analysis and investigation of ultrafast electron dynamics of molecules require accurate theoretical descriptions of electronic dynamics in the nonperturbative regime of light-matter interaction. To numerically solve the time-dependent Schrödinger equation of the system as accurately as possible, we have developed time-dependent multiconfiguration theory for electronic (ionization) dynamics [1,2]. In this theory, a time-dependent N -electron wave function $\Phi(t)$ is expanded as a linear combination of Slater determinants $\{\Phi_I(t)\}$ in which the molecular orbitals (MO) and the configuration interaction (CI)-coefficients $\{C_I(t)\}$ are both treated as time-dependent ones:

$$\Phi(t) = \sum_{I=1}^M C_I(t) \Phi_I(t) \quad (1)$$

where M is the number of Slater determinants. The equations of motion for MOs in the coordinate representation (grid point representation) and CI-coefficients were derived on the basis of the Dirac-Frenkel time-dependent variational principle [2].

Profound understanding of nonstationary processes in quantum many-body systems is indispensable for further development of the new research field of light-matter interaction. To characterize the energetics of individual electron configurations $\{I\}$, we defined the energies $\{E_I(t)\}$ by dividing the total energy $E(t)$ including the light-matter interaction as [3,4]

$$E(t) = \sum_{I=1}^M |C_I(t)|^2 E_I(t) \quad (2)$$

We have also proposed an approach of dividing $E(t)$ into the “chemical potentials” $\mu_j(t) \equiv \partial E(t) / \partial w_j(t)$ for natural orbitals $\phi_j(t)$, where $w_j(t)$ is the occupation number for $\phi_j(t)$:

$$E(t) = \sum_{j=1}^{N_o} w_j(t) \mu_j(t) \quad (3)$$

where N_o is the number of molecular orbitals used in $\Phi(t)$. By analyzing the near-IR induced electron dynamics of LiH, we found that a valence electron exchanges energy with inner shell electrons and that the change in $\mu_j(t)$ correlates with the dynamical motion of $\phi_j(t)$.

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Time-dependent MCSCF methods for multielectron dynamics in intense laser fields

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We propose a new time-dependent multiconfiguration wavefunction method for electron dynamics in intense laser fields, based on the concept of Complete-Active-Space Self-Consistent-Field (CASSCF) [1]. The method, called TD-CASSCF [2], allows compact yet accurate representation of ionization dynamics in many-electron systems, thus largely extends the applicability of the MCTDHF (multiconfiguration time-dependent Hartree-Fock) method [3, 4], while keeping the accuracy.

For a molecule interacting with high-intensity, long-wavelength laser, one reasonably expects that the deeply-bound electrons remain non-ionized, while only the higher-lying valence electrons ionize appreciably. For the bound electrons a closed shell description would be acceptable. However, correlated treatment is required for ionizing electrons to describe the seamless transition from the closed-shell-dominant ground state to the symmetry-breaking continuum. The CASSCF wavefunction provides an ideal *ansatz* for such problems. See Fig. 1.

Figure 2 shows the ionization probabilities of one-dimensional LiH-LiH model [2], induced by a 3-cycle laser pulse with wavelength 750 nm and peak intensity 4×10^{14} W/cm². As seen in the figure, TD-CASSCF with 4 active electrons closely reproduces the results of fully correlated MCTDHF with the same number of orbitals. Recently we also derived the equations of motion for general (arbitrary) MCSCF wavefunctions, and implemented the TD-MCSCF method within the framework of Occupation Restricted Multiple Active Spaces (ORMAS) model [5]. This extension will be discussed in the present contribution.

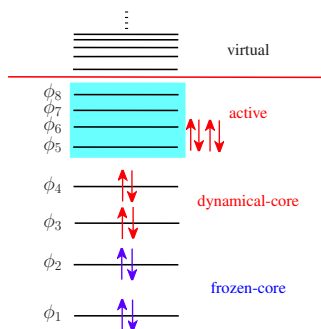


Fig.1: TD-CASSCF concept, illustrating a 12 electron system with 4/4/4 electrons in frozen-core/dynamical-core/active orbital subspaces, respectively.

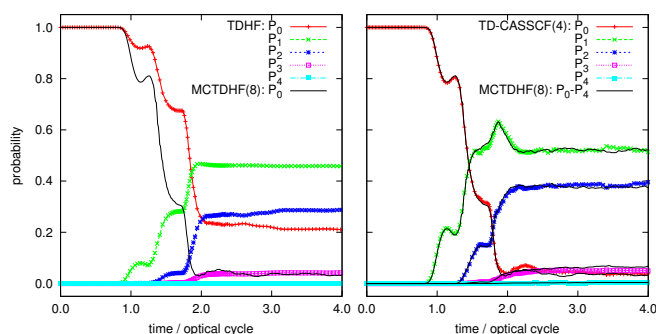


Fig. 2: Ionization probabilities (P_n ; n -electron ionization) of 1D LiH-LiH as a function of time. Results of TDHF (left), TD-CASSCF with 4 active electrons (right), and MCTDHF (black solid lines). Total number of orbitals in TD-CASSCF and MCTDHF is 8.

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First-principles simulations of chemical reactions at interfaces

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I. Introduction

Density functional theory (DFT) has been successfully applied to clarify atomic geometries and electronic properties of well-defined surfaces. It plays now important roles to elucidate chemical processes at “real” surfaces and interfaces in various fields such as catalysis, electrochemistry, semiconductor devices, corrosion, enzyme, and so on and it is now getting a powerful tool to “design” new functional materials. In this talk, I will present recent first-principles simulations on catalysts [1-4].

II. Self-regeneration mechanism of $\text{LaFe}_{1-x}\text{Pd}_x\text{O}_3$

The growth of metal particles is one of main reasons of catalyst degradation in three-way catalysts. Pd-containing perovskite-catalysts such as $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_3$ exhibit excellent durability by suppressing the sintering effect, resulting in dramatic reduction of precious metals by 70-90%[5]. The perovskite catalysts display quite peculiar behavior. Pd nano-particles are self-regenerated during catalytic reactions by reversibly moving into and out of the perovskite lattice depending on the fluctuations between the oxidative and reductive atmospheres in emission. We have carried out calculations based on DFT within the spin-polarized generalized gradient approximation (GGA) as implemented in the STATE code. We propose a possible mechanism of the self-regenerating perovskite-catalyst, based on our calculations, wherein O vacancies (V_{O} s) promote the surface segregation of precious metal atoms, which play the central role in the self-regeneration. We found that the Pd exists in the vicinity of LaFeO_3 surface as a LaPdO_{3-y} layer, which facilitates the segregation of Pd metal particles on the surface without diffusing long distance in the bulk.

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Theoretical calculations of ^{129}Xe NMR parameters

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We have been interested in theoretical calculations of ^{129}Xe NMR parameters in confined Xe atom systems¹ as well as in Xe molecules.² We aim at accurate calculations with inclusion of all physical conditions, such as solvent, temperature, dynamics,^{1b-1d} electron correlation, and relativistic effects.²

Summary of recent results for calculations of ^{129}Xe chemical shift of Xe atom confined in fullerene C_{60} cage will be presented. The essential role of the relativistic effects and dynamical solvent will be discussed.^{1b-1d}

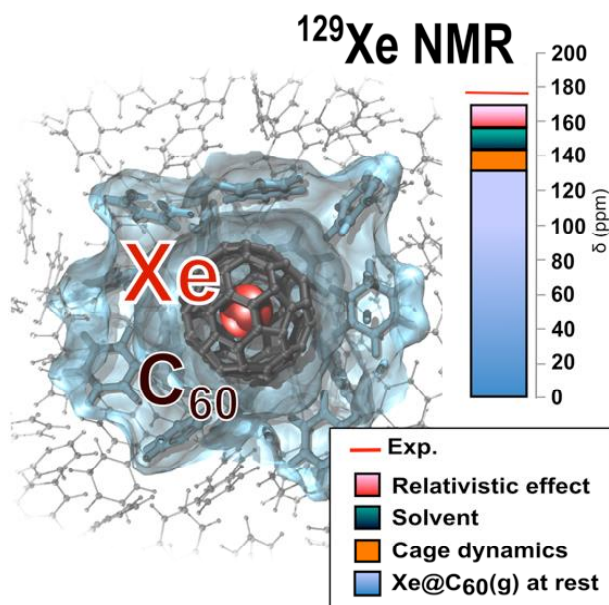


Figure shows a snapshot from molecular dynamics simulations of the $\text{Xe}@\text{C}_{60}$ dissolved in benzene. In the chart, different contributions to the total calculated ^{129}Xe NMR chemical shift are highlighted..

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Theoretical DFT Study on New Carbon K4 and Metal-Organic Framework Structures

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In the present talk we would like to bolster advantages of the cluster approach (being relatively very simple but complementary to other periodic slab model calculations) in proper modeling of extended systems [1-3]. Especially, the structure and chemical activity of the selected transition metal and metal oxide catalysts would be thoroughly discussed [3-5]. In line with combining of metal oxide connectors with organic linkers into extended metal-organic framework (MOF) networks, some solutions is given to stabilize and characterize modified new carbon K4 [6] and related new IRMOF structures. Based on these DFT cluster calculations results, some discrepancies with the results of other theoretical investigations and studies in literature have been critically pointed out.

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Localised Quantum States of Atomic and Molecular Particles Physisorbed on Carbon-Based Nanoparticles

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The vibrational states of atomic and molecular particles adsorbed on finite nanographenes are described using reliable theoretical potentials and appropriate vibrational (lateral) Hamiltonians. Although they rigorously obey the Bloch theorem only for the infinite nanographenes, the energy patterns of the probed states resemble closely the usual Bloch bands and gaps. In addition, for any finite nanographene, these patterns are enriched by the presence of "solitary" energy levels. While the band states are profoundly delocalized, due to a fast tunnelling of the adsorbed particle, the "solitary" states exhibit strong dynamical localization, similar to the behaviour of the states of the Wannier-Stark ladders in optical and semiconductor superlattices.

The present study of the localised states of the physisorbed particles on the finite nanographenes is focused on theoretically predicting their behaviour. As a matter of fact, the actual calculations have suggested not only their existence, but also the reasons causing this existence: Obviously, the gradual increase of the potential energy at the edges of the probed nanographenes plays the same role as the electric field applied to periodic semiconductor superlattices or the chirping of the frequency difference of the counterpropagating laser standing waves in optical lattices, being thus responsible for the same localisation effects as those ones faced in the superlattices. In other words, the localised states predicted in this study can be viewed as bound analogs of the famous Wannier-Stark ladder resonances. It is thus not unthinkable to view the probed nanographenes as nanoscopic/mesoscopic variants of the macroscopic semiconductor and optical lattices and, consequently, as possible candidates for formation of a novel kind of the Wannier-Stark-effect (WSE) based devices, for instance formation of nanoscopic analogs of the macroscopic electro-optical modulators. As these modulators can be operated at both low optical and low electrical powers, they appear attractive especially for optical computing.

Spin Orbit Effects in Re and Pt Organometallic Complexes

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Femtosecond fluorescence spectroscopy experiments on a series of Re complexes identified excited states which participate to the ultra-fast intersystem crossings (~ps time scale) and mainly contribute to the photophysical properties of these molecules [1]. In order to understand the character and dynamics of optically excited states quantum chemical calculations were performed on $[\text{Re}(\text{X})(\text{CO})_3(\text{L})]^n$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{py}$; $\text{L} = \text{bpy}$ (2,2'-bipyridine) or phen (phenantroline)) systems and tetrakis(pyrophosphito)diplatinatate(II) complexes $[\text{Pt}_2(\text{BF}_2\text{POP})_4]^{4-}$ and $[\text{Pt}_2(\text{POP})_4]^{4-}$.

Optimized excited-state geometry was calculated for the lowest singlet and triplet states of each complex by TD-DFT. The lowest triplets were optimized also by the unrestricted Kohn-Sham approach (UKS). DFT calculations employed the hybrid functionals either B3LYP or Perdew, Burke, Ernzerhof exchange and correlation functional (PBE0). The solvent was described by the polarizable continuum model (PCM) (G09) or conductor like screening model (COSMO) (ADF). Low-lying excitation energies and coupling elements between low-lying singlet and triplet states were calculated by several quantum chemical approaches which include spin orbit (SO): TD DFT (ADF), MRCI with the use of spin-orbit pseudopotentials by MOLPRO program and SO-RASSI of MOLCAS 7.8 package based on CASSCF/MS-CASPT2.

Computational results on $[\text{Re}(\text{X})(\text{CO})_3(\text{L})]$ complexes were compared with absorption spectra measured in different solvents and it was shown that calculations qualitatively explain the temperature-dependence of the phosphorescence decay parameters that were measured for the whole series of complexes. SO-TD-DFT calculated spectra of $[\text{Pt}_2(\text{BF}_2\text{POP})_4]^{4-}$ and $[\text{Pt}_2(\text{POP})_4]^{4-}$ well interpreted experimental spectra including the lowest lying singlet – triplet excitations. SO calculations shown the splitting the lowest triplet states and help to understand time – resolved IR experiments.

Acknowledgements: Support from the Czech Ministry of Education (grant LD11086) is gratefully appreciated.

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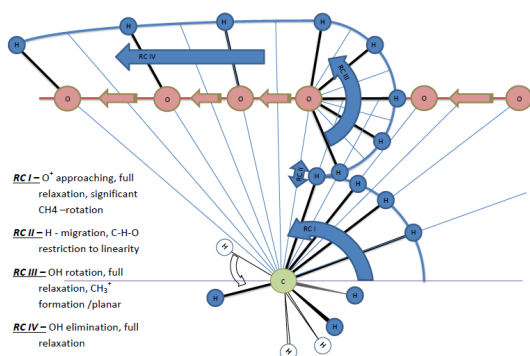
Towards theoretical description of state-selected reactions of O^+ with methane¹

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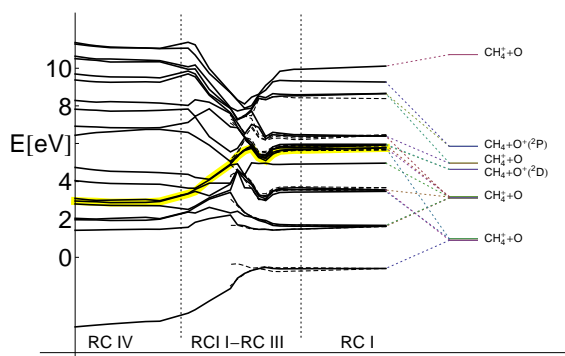
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The process of activation of methane and its conversion to other valuable compounds is of uttermost importance in combustion, catalysis, atmospheric and interstellar chemistry, reaction dynamics, and in many other related areas. The experiments on the state-selected $O^+(^4S, ^2D, ^2P)$ atomic ions with CH_4 (and CD_4), which have been performed using the CERISES setup at synchrotron SOLEIL in Paris[1], provide strong evidence that different reaction mechanisms may be acting for individual O^+ electronic states. This is the main motivation to investigate these processes also by means of quantum chemical methods. However, the high complexity of the system, the huge dimensionality of the corresponding surfaces and the sizeable number of electronic states make the use of standard ab initio approaches computationally extremely demanding or even prohibited. We present the first step towards the development of a robust computational strategy that allows chemically reasonable and computationally feasible construction of potential energy surfaces of the CH_4/O^+ system for future semi-classical dynamic studies[2].

The reactions of atomic oxygen ion with methane in several excited electronic states have been studied by the MCSCF approach. Relaxed guided scan was performed for the particular reaction $[CH_4 + O \rightarrow CH_3 + OH]^+$ along a “chemically reasonable intuitive reaction coordinate” (CRIRC). The lowest 19 electronic states of A' symmetry have been considered in these calculations.



Schematic diagram of the CRIRC. The principal movement of the oxygen is accompanied by CH_4 rotation (RC I), by hydride migration (RC II), by OH rotation (RC III), and OH departure (RC IV).



The energies of the 19 electronic states of the A' (C_s symmetry) are drawn along the CRIRC. The limit corresponding to the T_d symmetry group of CH_4 is connected by dashed lines with the corresponding C_s states. One low energy path for the reaction $CH_4 + O^+(^2D) \rightarrow CH_3^+ + OH$ is highlighted.

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First-principles calculation for positron binding to molecules

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Characteristic features of positron-binding structures for some polar [1, 2] and nonpolar [3] molecules are discussed with multi-component quantum Monte Carlo (QMC) [4] and configuration interaction scheme of molecular orbital (MO) calculations [5].

In the case of nitrile (-CN functional group) species, our vertical positron affinity (PA) value of HCN molecule with electronic 6-31++G(2df,2pd) and positronic [15s15p3d2f1g] GTF basis sets is 38 meV. This value is in reasonable agreement with our previous QMC result of 38(5) meV [4], though our variational energy of $[\text{HCN}; e^+]$ species is still 0.5 hartree higher than that by QMC. Our PA value of acetonitrile is calculated as 135 meV, which agrees to within 25% with the recent experimental value of 180 meV [6]. Our PA values of acrylonitrile and propionitrile (155 and 164 meV) are largest among these species, which is consistent with the relatively large dipole moments of the latter two systems [1]. In the case of carbonyl species, our vertical PA values of acetaldehyde and acetone are as 52 and 92 meV [2], which can be compared to the recent experimental values of 90 and 173 meV [7]. For formaldehyde we have also found that the PA values are enhanced by including the local C=O vibrational contribution from vertical PA value of 15 meV to 17, 21, and 25 meV after averaging over the 0th, 1st, and 2nd vibrational states, respectively, due to the anharmonicity of the potential.

We will also show the results of vibrational enhancement of positron affinities for nonpolar CO₂, CS₂ [3] and CSe₂ molecules. For nonpolar CSe₂ molecule, a positron can be attached even at the equilibrium structures, due to the effect of the induced dipole moment with large polarizability values. In these molecules, the vibrational averaged PA values become larger as the vibrational quantum number increases.

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Magnetism and spin transport in transition metal organometallic molecules

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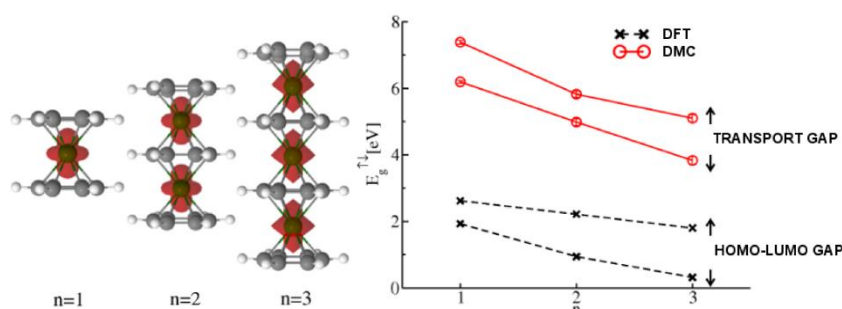
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Transition metal organometallics has recently attracted much attention due to its potential for applications in catalysis, polymers, molecular recognition, high-density storage, quantum computing, and spintronics. Despite these applications, reliable theoretical and experimental knowledge of energetics, dissociation energy, spin multiplicity, spin gaps, etc. of these systems is still missing. Therefore we have performed very accurate fixed-node quantum Monte Carlo (QMC) calculations [1] with the quest to elucidate electronic, magnetic, and atomic structure of these systems and thus to provide ultimate answers to the open questions.

Taking vanadium-benzene half-sandwich as an example [2], we find that, at variance with DFT results which favor either low- or high-spin state, depending on the functional used, QMC predicts degenerate energies for spin multiplicities 2, 4, and 6, irrespective of DFT functional used to fix the nodal hyper-surfaces. Our QMC results indicate that both DFT as well as experimental results may be strongly biased.

We have also studied full-sandwich vanadium-benzene multi-decker clusters, V_nBz_{n+1} , $n = 1-3$ [3]. The most important prospective applications of these and related systems was predicted in spintronics as spin filters. Use as spin filters requires them to be half-metal ferromagnets, in order to feature a metallic gap for the minority-spin electrons and semiconducting gap for the majority-spin electrons. We find that, while magnetic structure of these systems is consistent with ferromagnetic coupling, their electronic structure is not consistent with half-metallic behavior as previously assumed, but rather this system is a ferromagnetic insulator with large and broadly similar \uparrow/\downarrow -spin gaps, implying thus a limited potential of these and related materials for spintronics applications unless they are further modified or functionalized.



Model of vanadium benzene full-sandwich molecules featuring ferromagnetically coupled vanadium atoms. Right: \uparrow/\downarrow -spin gaps for vanadium-benzene full sandwich structures in DFT and QMC treatments.

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It is known that the Heisenberg and Robertson-Schrödinger uncertainty relations can be replaced by sharper relations in which the "classical" (depending on the gradient of the phase of the wave function) and "quantum" (depending on the gradient of the envelope of the wave function) parts of the variances $\langle(\Delta x)^2\rangle$ and $\langle(\Delta p)^2\rangle$ are separated. In this talk, the one-dimensional as well as the corresponding multi-dimensional form of these relations is summarized and discussed.

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Time evolution of quantum system based on QED: Formulation and Simulation

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We have developed our program package, QEDynamics [1, 2, 3], which computes the time evolution of quantum systems. Our program compute the evolution based on quantum field theory, Rigged QED [4]. Hence, quantum fields are defined by the combination of spatial expansion functions and creation-annihilation operators. As quantum fields, we consider electron, nucleus, and photon. Nucleus is included as a Schrödinger field. For expansion functions of matter fields, we do not use plane waves but wave packets in a manner of Furry picture. Photon fields are quantized by adopting the Coulomb gauge [4].

The operators at $t=t_i$ are expanded as the operators at $t=0$. Accordingly, our program code computes the coefficients of expansion of operators in Heisenberg picture. This expansion is not restricted to the first order, since the order of operators increases by interactions, and results in polynomials of operators. Due to the interactions of many body effects, the evolution of operators is very complicated and the order of the expansion polynomials increases exponentially in an instant. Hence, in practical computations, the expansion polynomials is truncated at some order, and some operators are evaluated by replacing the expectation values [2, 3].

The description of interaction photons are essentially important in QED. The computation of interaction photon requires all the information at $t < t_i$ due to the retardation effects. Hence we compute them with some approximations. Our method is explained in Ref. [3].

Another inevitable topic in quantum field theory is renormalization. In our case, the ordinary renormalization by using the asymptotic field cannot be used, and the renormalization is dependent on time. This topic is studied hardly in many physicist and however has not been settled yet [5]. For time dependent renormalization, we propose the prescription using the conserved quantities in a system.

Acknowledgement

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Search for a molecule with a measurable electronic energy shift due to parity violation

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A pair of chiral molecules that are mirror images of each other do not have the same energy; they slightly differ in all their properties owing to the so-called weak force acting between quarks and leptons. The weak force has been proven experimentally, for elementary particles and for atoms, to violate parity, the symmetry with respect to space inversion. As a result, it must violate also the otherwise perfect equivalence of enantiomers.

Many theoreticians have been struggling to find a molecule suitable for the long-awaited first unambiguous experimental proof of the correctness of this striking theoretical prediction. We have tried to achieve this goal by simplifying the problem so that manageable relations between the magnitude (and sign) of parity-violating effects and molecular structure could emerge.

Our approach stems from the simplest formula, adopted from nondegenerate perturbation theory, for the shift E_{pv} of the electronic energy of a nonrelativistic singlet S due to its interaction with a nonrelativistic triplet T through a 2-component spin-orbit Hamiltonian \hat{H}_{so} and a 2-component parity-violating Hamiltonian \hat{H}_{pv} ,

$$E_{pv}(S) = -2 \frac{\mathbf{a} \cdot \mathbf{b}}{E(S) - E(T)},$$

where \mathbf{a} is the axial vector of spin-orbit coupling and \mathbf{b} is the polar vector of parity-violating coupling between the singlet and the triplet (\mathbf{a} and \mathbf{b} are purely imaginary Cartesian vectors whose components are $a_u = -\langle S | \hat{H}_{so} | T_u \rangle = \langle T_u | \hat{H}_{so} | S \rangle$, $b_u = -\langle S | \hat{H}_{pv} | T_u \rangle = \langle T_u | \hat{H}_{pv} | S \rangle$, $u = x, y, z$), $E(S)$ and $E(T)$ are the nonrelativistic energies of the two unperturbed states.

Accordingly, if we want to maximize the ground-state electronic energy shift of a molecule, we should focus on dissymmetric molecules with small singlet-triplet gaps, e.g. biradicals. The aim is to find a molecule with a minute singlet-triplet gap for which the vectors \mathbf{a} and \mathbf{b} are both as large as possible and collinear. Such a choice must evidently enhance the effect of the state nearly degenerate with the ground state and thus effectively suppress the usually opposed effect of the other, higher excited, states.

However, the validity of nondegenerate perturbation theory decreases with the rising ratio $a/|E(S) - E(T)|$. As a result, the benefit derived from pushing the energies of two nonrelativistic states of a molecule towards each other is the greatest within the first row, and much smaller, *but still significant*, within the sixth row of the periodic table (atomic contributions to $a = |\mathbf{a}|$ grow roughly as Z^2).

Despite the limited ability of simple models (ignoring all but a small subset of nonrelativistic states) to estimate the magnitude, the sign of parity-violating effects is usually predicted “correctly”, i.e. in accordance with a moderate double-group CI calculation: even in chiral molecules containing atoms of the heaviest elements the energies of the two coupled electronic states turn out to be shifted in mutually opposite directions. Properly selected electronic excitation frequencies therefore seem to be, contrary to vibrational excitation frequencies, fairly sensitive measures of parity violation in molecules (vibrational levels of an electronic state of a chiral molecule are typically shifted all in the same direction by more than 99% the same amount).

We propose a few molecules likely to exhibit extraordinarily large electronic excitation frequency shift due to parity violation. The energy gap between the ground and the lowest excited states varies from a few wavenumbers to about 9000 cm^{-1} . Some of the suggested molecules might be exploited in future attempts to detect parity violation in chiral molecules by means of ultrahigh resolution spectroscopy.

Electron and nuclear wave packet modeling of chemical bonding and dynamics

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Recent development in nuclear and electron wave packet modeling of molecular systems will be presented. We first outline semiquantal nuclear WP molecular dynamics (MD) simulation of hydrogen-bond exchange dynamics in water [1]. The method takes account of the zero-point fluctuation and dynamic WP broadening in real-time and real-space, to describe WP delocalization over low-barrier hydrogen-bond, geometric isotope effects, and under-barrier shallow tunneling in nearly-adiabatic proton transfers. The equations of motion for both the WP center and width variables follow canonical Hamiltonian form that yield stable symplectic propagation. An enhancement of the accuracy by inclusion of quantum phase via the initial value representation of propagator with coherent-state path-integral is also presented briefly [2]. We then discuss an extension of the method to many-fermion systems with use of the non-orthogonal valence-bond (VB) theory [3], which fits better with the localized electron WP picture than the conventional molecular orbital theory does. However, in contrast with the conventional VB theory that employ frozen atomic orbitals (AOs) clamped on nuclear positions, we employ floating and breathing minimal WP per electron. That is, each electron is described by a single spherical Gaussian WP that can move in space (float) and change its width (breath). In spite of this simplicity, the method is found to yield accurate ground state potential energy surfaces of small molecules including H₂, LiH, BeH₂, CH₂ and H₂O. Roughly assigning, the polarization of electron distribution is described by the WP floating, the static electron correlation effect is by the VB coupling, and the dynamic correlation is by the WP breathing. The method is now being extended to excited-state calculations via dynamic response theory, computation of larger systems by decoupling electron group approximation, and combined electron-nuclear MD simulations that is free from the Born-Oppenheimer approximation.

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Fragmentation of Negative Ions - Theoretical Description

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Temporary negative ions formed by the collision of low energy electrons with neutral target molecules have an important function in a variety of chemical processes. It is generally considered that the types of damage induced by ionising radiation in deoxyribonucleic acids, peptides, their building units amino acids as well as other important biomolecules that lead to the most significant biological effects are double-strand breaks, clustered lesions and various fragmentation reactions. Dissociative electron attachment (DEA) is an efficient reaction between the electrons and molecules which produces the temporary negative ion with the energy lying above the previous molecule. The formation of negative ions and radicals may play important role in the radical formation in the living organism. The description of the resonant electron capture by molecules connected with the formation of negative ions represents still the challenge for the theory [1]. The reason is that the metastable resonance state is embedded in the continuum of scattering states and this plain application of bound state techniques will inevitably lead to a neutral molecule plus a free electron. This is the reason why many theoretical papers based on standard methods failed in the calculation of vertical electron affinities of halogenated molecules. A rigorous treatment of anion resonances needs, of course, quantum mechanical scattering methods such as R-matrix theory or the Kohn variation technique. Because of complications connected with the application of these methods to real size molecules some approximate techniques, based on stabilization methods have been proposed to describe the negative ions. There are many variants of them; the product of all these approaches is the determination of a series of eigenvalues of the molecular Hamiltonian as a function of some scaling parameter. The drawback of these methods consists in the determination of the

important physical quantity, resonance width, which is in many cases not possible to obtain.

In the contribution the simple schemes for the calculation of the resonance energies and resonance widths of temporary anions are presented. The advantage as well as the drawback of methods applied to the chosen molecules is discussed. This method is then applied to study of biomolecules where the effect of electron capture may cause the formation of negative ions following the fragmentation of molecules.

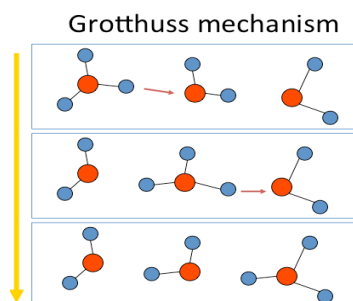
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Proton transport in biomolecular and aqueous systems: A molecular dynamics approach

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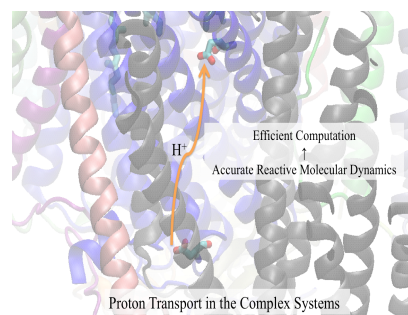
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The excess proton plays many essential roles not only in chemistry but also in biology and material science. While some proteins utilize protons to perform their enzyme function, the cellular respiration involves proton transporters to generate ATP. In the material science, for example, the power generating efficiency of the polymer electrolyte fuel cell is closely related to the efficiency of the proton transport. Furthermore, the excess proton is the basis of the acid-base reaction in aqueous solution systems, and therefore this fact is introduced to most high school students as the core of educational curricula of chemistry.



However, the properties of the excess proton are not fully understood at the atomic level. Even in the amphiphile/water solution, recent experimental and theoretical studies have suggested that the proton behavior is more complicated than researchers expected, mainly because the properties of the excess proton is very sensitive to its environment (see Ref. [1-4] and more references are therein). One of our projects aims at clarifying the properties of the excess proton in complex environments at the atomic level by performing the molecular dynamics (MD) simulations.

In the presentation, we discuss several examples showing the unique nature of the excess proton in aqueous and biomolecular systems [1-4]. In the proton transport in cytochrome c oxidase (CcO), in particular, our MD results clearly suggest a crucial effect of the electron transfer on the proton transport, which implies that this mechanism should be involved in controlling the gate of the proton channel [1]. Also, it is found that the change of the hydrogen bond network topology mediates interaction between the electron transfer and the proton transport in CcO.



It is noteworthy that the proton transport is usually associated with the chemical bond alternation in aqueous media, which is called Grotthuss mechanism. Such behavior of the excess proton cannot be described by the standard MD force field. Therefore, we introduce the idea of the multi-state empirical valence bond (MS-EVB) method to describe the unique proton motion. Although the MS-EVB MD calculation is slower than the classical MD, it is much faster than the ab initio MD. Therefore, the MS-EVB method can be applied to long-time simulations of large systems to obtain better convergence of statistical properties of the reactive system. In the presentation, we also propose several ideas to further accelerate the reactive MD calculations [5].

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New Ultrafast Relaxation Processes in Hydrogen Bonded Systems

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The processes initiated by ionization and excitation of core electrons are reasonably well described for the molecules in the gas phase. The X-ray photodynamics in solution is on the other hand only poorly understood. Upon the ejection of inner-valence or inner shell electron, the molecules lose energy via local relaxation processes such as X-ray fluorescence (leading to singly charged molecule) or Auger process (leading to doubly charged molecule). Relatively recently, non-local electronic relaxation processes such as Intermolecular Coulomb Decay (ICD) have been identified.^{1,2} The non-local auto-ionization processes turned out to represent rather important relaxation channels in the solution chemistry.

Using a combination of liquid photoemission, quantum chemistry and quantum dynamics methods, we have identified a novel type of relaxation process specific for hydrogen bonded systems, the so called proton transfer mediated charge separation (PTM-CS).³ In the PTM-CS process, the electron autoionization is preceded by an ultrafast (less than 10 fs) proton transfer between two neighboring water units, leading to Zundell-like $[\text{HO}^*\cdots\text{H}\cdots\text{OH}_2]^+$ structures. Ultimately, dicationic, charge separated species of the $[\text{H}_2\text{O}^+\cdots\text{H}_2\text{O}^+](\text{aq})$ and $[\text{OH}^+\cdots\text{H}_3\text{O}^+](\text{aq})$ type are formed. The implications for radiation chemistry will be discussed. We will present a detailed analysis of the PTM-CS process for liquid water and for solvated hydrogen peroxide.^{4,5} We will further discuss the limits of the efficiency of the inner valence ICD process imposed by a nuclear dynamics as well as the relevance for the non-local ionization processes for other hydrogen bonded systems. The potential applications of the new process will also be briefly mentioned.

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Intermolecular interaction as origin of red shifts in absorption spectra of Zinc-Phthalocyanine from first-principles

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Zinc-phthalocyanines (ZnPc) have currently attracted considerable attention as promising photoelectric device materials for energy conversion, such as dye-sensitized solar cells and organic thin-film solar cells. In tuning the excitation window, modification of the excited states of a chromophore molecule induced by molecularly stacked aggregation is of primary interest. Two stack configurations of chromophore molecules, *i.e.*, those with face-to-face cofacial configurations, often referred to as H-type aggregates, and slipped-cofacially stacked configurations, known as J-type aggregates, have been highlighted.

We investigate electronic origins of a redshift in absorption spectra of a dimerized ZnPc by means of hybrid density functional theoretical calculations [1]. In terms of the molecular orbital (MO) picture, the dimerization splits energy levels of frontier MOs such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the constituent ZnPc molecules. Consequently, the absorption wavelength seems to become longer than the monomer as the overlap between the monomers becomes larger. However, for a ZnPc dimer configuration with its cofacially stacked monomer arrangement, the calculated absorption spectra within the time-dependent density functional theory indicates no redshift but blueshift in the Q-band absorption spectrum, *i.e.*, a typical H-aggregate. The origin of the apparently contradictory result is elucidated by the conventional description of the interaction between monomer transition dipoles in molecular dimers [2]. The redshift is caused by an interaction between the two head-to-tail transition dipoles of the monomers, while the side-by-side arranged transition dipoles result in a blueshift. By tuning the dipole-dipole interaction based on the electronic natures of the HOMO and the LUMO, we describe a slipped-stacked ZnPc dimer configuration in which the Q-band absorption wavelength increases by more than 120 nm relative to the monomer Q-band.

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Force Field Refinements for RNA and DNA Simulations Derived from Accurate QM Calculations with Inclusion of Solvation Effects

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The relevance of RNA and DNA conformational dynamics in molecular dynamics simulations critically depends on the quality of the applied empirical force field and its dihedral angle parameters in particular. Dihedral parameters in force fields are often obtained with the help of quantum chemical calculations. These are usually performed in vacuum and it is assumed that the solvent model used in the molecular dynamics simulation (explicit or implicit) satisfactorily accounts for the major part of the solvation energy. However, there are certain nonspecific solvation effects that are not properly accounted for in this approach. A parameterization procedure is suggested that incorporates the missing conformation-dependent solvation effects into the torsion parameters, based on the difference between the quantum-mechanical self-consistent reaction field and Poisson-Boltzmann continuum solvation models. Here we focused on the glycosidic torsion angle χ , a key parameter for description of DNA and RNA structures, which has received particular attention recently. The derived χ torsion parameters are verified by extensive molecular dynamics simulations. We show that our parameters remove overstabilization of the high-*anti* region found in the ff99 force field and thus prevent formation of undesirable ladder-like structural distortions in RNA simulations. Also presented is reparameterization of backbone torsion angles ϵ and ζ for DNA molecular dynamic simulations.

Om-1

Benchmark databases and method development in the Cuby framework

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Over the last few years, we have generated a large body of benchmark data on noncovalent interactions. Our new data sets provide systematic coverage of interactions of organic (the S66 set)[1] and halogenated[2] (X40) molecules at the CCSD(T)/CBS level. Additional extensions (S66x8, S66a8, X40x10) cover also non-equilibrium geometries.

To facilitate the use of these data in validation of existing methods and in the parameterization of new ones, we are developing a software that can efficiently handle such data and automates the common workflows. It is based on the Cuby framework[3] developed by the author, a platform for integration various computational chemistry methods and protocols written in ruby programming language[4].

The capabilities of the Cuby framework in this area will be demonstrated on the parameterization of corrections for noncovalent interactions[5] on our benchmark data and their subsequent testing.

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Nature of proton transport in polymer electrolyte membranes for fuel cell applications

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I. Introduction

The polymer electrolyte fuel cells (PEFCs) have attracted a considerable amount of interest as a non-polluting power source for automobiles or mobile devices. One of the key components of PEFCs is a polymer electrolyte membrane (PEM) whose role is to facilitate proton transport from the anode to the cathode. While the amount of electricity generated by fuel cell is limited by the transport of protons, the necessary depth of comprehension on the proton transport mechanism has not yet been reached. This presentation reports on results of first-principles molecular dynamics (MD) simulation carried out to investigate the nature of proton transport in PEM.

II. Computations

For first-principles MD simulations, the electronic structures of the systems were evaluated by means of density functional theory (DFT) in the Kohn–Sham formalism, employing the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional. Separable norm-conserving pseudo potentials were employed for the inner core of electrons, and only the Γ -point was used to sample the Brillouin zone. For the basis set, adaptive finite elements were used in place of ordinary plane waves. In the molecular dynamics simulations, the temperature was controlled by the Berendsen thermostat with a target temperature of 353.15 K. All hydrogen atoms in the system were given the mass of deuterium to allow the use of a large time step of 1.21 fs in the production run. space.

III. Results and Discussions

The first-principles MD simulation reveals several new aspects on the proton transport mechanism in PEM. One finding is that the classical vehicular diffusion model, which has been employed to account for the slow diffusion process of protons in low water-content PEM, is an oversimplification and does not correctly describe proton dynamics. Furthermore, it is found that difference in the value of the proton diffusion coefficient with respect to water content inside PEM is related to the different character of proton hopping occurring in the water hydrogen bond network. Those new findings allow us to explain phenomena related to proton transport such as proton coupled water transport in PEM.

RNA catalyzes: An Insight from molecular dynamics simulations and QM/MM calculations.

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The RNA enzymes (ribozymes) are non-coding RNAs that are able to catalyze site-specific cleavage of their own sugar-phosphate backbone.^{1,2} This RNA-catalyzed self-cleavage reaction is involved in several biological processes such as replication of viral RNAs or self-splicing processes.³ Among the catalytic RNAs, the most theoretically studied are small self-cleaving ribozymes having typically less than ~200 nucleotides that catalyze the self-cleavage of the sugar-phosphate backbone. The self-cleavage is classified as internal trans-esterification reaction that starts with nucleophilic attack of the 2'-O oxygen toward the adjacent 3'-phosphate group (scissile phosphate) and ends with 2',3'-cyclic phosphate and 5'-hydroxyl termini.⁴

The study of the mechanisms that are utilized by the ribozymes is complicated by the fact that it is quite challenging to obtain the experimental structural data of the reactive (pre-cleavage) conformation of the ribozyme as some chemical modifications of the active site should be typically introduced in order to inhibit the self-cleavage. However, all these modifications are prone to perturb the conformation of the active site to such extent that seriously complicates the interpretation of the structural data.

The molecular dynamics (MD) simulations might significantly contribute to the interpretation of these experimental structural data and to the structural characterization of the active site arrangement in its native reactive form. Namely, the simulation should be in principle able to explicitly examine the effect of inhibiting modification and suggest the reactive pre-cleavage conformation of the ribozyme active site. However, MD simulations are substantially limited by two factors: (i) limited accuracy of the utilized empirical force field, and (ii) bias coming from the starting structure, which might affect the simulation behavior due to the limited sampling.

If experimental structural data combined with MD simulations are enough to be able to suggest the reactive conformation of the active site of the native ribozyme, the QM/MM technique might be used to determine the mechanism of the self-cleavage reaction and to reveal the role of the active site nucleotides in the catalyzes. There are increasing experimental as well as theoretical evidences that the small self-cleaving ribozymes might utilize the active site nucleotides in the minor protonation states as direct participants of the self-cleavage reaction in the role of general base or general acid.

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The Role of Delocalized Electrons in Infrared and Terahertz Intensities of Hydrogen- and Halogen-Bonding Systems

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I. Introduction

We can observe many kinds of dynamics in condensed-phase systems with different choices of spectroscopic methods, and theoretical analysis is often helpful to elucidate what the spectral profiles really mean. With regard to the IR and far-IR (THz) spectra, it is well known that the spectral profiles are determined by the correlation function of the system's dipole, and since the motions of any charged particles are involved, one sometimes faces the problem of the coupling between the motions of electrons and atomic nuclei. A simple idea would be that the electrons faithfully follow the atomic nuclei, and this is employed in the models with fixed atomic partial charges. The next step would be to take into account the intramolecular polarizations induced by intermolecular electrostatic interactions, for example, with the dipole-induced dipole model. However, there is no guarantee that this is (practically) sufficient for all cases.

Detailed analyses of the behavior of electrons induced by molecular motions that we have recently done have clarified that such a problem really exists for many important cases of hydrogen- and halogen-bonding systems [1–5]. The present talk will give an overview on this subject. Two of such cases are briefly described in the following.

II. Terahertz spectral intensity of liquid water at 6 THz

The band at ~6 THz (200 cm^{-1}) in the terahertz spectrum of liquid water is known to arise from the H...O hydrogen-bond stretching motions, but it has long been pointed out that the intensity arising from intramolecular polarizations induced by intermolecular electrostatic interactions is not sufficiently strong. The analysis of the electron density modulations induced by molecular motions [3,5] has shown that intermolecular transfer of electron density (called *intermolecular charge flux*) is induced by molecular translations of hydrogen-bonded water, and this is the main origin of the intensity of this band.

III. IR intensity of the amide I band of halogen-bonding peptide group

In many cases of halogen bonding in ligand-protein complexes, the C=O group of the peptide group is directly involved in the halogen bonding. Since the amide I mode (mainly C=O stretch) is known to be sensitive to the environment and secondary structure, it is interesting to see how the halogen bonding affects the properties of the amide I band. Our analysis [1] has shown that the IR intensity is significantly enhanced in those cases, and this arises from the intermolecular charge flux induced by the amide I mode.

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Multiple oxygen entry pathways in T-state human hemoglobin revealed by ensemble MD simulation

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I. Background

Hemoglobin function of O₂ transport is achieved by O₂ binding to the heme binding site. The binding site is buried inside protein, indicating the necessity of O₂ migration into the site. However, it is still under debate over the ligand migration pathway. Therefore, we examined the migration pathways into the binding site in tetramer human hemoglobin (HbA) [1].

II. Computational methods

Intrinsic pathway identification (IPIC) method with the combination of ensemble MD simulation [2-4] and clustering was applied to clarify the O₂ migration pathways. First, we executed 128 independent MD simulations of T-state HbA for 8 ns under oxygen-rich condition and obtained O₂ entry trajectories into the binding site. Then we classified them by clustering and visualized the multiple migration pathways (Fig.1).

III. Results & Discussion

We found that O₂ molecules enter the binding site through multiple pathways and His-gate, which has traditionally been assumed to be the main entry pathway, was merely one of minor pathways. Moreover, the rate constants of O₂ entry estimated from our simulations were consistent with the experimentally observed rate constants and able to explain the faster O₂ entry into the β subunit binding site. The correspondence with experiments indicates that the IPIC method is useful to analyze multiple ligand entry pathways in complicated proteins.

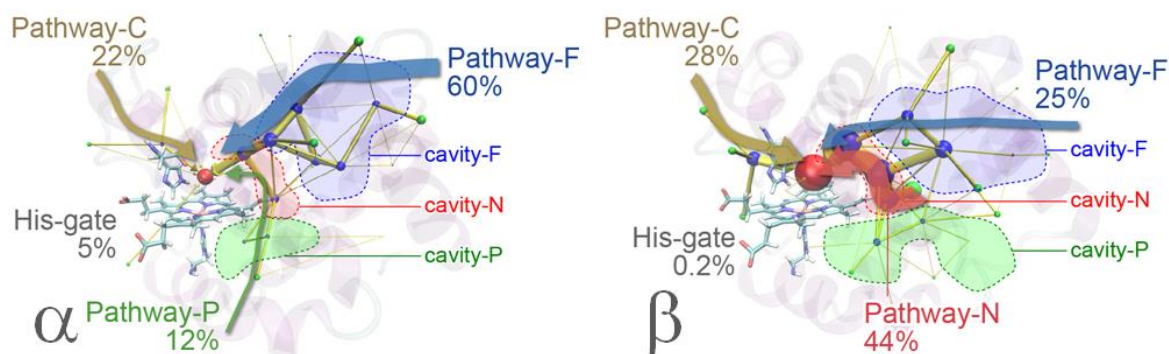


Fig. 1. Multiple O₂ entry pathways from solvent to the binding site in the α subunit (left) and β subunit (right). The red sphere is the center of the binding site, blue spheres are centers of inside clusters, and green spheres are those of surface clusters or O₂ entry portals. Yellow cylinders represent ligand migration between two clusters.

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Elucidation of the Fe^{IV}=O intermediate in the catalytic cycle of Halogenase: Chlorination versus Hydroxylation Selectivity

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High-spin ($S=2$) Fe^{IV}=O species are key intermediates in the catalysis of most non-heme iron enzymes. Here we present spectroscopic (magnetic circular dichroism) and high-level computational studies on a structurally-defined $S=2$ Fe^{IV}=O model complex that define its frontier molecular orbitals, which allow its high reactivity towards C-H bond cleavage.¹

We also present the structural characterization of the reactive Fe^{IV}=O intermediate in non-heme iron halogenase (SyrB2) by using synchrotron-based nuclear resonance vibrational spectroscopy (NRVS) that defines the dependence of the vibrational modes involving Fe on the nature of the Fe^{IV}=O active site.² This intermediate reacts via an initial hydrogen-atom abstraction step, performing subsequent halogenation of the native substrate or hydroxylation of non-native substrates.³ A correlation of the experimental NRVS data to electronic structure calculations indicates that the substrate directs the orientation of the Fe^{IV}=O intermediate, presenting specific frontier molecular orbitals that can activate either selective halogenation or hydroxylation.

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Theoretical Investigation for the Catalytic Activities of Au Cluster Catalysts

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I. Introduction

It is well known that Au cluster can exhibit high catalytic activity with the stabilizing polymers, such as PVP. Our previous work was found that the anionic Au clusters played an important role for the activation of oxygen molecule on the Au clusters. However, the catalytic activity of neutral Au clusters for the aerobic oxidation reaction of alcohol is not still investigated in detail. In order to examine the catalytic activity of neutral Au clusters, the aerobic oxidation of *p*-hydroxybenzyl alcohol to the corresponding aldehyde catalyzed by Au₆ has been investigated quantum chemically using density functional theory. Possible reaction pathways are investigated taking account of full structure relaxation of the model systems. From the calculation results, it was found that the formations of both a hydroperoxyl anion and a hydride were the important steps for the aerobic oxidation of *p*-hydroxybenzyl alcohol over Au₆ cluster

II. Presentations

In all calculations, DFT with PBE0 functional was used. The scalar relativistic effective core potential (ECP) with double-zeta basis sets (LANL2DZ) for all gold atoms and 6-31+G(d) basis sets were applied for the hydrogen, carbon, and oxygen atoms. All the geometries of the model systems were fully optimized.

III. Abstract deadline

The calculation results showed that the production of *p*-hydroxybenzyl aldehyde was generated by both C-H bond dissociation of 1-carbon position of hydroxybenzyl alcohol by oxygenated Au₆ cluster and hydride elimination from *p*-hydroxybenzyl alcohol by Au₆ cluster. Accordingly, hydrogen peroxide was produced in all reaction pathways investigated. Au₆⁻² cluster was presented by the charge donation from the deprotonated *p*-hydroxybenzyl alcohol and decomposed hydrogen peroxide to two OH⁻. Finally, neutral Au₆ with its original structure was regenerated after desorption of OH⁻ from Au₆. The calculation results also suggested that hydration of hydrogen peroxide was important for the decomposition of hydrogen peroxide to OH⁻ on the cluster.

Reaction Mechanism of Ru(II) Piano-Stool Complexes; Umbrella Sampling QM/MM MD Study

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Abstract

Biologically relevant interactions of piano-stool ruthenium(II) complexes with ds-DNA are studied in this paper by hybrid QM/MM computational technique. The whole reaction mechanism is divided into three phases: i) hydration of the $[\text{Ru}^{\text{II}}(\eta^6\text{-benzene})(\text{en})\text{Cl}]^+$ complex, followed by ii) monoadduct formation between the resulting aqua-Ru(II) complex and N7 position of one of the guanines in the ds-DNA oligomer model and the final phase – iii) formation of the intra-strand Ru(II) bridge (cross-link) between two adjacent guanines. Free energy profiles of all the reactions are explored by QM/MM MD umbrella sampling approach where the Ru(II) complex and two guanines represent a quantum kernel, which is described by DFT methods. The combined QM/MM scheme is realized by our own software (QMS v. 1.4), which was developed to couple several quantum chemical programs (in this study Gaussian 09) and Amber 11 program. Calculated free energy barriers of the both ruthenium hydration and Ru(II)-N7(G) DNA binding process are in good agreement with experimentally measured rate constants. Then this method was used to study a possibility of cross-link formation. One feasible pathway leading to Ru(II) guanine-guanine cross-link with synchronous releasing of benzene ligand is predicted. The cross-linking is exergonic process with energy barrier lower than for monoadduct reaction of Ru(II) complex with ds-DNA.

Orbital Views of Electron Transport in Molecules

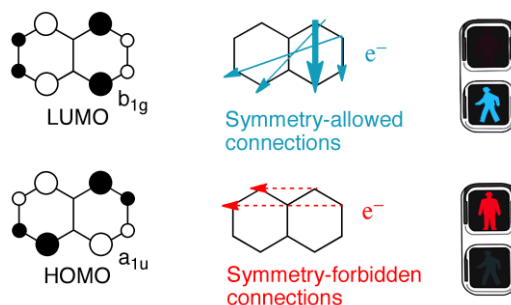
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We have developed a chemical way of thinking about electron transport in molecules in terms of frontier orbital theory [1-4]. The phase and amplitude of the HOMO and LUMO of π -conjugated molecules determine the essential properties of their electron transport. By considering a close relationship between Green's function and the molecular orbital, we derived an orbital rule that would help our chemical understanding of the phenomenon. First, the sign of the product of the orbital coefficients at sites r and s in the HOMO should be different from the sign of the product of the orbital coefficients at sites r and s in the LUMO. Secondly, sites r and s in which the amplitude of the HOMO and LUMO is large should be connected. Recently we confirmed these theoretical predictions experimentally by using nanofabricated mechanically controllable break junctions to measure the single-molecule conductance of naphthalene dithiol derivatives [5]. The measurement of the symmetry-allowed 1,4-naphthalene dithiol shows a single-molecule conductance that exceeds that of the symmetry-forbidden 2,7-naphthalene dithiol by two orders of magnitude.



Spintronic properties of cyclobutadiene (CBD) systems are investigated based on a qualitative frontier orbital analysis [6]. CBD undergoes a Jahn-Teller distortion from the square triplet state to the rectangular singlet state. According to the qualitative Hückel molecular orbital analysis, the electron transport through the square triplet state is symmetry allowed while that through the rectangular singlet state is symmetry forbidden. The magnetic triplet state is a possible coexisting system of conductivity and magnetism. Sophisticated first-principles quantum chemical calculations are performed by using a realistic molecular junction model. Interesting spin filtering properties are found in the square-shaped CBD system. The high- and low-spin states of the square-shaped CBD system produce the spin- α and - β polarized conductance, respectively.

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