

Development and parallelization of DC-DFTB method aimed at large scale molecular dynamics

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I. Introduction

There is great interest in developing molecular simulation force fields that are able to treat large scale molecules, such as chemical reaction in lithium battery, and carbon dioxide adsorption. Recently, the DFTB theory, which is semi-empirical theory based on *ab initio* DFT, is applied to large scale molecules. Although DFTB is fast and good accurate method, the computational cost is proportional to $O(N^3)$, and the limit of molecular size is not so large. To solve the problem, we have applied the DC technique to DFTB; this approach is termed DC-DFTB. In this presentation, we explain the development of DC-DFTB and its numerical assessments. The efficient technique for massive parallelization will be also presented.

II. Numerical assessment for DC-DFTB

Fig. 1 shows the computational cost for energy calculation of $C_{2n}H_{2n+2}$ molecules by the DC-DFTB and standard DFTB (the gray line) methods. In the DC-DFTB theory, a subsystem is 1 unit and each buffer region is left and right 8 units, treating C_2H_2 (or C_2H_3) as a unit. As shown in left-side of Fig. 1, DC-DFTB cost is drastically decreased in comparison with standard DFTB one. Furthermore, focused on the DC-DFTB results, the diagonalization cost changes from $O(N^3)$ to $O(N)$. As a result, the computational time is 68.2 second even in the case of $C_{10000}H_{10002}$ molecule.

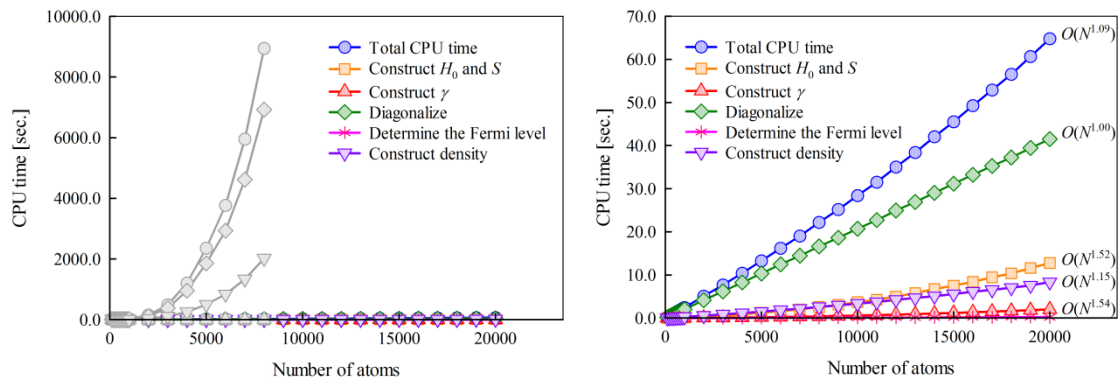


Fig. 1. Computational time for energy calculation of $C_{2n}H_{2n+2}$ obtained by DC-DFTB and DFTB.

MP2-F12 study of interaction energies of large molecules with K computer

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The explicitly correlated many-body perturbation theory (MP2-F12)[1], which considerably accelerate the basis set convergence, has been implemented for the massively parallel computational environment such as K computer, and applied to the evaluation of the intermolecular interaction energies of large molecules like a C₆₀ fullerene dimer. It has been found that the MP2-F12 theory significantly overestimates the interaction energy of fullerene dimer compared to the experimentally estimated value. Moreover, SCS-MP2 (spin component scaled) method[2], which is famous for the improvement of the description of the dispersion energy of small molecules such as benzene, also somewhat overestimates the interaction energy in the fullerene dimer. We considered that the reason of the failure of the SCS method is that it does not include the information about the orbital energy of the system. In fact the HOMO-LUMO gap of the fullerene is significantly small. Based on this observation, we designed the new scaling scheme in the MP2 method, of which scaling factors depend on the orbital energies. The new scheme presents reasonable interaction energy from small benzene dimer to large fullerene dimer as well as the hydrogen bonded water dimer.

The details of the implementation, the theory of MP2-F12 and new scaling scheme, and the results in the S66 test set[3] will be presented in the poster session.

[1] W. Klopper, F. R. Manby, S. Ten-no, E. F. Valeev, *Int. Rev. Phys. Chem.* 25, 427–468 (2006)

[2] S. Grimme, L. Goerigk, and R. F. Fink, *WIREs Comput. Mol. Sci.* 2, 886–906 (2012)

[3] J. Řezáč, K. E. Riley, and P. Hobza, *J. Chem. Theory Comput.* 7, 2427–2438 (2011)

Multiple-input parallel RHF calculation for improving SIMD operation efficiency

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Introduction

Currently, there are many research projects developing exascale supercomputer systems. To build up exascale computer systems, it is imperative to use many-core processors, which will have 16 or larger-ways SIMD functional units from requirements of high performance and low power consumption[1]. However, conventional Hartree-Fock programs have quite low SIMD operation level parallelization for the two-electron Fock-matrix (G-matrix) calculation which is the bottleneck of RHF program, since each loop length of contraction of primitive molecular integrals is determined at runtime and there are many complex data-dependencies in each primitive molecular integral calculation. In this research, we propose a Hartree-Fock method which calculates multiple-inputs of different molecular structures in parallel, and those calculations are applied for SIMD parallel operations. We evaluate maximum performances for our method with test inputs whose structure data are same.

Multiple-input parallel RHF calculation

Generally, for improving SIMD operation efficiency, target program has to be implemented as follows: (1) array elements of multiple-input data are aligned as continuous memory addresses for efficient vector-load and store operations, (2) data are aligned in adequate memory address boundaries, and (3) array notations are utilized for the SIMD operation regions. According to these rules, we implemented the G-matrix calculation of multiple-input data. Except for G-matrix calculation, data were allocated at independent memory regions and original sequential codes were reused at loop body regions of multiple-input loop calculations.

Performance evaluations

We evaluated our proposed methods by three types of desktop computers with Xeon 2-way X5650, 2 and 4-way E5-2650, and 8-way Phi processors. For parallel G-matrix computations, we achieved 1.82, 1.97 and 5.84 times speed-ups for Intel Xeon X5650, E5-2650, and Phi processor computers, respectively. It is expected that multiple-input parallel calculation will improve the SIMD operation efficiency for practical calculations of potential energy surfaces.

[1] "Exascale Computing Study Report", [Online]. Available:
http://users.ece.gatech.edu/mrichard/ExascaleComputingStudyReports/ECS_reports.htm.

Essentially exact ground-state calculations of few-electron molecular systems by superpositions of nonorthogonal Slater determinants

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I. Introduction

A tractable calculation algorithm to calculate essentially exact electron-electron correlation energies by the superposition of nonorthogonal Slater determinants (SDs) [1] is presented. The key to the proposed procedure for updating nonorthogonal one-electron wavefunctions to ground states is that linearly independent multiple correction functions are employed and optimized on the basis of a variational principle [2-7]. The accuracy and applicability are demonstrated through calculations of the ground-state energies for atoms and molecules.

II. Applications to few-electron systems

Figs. 1 and 2 show the numbers of SDs required to count 98% of the electron-electron correlation energy for few-electron atoms and the potential energy curve of a HF molecule, respectively.

III. Summary

The convergence performance to the ground state is improved by multiplying the correction functions. A drastic reduction of the number of SDs required to determine the ground-state energies and a modest increase with the system size are illustrated.

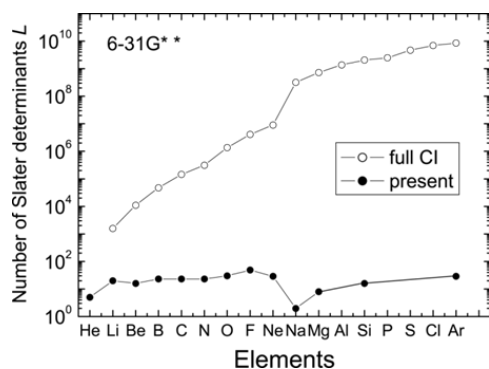


Fig. 1 Required number of SDs to obtain ground states of atoms.

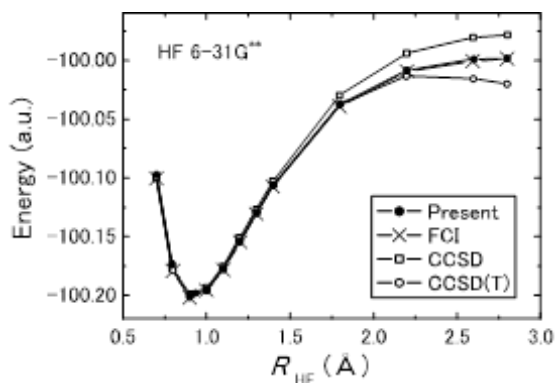


Fig. 2 Potential energy curve of a HF molecule obtained by using the proposed algorithm.

- [1] H. Fukutome, Prog. Theor. Phys. 80, 417 (1988)
- [2] H. Goto and K. Hirose, J. Phys.: Condens. Matter 21, 064231 (2009)
- [3] H. Goto, T. Yamashiki, S. Saito and K. Hirose, J. Comput. Theor. Nanosci. 6, 2576 (2009)
- [4] H. Goto and K. Hirose, J. Nanosci. Nanotechnol. 11, 2997 (2011)
- [5] A. Sasaki, M. Kojo, K. Hirose and H. Goto, J. Phys.: Condens. Matter 23, 434001 (2011)
- [6] A. Sasaki, K. Hirose and H. Goto, Curr. Appl. Phys., 12, S96-S99 (2012)
- [7] H. Goto, M. Kojo, A. Sasaki and K. Hirose, Nanoscale Research Letters, 8:200 (2013)

Recent progress in quantum chemical density matrix renormalization group methods

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The multireference electronic structure methods based on the density matrix renormalization group (DMRG) theory have been emerging as a robust tool for describing quantum chemical systems where single-particle methods, such as density functional theory (DFT), is no longer reliable due to strong electron correlation. In our poster presentation, we will demonstrate applicability of DMRG and associated dynamical correlation methods to challenging multireference systems. The calculations of near-exact entangled wavefunction of the photosystem II Mn₄Ca cluster of Shen and Kamiya's XRD structure will be shown, which efficiently dealt with more than 10^{18} quantum degrees of freedom for the physical electronic states. The recent development of the combination of DMRG and MRCI methods as well as the methods to compute magnetic properties with/without inclusion of relativistic effects will be discussed.

New Orbital Optimization Approach via Thouless Theorem.

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Recently, we have proposed a new approach which is equivalent to orbital optimized second order Møller-Plesset perturbation theory[1]. It is based upon using the Thouless theorem, namely expressing the zeroth order wave function as an exponential cluster expansion using merely the single excitation operator whose amplitudes are variationally determined by minimizing the total energy functional[2; 3] that includes a modified second order Hylleraas functional. This Thouless expansion optimized MP2 approach works with the same set of reference orbitals during the whole optimizing procedure, hence it can be ideally utilized also with localized orbitals. The implementation has been numerically tested on a set of small molecules, while the convergence properties have been investigated with respect to the starting reference determinant. In addition, the performance of the method is shown for a set of reaction enthalpies for reactions of small molecules as well as for the S22 set of interaction energies . Based on our previous work, we propose Brueckner coupled cluster method via optimized Thouless expansion. Comparison with conventional CCSD and CCSD(T) approach will be presented for small set of reactions and for interaction energies.

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[1]J. Šimunek and J. Noga, Mol. Phys. 111, 1119 (2013).

[2]J. Šimunek and J. Noga, in ICCMSE 2009, edited by T. E. Simos and G. Maroulis (American Institute of Physics, Melville, New York, 2012), vol. 1504 of AIP Conf. Proc., p. 143.

[3] J. Noga and J. Šimunek, J. Chem. Theory Comput. 6, 2706 (2010).

Statistical mechanics based on cumulant dynamics

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We have proposed a quantal cumulant dynamics (QCD) method for the investigation of weak quantum effects on model and molecular systems such as zero-point vibrational effects, proton transfer reactions and so on [1-4]. The essence of this method is to treat with an extended dynamics of distribution characterized as expectation values generating from the distribution. Within this scheme, not only the position and momentum but also the cumulant variables, which are functions of mixed position and momentum moment operators, play a central role in their propagation. In the present study we utilized the same procedures to treat problems appearing in classical statistical mechanics. We referred to it as classical cumulant dynamics (CCD). The same kind of methodology was proposed by Prezhdo and co-workers. In their method, the expectation value of the total energy is directly substituted into the Boltzmann factor that results in introduction of an additional prefactor for rescaling the inverse temperature in order to apply their theory to the exactly soluble models such as the free-particle and harmonic oscillator [5].

In this study, we formulated statistical mechanics on the basis of CCD and proposed a method for the variational determination of free energy within cumulant mechanics. For the many body systems interacting with two-body interaction, the free energy of the system is given by the second-order CCD as

$$F = \sum_i \frac{(\mathbf{p}_i^2 + \hbar \mathbf{l} \cdot \boldsymbol{\sigma}_i)}{2m_i} + \sum_{ij} \int \frac{ds_i ds_j}{(2\pi)^3 \sqrt{\det|\sigma_i \lambda_i|}} e^{-\frac{1}{2}(\mathbf{s}_i - \mathbf{q}_i)^T \lambda_i^{-1} (\mathbf{s}_i - \mathbf{q}_i) - \frac{1}{2}(\mathbf{s}_j - \mathbf{q}_j)^T \lambda_j^{-1} (\mathbf{s}_j - \mathbf{q}_j)} V(s_{ij}) \\ - \frac{k_B T}{2} \sum_i \ln(\det|\sigma_i \lambda_i|)$$

The first and second terms come from the enthalpy contribution and the third from the entropy one. We have applied the method to 7-particle Morse clusters, where particles interact with the inter-particle Morse potential $V_M(r_{ij}) = \exp(-2(r_{ij} - R_e)) - \exp(-(r_{ij} - R_e))$. Free energy landscape along two-dimensional reaction coordinates for a deformation of cluster from PBP (pentagonal bipyramid) to COCT (capped octahedron) structures is evaluated, where we set temperature as $k_B T = 0.01$ (/unit) and mass as $m = 1000$. It is found that the method well reproduces the free energy difference obtained by the conventional method with less computational cost indicating a promising method to evaluate free energy surfaces of large clusters.

References

- [1] Y. Shigeta, H. Miyachi, K. Hirao, **JCP** **125**, 244102 (2006). [2] Y. Shigeta, **JCP** **128**, 161103(2008). [3] Y. Shigeta, T. Matsui, H. Miyachi, K. Hirao, **BCSJ** **81**, 1230 (2008). [4] Y. Shigeta **BCSJ** **82**, 1323 (2009). [5] E. Heatwole, O. Prezhdo, **JCP** **121**, 10967 (2004).

Time Evolution of Atomic and Molecular Systems by Rigged QED

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We discuss a method to follow the step-by-step time evolution of atomic and molecular systems based on Rigged QED (Quantum Electrodynamics) [1]. In our formulation, both electron and photon fields are treated as quantized fields. We show that the “electron-positron oscillations”, the fluctuations originated from virtual electron-positron pair creations/annihilations, are found in the time evolution of the charge density of a hydrogen atom and molecule. We also show that the oscillations are affected by considering the self-energy process, in which the electron emits a photon and then absorbs it again.

In Ref. [2], we have studied the time evolution of one of the most basic physical quantity operators, the electronic charge density operator, and have discussed approximation methods to obtain the time evolution of its expectation value. The charge density operator is expressed by the product of one creation operator and one annihilation operator, which is called an excitation operator, but since the time derivative of creation/annihilation operators contains more than one of these operators, the time differential equation of the excitation operator is not closed. In Ref. [2], we have introduced several approximations to obtain the time evolution equation for the expectation value of the excitation operator, which is called a density matrix, and numerically solved the time evolution of the density matrix. The time evolution of the expectation value of the charge density operator has been obtained by multiplying the density matrix by the expansion functions of the field operator. Then, we have found that the time evolution of the charge density of a hydrogen atom exhibits very rapid oscillations of the period $\approx 1.7 \times 10^{-4}$ a.u., which corresponds to the inverse of twice the electron mass. This is interpreted as the fluctuations originated from the virtual electron-positron pair creations and annihilations, showing the effect of QED, and we have designated the phenomenon as “electron-positron oscillations”.

In the present paper, we improve one of the approximations employed in Ref. [2] with respect to the terms which include the photon creation/annihilation operators. In our formalism, the time derivative of the electron excitation operator has the terms which consist of an electron creation operator and an annihilation operator sandwiching a photon creation or annihilation operator (we call this type of operator by “ $\hat{e}^\dagger \hat{a} \hat{e}$ -type operator” for short). In Ref. [2], when we take the expectation value of these terms, we have factorized the terms into the expectation value of the excitation operator and that of the photon creation/annihilation operator. After this approximation, these terms give finite contribution only when an initial photon state is a coherent state, which is an eigenstate of the photon annihilation operator. In particular, they vanish for the photon vacuum state. To go one step further, we, in this paper, do not perform the above factorization, and solve the time evolution equation of the $\hat{e}^\dagger \hat{a} \hat{e}$ -type operators simultaneously with that of the excitation operator. This procedure corresponds to counting the self-energy process of the electron (the electron emits a photon and then absorbs it again), and, consistently, it gives non-zero contribution even when the initial state is the photon vacuum state. In fact, it is shown that the period of the electron-positron oscillations is affected by including this process.

The numerical calculation is performed by the QEDynamics code [3] developed in our group.

References

- [1] A. Tachibana, Field Energy Density In Chemical Reaction Systems. In *Fundamental World of Quantum Chemistry, A Tribute to the Memory of Per-Olov Löwdin*, E. J. Brändas and E. S. Kryachko Eds., Kluwer Academic Publishers, Dordrecht (2003), Vol. II, pp 211-239.
- [2] K. Ichikawa, M. Fukuda and A. Tachibana, *Int. J. Quant. Chem.* **113**, 190 (2013)
- [3] QEDynamics, M. Senami, K. Ichikawa and A. Tachibana
<http://www.tachibana.kues.kyoto-u.ac.jp/qed/index.html>

Surface effects on the reactivity of CeO₂ for hydration of cyanopyridine

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I. Introduction

CeO₂ shows very high activity and substrate specificity for nitrile hydration to amide [1]. For example, hydration of 2-cyanopyridine yielded 2-picolinamide quantitatively, while little amide for 3-cyanopyridine or 4-cyanopyridine was produced. Although the adsorption states of nitriles on Lewis acid site are experimentally suggested to be a key to understand the substrate specificity, there is no observation on the adsorption structures. In this study, we have calculated the adsorption structures of 2-cyanopyridine (hereinafter 2CNPy) and 4-cyanopyridine (4CNPy) on CeO₂(110) and CeO₂(111) surfaces. Furthermore, intermediates for nitrile hydration on CeO₂(110) were calculated.

II. Method

Spin-polarized DFT calculations were performed with the PWscf code. GGA+U approximation was adopted using Perdew-Burke-Ernzerhof (PBE) functional and the Hubbard U value for Ce atoms of 1.5 eV. Vanderbilt's ultrasoft pseudo-potentials were adopted with the kinetic-energy cutoff of 30 Ry for the plane-wave basis. CeO₂ surfaces were represented by slab models which are separated by a vacuum region of 15 Å. The Brillouin zone was sampled with the 2 × 2 × 1 Monkhorst-Pack grid k-points.

III. Results and discussion

Fig. 1 shows optimized structures and relative energies of 2CNPy and 4CNPy on the CeO₂(111) surface. The preferred adsorption for 2CNPy is Fig.1a and that of 4CNPy is Fig.1c. This is because basicity of nitrogen of pyridine ring (N_{pyridine}) is stronger than that of N of nitrile (N_{nitrile}). In the case of the adsorption of 2CNPy, two point's interaction takes place with the bonds of N_{pyridine}-Ce and N_{nitrile}-Ce. This two point's interaction also occurs for the adsorption modes of 2CNPy on a CeO₂(110) surface. In this configuration, nitrile group is so close to the surface that reactive OH adspecies produced on the surface can easily approach the CN group. On the other hand, nitrile of the stable adsorption of 4CNPy is far away from the surface. The relative position of nitrile mainly determines the reactivity for nitrile hydration. Thus, substrate specificity comes from the two point's interaction which is possible with the adequate position of Lewis acid sites on CeO₂ surface structures.

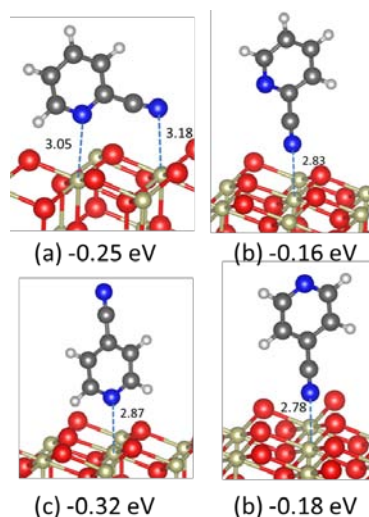


Fig.1 Optimized structures and relative energies of 2CNPy (a), (b) and 4CNPy (c), (d) on CeO₂(111) surface. Ce atoms are in yellow, N in blue, O in red, and H in white.

Development of model effective Hamiltonian to study low-lying d–d excited states of $[\text{Fe}(\text{bpy})_3]^{2+}$

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Photophysical properties of transition metal (TM) complexes have been paid attention due to their fundamental importance as well as potential applications in various technologies. Recently, electronic relaxation processes have been studied experimentally for several prototypical TM complexes such as $[\text{Fe}(\text{bpy})_3]^{2+}$ [1]. However, because various processes such as internal conversion, intersystem crossing, and vibrational relaxation often occur in a competing fashion, underlying mechanisms have not been fully clarified [2].

Molecular dynamics (MD) simulation could be an effective tool to clarify the relaxation processes. However, high-level electronic structure calculations such as CASPT2 are generally required for describing electronic excited states of TM complexes. Such *ab initio* calculations are computationally too demanding to be used in dynamics simulations. In addition, the description of spin–orbit (SO) and non–adiabatic couplings is necessary for dynamics studies. In this regard, it would be meaningful to develop a simple method to describe TM electronic structures for use in dynamics simulations.

For this reason, we have been developing a simple model effective Hamiltonian for describing the ground and d–d excited states of $[\text{Fe}(\text{bpy})_3]^{2+}$ on the basis of benchmark density-functional theory calculations for the lowest energy states within singlet, triplet, and quintet states [3,4] (Fig.1). The SO couplings were included through simple one-electron one-center operator within the framework of the model Hamiltonian. It was shown from MD simulations that the constructed model Hamiltonian reasonably describes potential energy surfaces and solvation structures of the lowest singlet and the lowest quintet states in aqueous solution. The MD simulation results have also demonstrated that the model Hamiltonian provides a reasonable description of excited states not only around equilibrium structure regions but also around surface crossing regions.

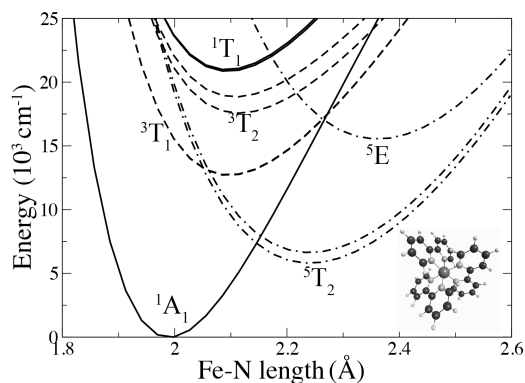


Fig. 1. Potential energy curves obtained by the model Hamiltonian for several low-lying d–d states along the linearly interpolated path between the lowest singlet and the lowest quintet states. Ref. [3].

- [1] e.g., Ch. Bressler *et al.*, *Science* **323**, 489 (2009).
- [2] M. Chergui, *Dalton Trans.* **41**, 13022 (2012).
- [3] S. Iuchi, *J. Chem. Phys.* **136**, 064519 (2012).
- [4] S. Iuchi and N. Koga, *to be submitted*.

Crystal Structure Prediction by using the GRRM method

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I. Introduction

We are trying to predict crystal structures by using the GRRM method [1] and the generalized scaled hypersphere search method [2]. In this study, not only coordinates of atoms or molecules but also lattice vectors are optimized. Energy of crystals were estimated by using *ab initio* calculation or SCC-DFTB method [3] or Buckingham potential.[4]

II. Results and Discussion

As an example of crystal structure prediction by using the GRRM method, Fig. 1 shows predicted crystal structures for four carbon atoms in a unit cell. Fig.2 shows one of predicted crystal structures of benzene by using Buckingham potential. It is remarkable that experimental structures are reproduced in these calculations.

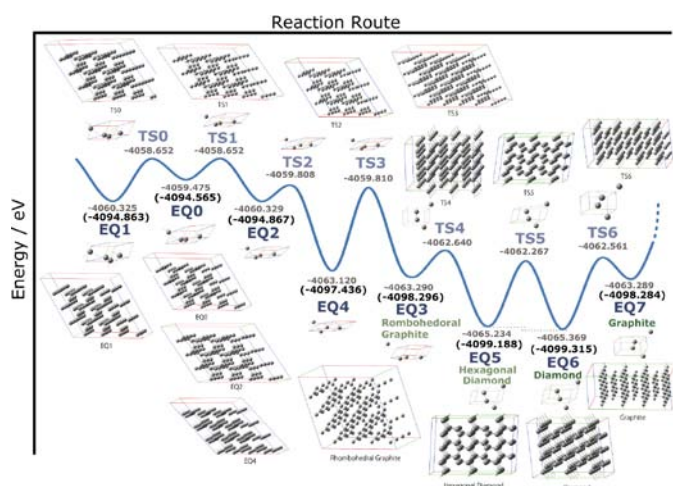


Fig. 1. Predicted crystal structures for carbon atoms. (C_4 / unit)

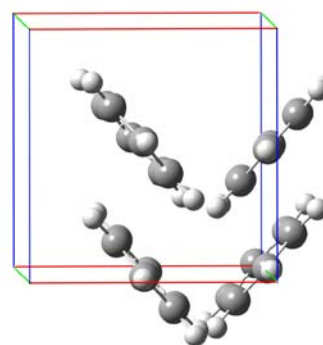


Fig. 2. The most stable crystal structure of benzene.

[1] K. Ohno, S. Maeda, *Chem. Phys. Lett.*, **348**, 277 (2004); S. Maeda, K. Ohno, *J. Phys. Chem. A* **109**, 5724 (2005); K. Ohno, S. Maeda, *J. Phys. Chem. A* **110**, 8933 (2006).

[2] K. Ohno, Y. Osada, S. Maeda, *Bunshikagaku touronkai 2010*, 1E15 (2010).

[3] M. Elstner, T. Frauenheim, S. Suhai and M. Karplus, *Phys. Rev. B*, **58**, 7260 (1998).

[4] D.E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966)

Density Functional Study of Selective Binding to Negatively Charged N₂S₂-type Co(III) complex

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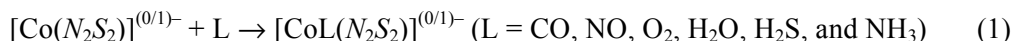
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I. Introduction

A series of N₂S₂-type Co(III) complexes modeled on an active site of nitrile hydratase (NHase) are potential complex of binding selectivity in bioactive small molecules CO, NO, and O₂ having 14, 15, and 16 valence electrons, respectively. It is expected that the binding selectivity comes from negatively charged coordination environment like porphyrin complex.

In this work, we studied binding of neutral small molecules L (L = CO, NO, O₂, H₂O, H₂S, and NH₃) to N₂S₂-type Co(III) complexes having different number of amido-type N atom ([Co(N₂S₂)]^{(0/1)-}, Figure 1) in order to investigate an effect of negatively charged coordination environment on NO-selectivity. We calculated complexation energies of reaction (1) at DFT level with OPBE functionals and analyzed electronic structure to elucidate the bonding interaction.



II. Results and Discussion

The binding interaction of L with the both N₂S₂-type Co(III) complexes increases in order of L = H₂O, H₂S, O₂, NH₃, CO, and NO. The strong binding of NO arises from pairing of an unpaired electron of NO with an electron in a *d_π* orbital of the Co complex.¹ The bonding interaction of the negatively charged complex with a NO ligand is small in contrast to its large NBO bond order. A negatively charged coordination environment excludes a σ-donation but enhances a π-back donation as a result of expansion of the *d_π* orbital on the Co(III) ion. Simultaneously, the paired *d_π* electrons in the negatively charged complex have a large repulsive interaction with 3*d_π* orbitals to the ligand.

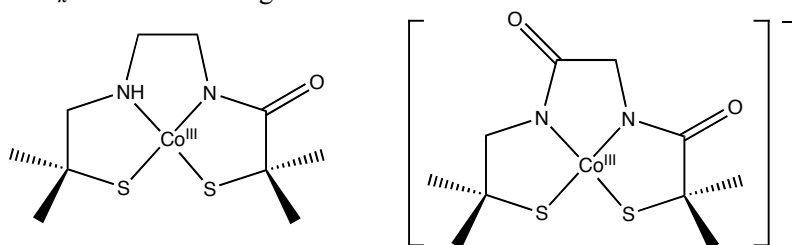


Fig. 1. Co-centered N₂S₂ complexes of NHase analogues.

[1] Hoffmann, R.; Chen, M. M.-L.; Elian, M.; Rossi, A. R.; Mingos, D.M. P. *Inorg. Chem.* **1974**, 13, 2666-2675.

Unique Spin State of Inverted Sandwich Type Complexes with Hetero Dinuclear Transition Metals Bridged by Dinitrogen Molecule

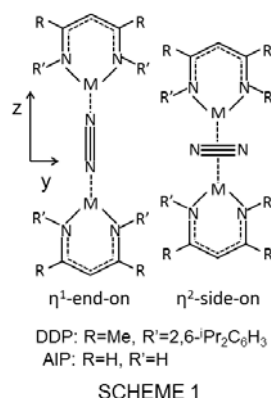
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The spin state of inverted sandwich type complex (ISTC) significantly depends on metal and sandwiched organic molecule. In particular, di-nitrogen bridged ISTC with DDP ligand (DDPH = 2-(4-{(2,6-diisopropylphenyl)-amino}pent-2-ene; SCHEME 1) is very interesting, as follows: The Fe-ISTC takes a septet spin state and an η^1 -end-on N_2 coordination form. On the other hand, the Cr-ISTC takes an open-shell singlet state and an η^2 -side-on coordination form. In previous study, we clarified that these differences in N_2 coordination mode and spin multiplicity result from the difference of the d_π - π^* bonding interaction between N_2 and metal atoms. In this study, we focus the electronic structure and spin state of the ISTC with hetero dinuclear transition metals.

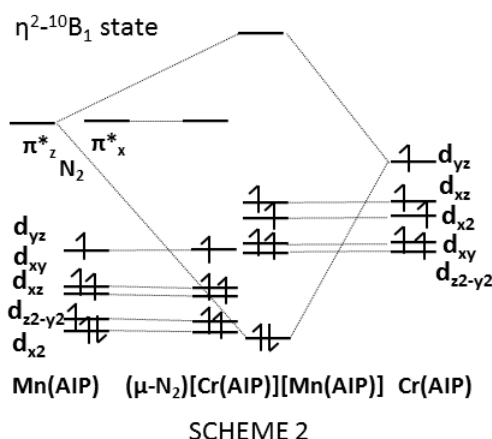


We employed AIP (AIPH = 1-amino-3-imino-prop-1-ene; SCHEME 1) was employed as a model of DDP, for brevity. The combinations of two metals (M_1, M_2) = {(Cr, Mn), (Cr, Fe), (Cr, Co)} were investigated. The geometry optimization was performed at each spin state with the CASSCF method. The relative energies of various spin states were calculated by the CASPT2 method.

In the (Cr, Mn) complex, the $^{10}B_1$ state with η^2 -side N_2 coordination is the ground state (Table 1). In the B_1 state, the Cr d_{yz} orbital forms the bonding MO with the N_2 π^* orbital, which are doubly occupied, and other d orbitals are singly occupied (SCHEME 2). Another electronic state (A_2 state) was also found, in which the bonding d_π - π^* orbital is formed between Mn and N_2 . The 2A_2 state is 4.4 kcal/mol higher than the $^{10}B_1$ state. However, the A_2 state becomes more stable in the (Cr, Co) complex. Based on these results, it is calculated that the highest spin multiplicity of the dectet is presented in the (Cr, Mn) complex.

Table 1. Relative energies (kcal/mol) of various spin multiplicities of $(\mu-N_2)[Cr(AIP)][Mn(AIP)]$

(M ₁ ,M ₂)	(Cr,Mn)			
	η^1 -end		η^2 -side	
	B ₂ state	B ₁ state	A ₂ state	B ₁ state
multiplicity				
10tet	13.5	14.1	18.3	0.0
8tet	7.6	15.5	6.2	1.4
6tet	8.2	16.0	5.7	2.3
4tet	9.5	16.2	5.5	2.8
2let	11.4	16.1	4.4	3.0



Theoretical Study of the TiO₂-TCNX Surface Complex Showing Interfacial Charge-Transfer Transitions

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Dye-sensitized solar cells (DSSCs) are devices for renewable energy sources that have been extensively investigated from both experimental and theoretical points of view. To achieve practical use of DSSCs, many studies have focused on enhancing the light-to-electron conversion efficiency (η), which is defined by the following equation: $\eta = J_{SC} V_{OC} ff / P_{in}$, where J_{SC} is the short-circuit current density, V_{OC} is the open circuit photovoltage, ff is the fill factor, and P_{in} is the power density of the incident light. The device made from current efficient ruthenium dye, N749, shows over 11% for η with $J_{SC} = 22.47 \text{ mA / cm}^2$ and $V_{OC} = 0.744 \text{ V}$.

A straightforward way to improve η is to increase the values of J_{SC} and V_{OC} . According to the theoretical estimation of the maximum efficiency of solar cells, the most effective system should absorb photons in the range from 400 nm to 1000 nm and have about 1.2 V for V_{OC} . In this situation, to develop dyes or molecules using the photons in the range to 1000 nm is needed. From the view point of using the photons in near IR region, we calculated the photo-properties of TiO₂-TCNQ surface complex showing interfacial charge transfer transitions and revealed the mechanism of making the surface complex. The nucleophilic addition reaction between strong electron acceptors induces the electron flow from TiO₂ to TCNQ in ground state, and then, the electron directly injects from TCNQ to TiO₂ under irradiance.

[1] R. Jono, J. Fujisawa, H. Segawa, K. Yamashita

J.Phys.Chem.Lett. **2**, 1167 (2011)

[2] S. Manzhos, R. Jono, K. Yamashita, J. Fujisawa, M. Nagata, H. Segawa

J.Phys.Chem.C **115**, 21487 (2011)

[3] R. Jono, J. Fujisawa, H. Segawa, K. Yamashita

Phys.Chem.Chem.Phys. **15**, 18584 (2013)

Computational Modeling of Protein Functions: Molecular Recognition and Enzymatic Catalysis

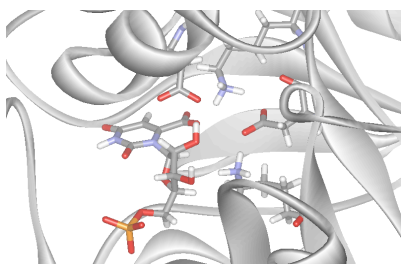
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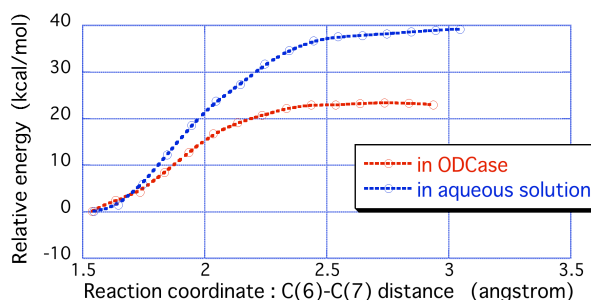
Recent progress in chemical theory and computational methods has opened the way for computer simulations to clarify the structure-function relationship in biomolecules. Given the wide variety of biological functions found in nature, understanding the molecular mechanism of ligand recognition and the catalytic power of enzyme reactions are two major challenges of modern theoretical chemistry. To address these important but difficult issues, the author has been investigating the computational methods (including hybrid QM/MM computations, free energy calculation based on molecular dynamics simulations, and all-electron QM calculations based on the fragment molecular orbital approximation), and applying these newly developed methods to various protein systems. In this 5th-JCS symposium, we would like to present some of recent simulation studies.

Effects of substrate distortion on enzymatic process: Case study of ODCase reaction

Although the general catalytic principle, so-called *the transition state stabilization* (TST), was proposed over half century ago, atomistic details of TS binding has not yet been clarified. Besides TST, another appealing hypothesis, such as *the substrate distortion*, is still actively debated issue in modern enzymology. One such example is orotidine-5'-monophosphate decarboxylase (ODCase), the enzyme that catalyzes the decarboxylation of orotidine-5'-monophosphate to uridine-5'-monophosphate in the last step of pyrimidine biosynthesis. To answer the controversial proposal for this enzymatic mechanism, we performed systematic *ab initio* QM/MM computational analyses combined with MD-FEP simulations, and *all-electron* QM calculations for the entire protein matrix. Our hybrid modeling analyses clearly showed that the reactive substrate has rather distorted geometry compared to the reactant in the aqueous phase, and this distortion can contribute up to ~4 kcal/mol energy reduction in the activation process.



(left) active site geometry of ODCase,



(right) free energy profiles of catalytic process

Ion mobility mass spectrometry and MM conformational search of glycopeptides

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Introduction

Glycosylation alters the physicochemical properties and biological activities of proteins. During biosynthesis, N-linked glycosylation promotes folding and overall stability of proteins. In fact, physicochemical analysis indicated that the innermost GlcNAc contributes to the entire acceleration of folding and to two thirds of the native state stabilization of glycoproteins, while the remaining one third is derived from the next 2 saccharide units^[1]. These facts prompted us to investigate the interaction between protein and glycan in the vicinity of the attachment site by using ion mobility MS of glycopeptides and furthermore to compare the data with the conformations calculated by molecular mechanics (MM). Herein, we analyzed the glycopeptide isoforms corresponding to the sequence 293-301 of four different IgG subclasses, which differ each other at either or both of residues 296 and 300 and have the N-glycosylation site at Asn297.

Method

Four different peptides EEQ(Y/F)NST(Y/F)R and their glycosylated species bearing a single GlcNAc at Asn were synthesized. The (glyco)peptide samples were analyzed by ion mobility MS using a Waters SYNAPT G2 system or in-house IMS-TOFMS instrument (David Clemmer's laboratory, Indiana University)^[2]. The drift time of doubly protonated molecules of (glyco)peptides was measured and converted into collision CCSs by a theoretical equation^[3].

The MM conformational searches (using MMFF94s force field) were performed by CONFLEX 7 (CONFLEX Co.).

Result

The amino acid sequences of tryptic glycopeptides from the IgG1 and IgG2 Fc regions are EEQYNSTYR (exact mass 1188.5; 296Y/300Y) and EEQFNSTFR (1156.5; 296F/300F), respectively. The IMS MS of doubly protonated molecules indicated that IgG1 glycopeptide displayed smaller CCS than IgG2 in spite of higher molecular mass. Interestingly, this conformational feature was observed in an artificial glycopeptide with a single GlcNAc, suggesting specific interaction between the innermost GlcNAc and peptide backbone sequence. The CCS of IgG3 (296Y/300F) was larger than IgG4 (296F/300Y), although the molecular mass was the same.

The MM gave the calculated CCSs consistent with the observations described above. The plausible conformations include hydrogen bonds between GlcNAc and peptide backbone. In addition, the conformation of these four unglycosylated peptides was considerably different each other and that of the GlcNAc-bearing species was as well, indicating that the hydrogen bonding between glycan and peptide within glycopeptides ions was dependent on the peptide sequence.

In general, the CCSs of glycopeptides are smaller than those of peptides. Our findings from IMS MS and MM calculation suggested that the interaction between the innermost GlcNAc and peptide backbone largely contributes to the compactness of glycopeptide ions in gas phase.

[1] Hanson, S. R.; Culyba, E. K.; Hsu, T. L.; Wong, C. H.; Kelly, J. W.; Powers, E. T. *Proc Natl Acad Sci U S A*. **2009**, *106*, 3131-3136.

[2] Koeniger, S. L.; Merenbloom, S. I.; Valentine, S. J.; Jarrold, M. F.; Udseth, H. R.; Smith, R. D.; Clemmer, D. E. *Anal. Chem.* **2006**, *78*, 4161-4174.

[3] Mason, E. A.; McDaniel, E. W. *Transport Properties of Ions in Gases*; Wiley: New York, **1988**.

Theoretical Calculations of Electronic Circular Dichroism for Single and Double Helicenes

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Helicenes are ortho-fused polyaromatic hydrocarbons that exhibit unique (chir)optical properties due to their inherent helical structure. For instance, (*P*)-(+)-[6]helicene exhibits apparently bisignate, strong positive and negative Cotton effects (CEs) at the 1B_b and 1B_a bands ($\Delta\epsilon \approx +259$ and $-272 \text{ M}^{-1} \text{ cm}^{-1}$) together with a smaller CE at the 1L_b band in circular dichroism (CD) spectrum. Such distinctive properties are potentially useful for preparing advanced (chir)optical materials, if designed appropriately.

We have recently investigated the CDs of a series of carbo[n]helicenes by using a combination of the state-of-the-art theoretical calculations and the experimental CD spectral examinations. Thus, the coupled cluster calculations successfully reproduced the experimental features both in excitation energy and rotational strength. The excitation energies at the 1B_b and 1B_a bands were found linearly dependent on the reciprocal number of aromatic ring ($1/n$; $n \geq 4$) and the anisotropy ($g = \Delta\epsilon/\epsilon$) factor at the $1B_b$ band was also a linear function of $1/n$, but only at $n \geq 6$. Such behaviour is best correlated with the helical pitch throughout the helicene series. We also elucidated the effects of substitution on the CD spectra of [6]helicenes, in terms of the distortion of helical structure as well as the electronic effects. These effects were again theoretically reproduced properly, but the changes in chiroptical properties, caused by substitution, were rather marginal, revealing that simple substitution is not sufficient for significantly manipulating the chiroptical properties of helicenes.

Accordingly, we designed a set of S- and X-shaped double, or fused, helicenes, i.e. phenanthro[3,4-*c*;3'4'-*j*]chrysene and dinaphtho[2,1-*i*;2'1'-*l*]-[6]helicene, where the electric and magnetic transition dipole moments are expected to be aligned in the same direction, by which the rotatory strength in CD spectrum can be significantly augmented. In the presentation, we will report the experimental and theoretical CD spectra of these double helicenes, and explain the origin of the strong CEs observed for these helicenes by using the model systems based on parent [6]helicene. Successful enhancement of CEs in these double helicenes may provide us with a new strategy for designing advance chiroptical materials and devices based on helical structure.

[1] Y. Nakai, T. Mori, K. Sato and Y. Inoue, J. Phys. Chem. A, 117, 5082 (2013).

[2] Y. Nakai, T. Mori and Y. Inoue, J. Phys. Chem. A, 117, 83 (2013).

[3] Y. Nakai, T. Mori and Y. Inoue, J. Phys. Chem. A, 116, 7372 (2013).

Spectroscopy and Dynamics of Molecular Multiply Excited States

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Multiply excited states of molecules are short-lived resonance states which decay through autoionizations and neutral dissociations. The wave functions of such states cannot simply be described by the Born-Oppenheimer products due to the mixing with the electronic continua, hence the dynamics of the formation and decay of them has attracted many theoretical and experimental investigations. We have studied the dynamics of the multiply excited neutral states by measuring (i) the cross sections for the generation of a pair of two photons emitted by neutral fragments [1,2], and (ii) the cross sections for the formation of metastable atomic hydrogen in the 2s state [3,4], in photoexcitation of molecules. With the former measurements, we are able to observe the multiply excited states around the double ionization potentials that dissociate into neutrals. Those states are higher than any ever found in the extreme ultraviolet range (see Fig. 1). With the latter measurements, the cross section curves with the symmetry of electronic states being separated can be obtained for the case of linear molecules, which has great benefit for understanding the dynamics. We also measured the angular distribution of two Lyman- α photons so as to show the generation of an entangled pair of two H(2p) atoms in photodissociation of H₂ [5]. A brief review will be given in the presentation.

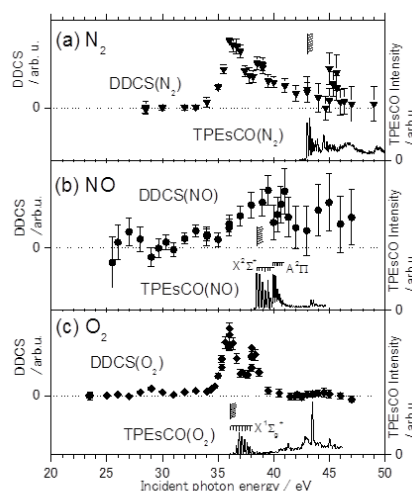


Fig. 1. The doubly differential cross sections for the generation of a photon pair in photoexcitation (DDCS) and the threshold photoelectrons coincidence spectra (TPEsCO) (G. Dawber et al., J. Phys. B 27 (1994) 2191) of N₂ (a), NO (b) and O₂ (c) [1].

- [1] T. Odagiri et al.: "The generation of a pair of photons from superexcited states of nitric oxide around the double ionization potential", J. Phys. B: At. Mol. Opt. Phys. **42** (2009) 225101 and references therein.
- [2] T. Odagiri et al.: "Three-body neutral dissociations of a multiply excited water molecule around the double ionization potential", J. Phys. B: At. Mol. Opt. Phys. **45** (2012) 215204.
- [3] T. Odagiri et al.: "Formation of metastable atomic hydrogen in the 2s state from symmetry-resolved doubly excited states of molecular hydrogen", Phys. Rev. A **84** (2011) 053401.
- [4] Y. Kumagai et al.: "Cross sections for the formation of H(n = 2) atom via superexcited states in photoexcitation of methane and ammonia", J. Chem. Phys. **139** (2013) 164307.
- [5] T. Tanabe et al., "Large Pressure Effect on the Angular Distribution of Two Lyman- α Photons Emitted by an Entangled Pair of H(2p) Atoms in the Photodissociation of H₂", Phys. Rev. Lett. **103** (2009) 173002

Auger decay spectra calculations for some small molecules

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I. Introduction

Auger decay process is one of decay process following core-excitation. A core-hole state is unstable, so decay processes take place rapidly within femtoseconds order, which corresponds to the lifetime of the core-hole state. For lighter atom system, dynamics induced by core-hole creation is also reflected in the observed spectra [1]. To reproduce experimental spectra, these all effects should be included properly.

Previously, we developed Auger decay calculations with population analysis [2]. Although this approximation looks quite rough, correspondence with experiments is reasonable, and our procedure can be applied to much system due to the simplicity. Recently, Auger spectrum of unstable chemical species such as H_2O^+ has been reported through core-valence excited state.[3] In the present study, our previous procedure is extended to open shell system such as H_2O^+ .

II. Computational methods

Auger decay rates were estimated within the two-step mechanism. The geometry sampling of at the ground state was performed by long molecular dynamics trajectories randomly. For each geometry, core-hole excited state dynamics at the core ionized state was propagated within 20 fs. Auger final states were estimated by multi-reference single and double CI calculations of triple ionized state for H_2O^+ . Auger decay calculations were performed along these trajectories. Each Auger spectrum along a trajectory were summed with decay ratio, and obtained Auger spectra were summed with weights estimated by vibrational wavefunctions quantum mechanically.

III. Results and Discussion

Normal Auger spectrum of H_2O^+ was shown in Fig. 1. Experimental spectrum was referred from Ref. [3]. Calculated spectrum is consistent with experiments. Time propagation of Auger spectra for core-hole and core-valence-hole states are examined. For both cases, a start geometry sets to the equilibrium geometry at the ground state. For the core-hole state, which is excited bending mode slowly, main peak positions are not changed. On the other hand, for the core-valence state, which is rapid three-body dissociation, all peaks are shifted to lower binding energy. These changes are reflected to the total Auger spectra.

[1] O Talahashi *et al*, *J Chem. Phys.*, **124**, 064307(2006). [2] M Mitani *et al*, *J. Electron Spectrosc. Relat. Phenom.*, **128**, 103(2003).

[3] M Muche *et al*, *Chem. Phys. Lett.*, **558**, 82(2013).

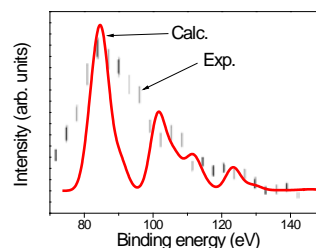


Fig.1: Auger spectra of H_2O^+ .

A Hybrid CASSCF/MRMP2 Method for the Quantitative Calculations of the Spin–Orbit Term of Zero-Field Splitting Tensors: A Case Study on Halogen-Substituted High-Spin Nitrenes

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Quantitative ab initio calculations of zero-field splitting (ZFS) tensors (**D** tensors) are one of the long-standing issues in theoretical chemistry as well as in electron spin science. Origins of ZFS are spin–spin dipolar (SS) and spin–orbit (SO) couplings. In 2009, we have proposed a hybrid CASSCF/MRMP2 method for the quantitative calculations of the SO term of **D** tensor (**D**^{SO} tensor). [1,2]

In 2012, Misochko and coworkers reported that dibromo-substituted trinitrenopyridine **3** has an unprecedentedly large $|D|$ value compared with difluoro and dichloro derivatives **1** and **2** (see Figure 1) [3–5]. With the aid of DFT calculations, they concluded that SOC plays an essentially important role in the contribution to the **D** tensor of **3**. However, origin of the heavy atom effects has not been discussed.

In this work, we have applied the CASSCF and the hybrid CASSCF/MRMP2 methods to the **D**^{SS} and the **D**^{SO} tensors, respectively, of halogen-substituted trinitrenopyridines **1–3** and *p*-phenylnitrenes **4–7**, focusing on the heavy atom effects on the **D**^{SO} tensors. These nitrenes give testing grounds for the methods of the **D** tensors.

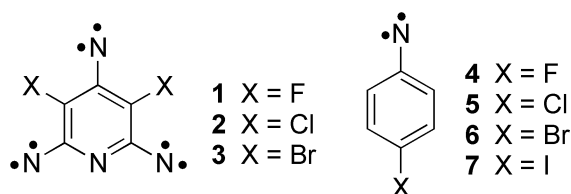


Figure 1. Target molecules.

[1] K. Sugisaki, K. Toyota, K. Sato, D. Shiomi, M. Kitagawa and T. Takui, *Chem. Phys. Lett.* **2009**, 477, 369-373.

[2] K. Sugisaki, K. Toyota, K. Sato, D. Shiomi, M. Kitagawa and T. Takui, In *EPR of Free Radicals in Solids I*, 2nd Edition, Springer: 2013, chapter 8, pp. 363-392., and references therein.

[3] S. V. Chapyshev, D. Gtote, C. Finke and W. Sander, *J. Org. Chem.* **2008**, 73, 7045-7051.

[4] E. Y. Misochko, A. V. Akimov, S. V. Chapyshev, *J. Chem. Phys.* **2008**, 129, 174510.

[5] E. Y. Misochko, A. V. Akimov, A. A. Masitov, D. V. Korchagin, I. K. Yakushchenko and S. V. Chapyshev, *J. Chem. Phys.* **2012**, 137, 064308.

DFT Calculations of the Spin–Orbit Term of Zero-Field Splitting Tensors: An Orbital Region Partitioning for the Analysis of PK-DFT, and Proposal of a Modified QRO Method

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Recently quantum chemical calculations of zero-field splitting (ZFS) tensors (**D** tensors) have attracted attention in theoretical chemistry as well as in high-spin chemistry. Major physical origins of ZFS are spin–spin dipolar (SS) and spin–orbit (SO) couplings. Those appear as the first- and second-order terms, respectively, in the perturbation expansion starting from non-relativistic Schrödinger equation.

In transition metal complexes and single molecule magnets, the SO terms of the **D** tensors (**D**^{SO} tensors) are generally more important than the SS terms (**D**^{SS} tensors). For the calculations of the **D**^{SO} tensors of such large molecular systems, DFT-based approaches are preferable than ab initio methods from the viewpoint of computational costs. Unfortunately DFT-based approaches sometimes give the **D**^{SO} tensors far from those obtained by means of sophisticated ab initio calculations such as a hybrid CASSCF/MRMP2, previously proposed by us.[1–4] Establishment of theoretical methodologies for the analysis of the calculated **D**^{SO} tensors and improvement in the theoretical framework for the DFT-based **D**^{SO} tensor calculations are the focus of current issues in theoretical chemistry.

In this work we will discuss two topics: In the first topic we will propose an orbital region partitioning technique for the analysis of the **D**^{SO} tensors calculated in terms of a Pederson–Khanna (PK) approach.[5] This approach enables us to determine which excitations are important in respect of the **D**^{SO} tensors very easily. In the second topic we will propose a modified version of the quasi-restricted orbital[6] (modified QRO) method, which is derived on the basis of the structure of spin eigenfunctions. The basic concept of the modified QRO method is "summing over all possible singly excited configurations from the reference determinant". Derivations and some preliminary applications will be given.

- [1] K. Sugisaki, K. Toyota, K. Sato, D. Shiomi, M. Kitagawa and T. Takui, *Chem. Phys. Lett.* **2009**, 477, 369–373.
- [2] K. Sugisaki, K. Toyota, K. Sato, D. Shiomi, M. Kitagawa and T. Takui, *ChemPhysChem* **2010**, 11, 3146–3151.
- [3] K. Sugisaki, K. Toyota, K. Sato, D. Shiomi, M. Kitagawa and T. Takui, *Phys. Chem. Chem. Phys.* **2011**, 13, 6970–6980.
- [4] K. Sugisaki, K. Toyota, K. Sato, D. Shiomi, M. Kitagawa and T. Takui, in *EPR of Free Radicals in Solids I*, Springer, 2013, Chapter 8, pp. 363–392.
- [5] M. R. Pederson and S. N. Khanna, *Phys. Rev. B* **1999**, 60, 9566–9572.
- [6] F. Neese, *J. Am. Chem. Soc.* **2006**, 128, 10213–10222.

Transition-Density-Fragment Interaction Combined with Transfer Integral Approach for Excitation-Energy Transfer via Charge-Transfer States

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Excitation-energy transfer (EET) is a well-known phenomenon observed in pair or aggregates of molecules, and its feature is widely used in biological systems such as green-plant photosynthesis.

As a pioneering study, Förster derived the rate constant of EET using Fermi's golden rule. In the framework of the Förster theory, an electronic coupling required for the EET rate is reduced to the Coulomb coupling termed as "pseudo Coulombic interaction", and hence the coupling is approximated to the dipole-dipole (DD) interaction using the transition dipole moments for individual chromophores. Although the DD method has been applied to various EET studies because of its practical usefulness, this method is limited for donor (*D*)-acceptor (*A*)

molecules that are separated largely compared with their molecular sizes. As shown in **Fig. 1**, the intermolecular distance between RET and SXN (~13 Å) are smaller than their molecular sizes (~36 Å). In this case, the DD method becomes out of range for the EET study.

To circumvent this problem, the transition-density-fragment interaction (TDFI) method was developed [1,2]. In the TDFI method, the electronic coupling is represented using transition densities. Compared with the DD and transition charge from ESP (TrESP) methods, TDFI showed a much improved description of the electronic coupling, which led to the clarification of the underlying mechanisms of the EET in xanthorhodopsin (xR) [1] and of the exciton-coupled circular dichroism (ECCD) spectra observed in a retinal dimer [2]. The TDFI method was further combined with the transfer integral (TI) method so as to describe the charge-transfer (CT) interaction. This extension, named TDFI-TI, succeeded in analyzing the mechanism of EET via CT states (**Fig. 2**) [3]. TDFI-TI was also applicable to the excitation energy calculations for molecular crystals [4]. This method successfully reproduced the experimental absorption energies of solid-state tetracenes, which allowed us to analyze and understand the molecular mechanism of crystallochromy [4].

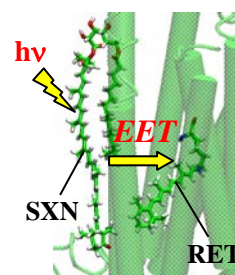


Fig. 1. EET in xR.

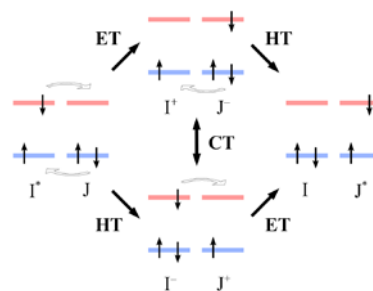


Fig. 2. EET via CT states.

[1] K. J. Fujimoto and S. Hayashi, *J. Am. Chem. Soc.* **131**, 14152 (2009). [2] K. J. Fujimoto, *J. Chem. Phys.* **133**, 124101 (2010). [3] K. J. Fujimoto, *J. Chem. Phys.* **137**, 034101 (2012). [4] K. J. Fujimoto and C. Kitamura, *J. Chem. Phys.* **139**, 084511 (2013).

Electronic excitations of conjugated molecules in vacuum and in solution

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Optical properties of large conjugated systems such as phthalocyanines and fullerenes have been receiving increasing attention since they are materials for molecular-based solar cells. Performing reliable calculations for the electronic excited states of large conjugated systems is still a challenging subject. Electron correlated computations for delocalized electronic states of large molecules are quite expensive but the direct SAC-CI method with perturbation-selection technique is found to be useful for the calculations of electronic excited states of large conjugated systems.

The optical absorption spectrum of C_{60} fullerene below 6.2 eV (200 nm) were calculated using the SAC-CI; our calculation included low-lying 61 excited states in I_h symmetry, which correspond to 230 states in abelian symmetry. The SAC-CI results were different from the previous assignment of the spectrum based on semi-empirical calculations.[1]

Solvent and other environmental effects are often considerable for the UV-vis spectra and other optical properties; therefore, we developed such a theory for solvated electronic excitations based on the SAC-CI method combining the polarizable continuum model (PCM).[2] Recently we developed a perturbative approach for the PCM SAC-CI; the solvent effects are considered by perturbation theory without performing costly self-consistent field iterations. This first-order PCM SAC-CI method is found to be a good approximation of the iterative PCM SAC-CI. The first-order PCM SAC-CI was applied to a solvatochromism of transition metal complexes.

The van der Waals interactions in excited states are another source of environmental effects particularly for nonpolar molecules in π - π^* state. The effects of van der Waals interactions in excited states for the free-base porphyrin were studied using the SAC-CI method that includes dispersion interaction in the excited states.[3]

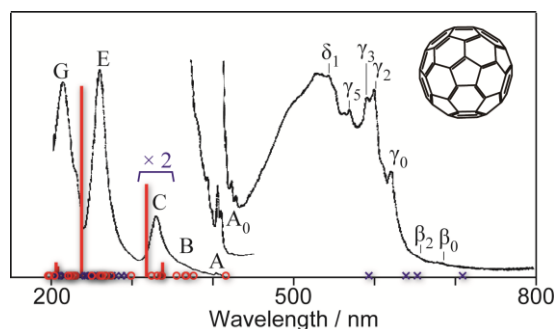


Fig. 1. Experimental absorption spectrum of C_{60} in n -heptane and the SAC-CI computational results.

[1] R. Fukuda and M. Ehara, *J. Chem. Phys.* **137**, 134304 (2012).

[2] R. Cammi, R. Fukuda, *et al*, *J. Chem. Phys.* **133**, 024104 (2010); *ibid* **134**, 104109 (2011).

[3] R. Fukuda and M. Ehara, *J. Chem. Theory Comput.* **9**, 470 (2013); *J. Chem. Phys.* **139**, 074303 (2013).

Efficient algorithm to optimize structures and reaction paths on free energy surface using QM/MM MD simulation

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In order to investigate reaction mechanisms in solution or proteins, free energy potentials along the reaction pathway should be obtained. For these purposes, both the free energy gradient (FEG) and the nudged elastic band (NEB) methods are introduced in QM/MM MD simulations. Although *ab initio* QM/MM calculations can be applied on reactive complexes to describe bond breakings or formations, it is very time consuming to obtain converged properties. Therefore, the charge response kernel and the structure response kernel are used to account the response of the QM ESP charges to MM and QM geometric perturbations¹ instead of using the expensive QM calculations. These response kernel approximations can reasonably reproduce not only electrostatic interactions between QM and MM regions but also QM gradients without QM calculations.

The FEG-NEB method (see Fig.1) can optimize reaction pathways as a chain of conformations on the free energy surface (FES). Since response kernel approximations drastically reduce the computational time, this method becomes a powerful approach to optimize structures and reaction pathways on FES.

This optimization method was applied on decarboxylation reactions of propylene carbonate² (PC) which is used as an electrolyte in the lithium battery. The solvation effect significantly lowered the free energy barrier as shown in Fig.2. The present simulation results indicate that the change of the dipole moment of PC during the reaction process is a key factor to control the free energy barrier.

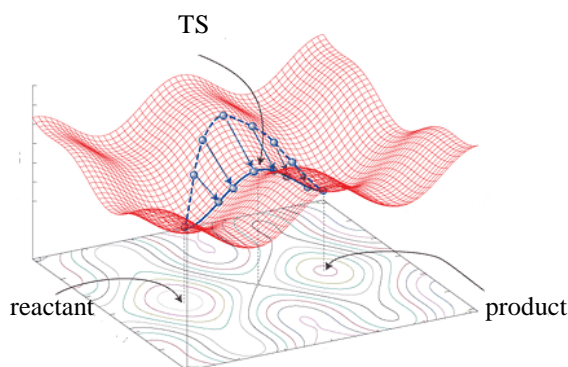


Fig. 1. Reaction path optimization on FES using FEG-NEB method.

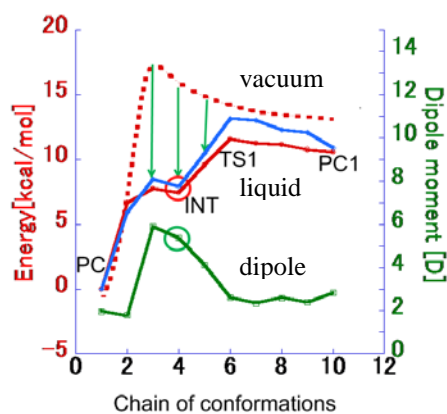


Fig. 2. Free energy profile of the decarboxylation reaction of PC molecule.

- [1] H.Hu, Z.Lu, J.M.Parks, S.K.Burger, W.Yang, *J.Chem.Phys.*, **128**, 034105 (2008).
[2] L.Xing, O.Borodin, G.D.Smith, W.Li, *J.Phys.Chem.A*, **115**, 13896 (2011).

Analysis and efficient time evolution of real-time TDHF/TDDFT calculation for electron dynamics

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I. Introduction

Electron dynamics, which is an ultrafast phenomenon occurring in femtoseconds, was recently observed by experiments and has attracted much attention. To theoretically describe electron dynamics, we can use real-time propagation (RT) method of time-dependent theories, such as the time-dependent Hartree-Fock (TDHF) method and time-dependent density functional theory (TDDFT). In previous studies, electron dynamics described by RT-TDHF/TDDFT calculations were analyzed by the Fourier transform technique to obtain frequency-domain properties and directly through time evolution of molecular properties [1-3]. Furthermore, the RT-TDHF/TDDFT calculations have limited applications than the conventional frequency-domain TDHF/TDDFT for evaluating excitation spectra and frequency-dependent polarizabilities, because evaluation of the time evolution operator is computationally demanding. In this study, we proposed two analyzing methods for electron dynamics, short-time Fourier transform (STFT) analysis and multidimensional spectroscopy (MDS) for electronic excited states, and developed efficient time evolution method with Chebyshev recurrence relation.

II. Analysis of electron dynamics

STFT has been utilized as a time-frequency analysis in the field of molecular dynamics simulation. We applied the STFT analysis to a time series of induced polarization vectors obtained by RT-TDHF/TDDFT calculation. The STFT analysis revealed that the induced polarization involving specific excited states propagated through intermolecular interaction [4]. MDS, such as two-dimensional IR and Raman spectroscopy [5,6], has been utilized for observing state-state coupling. We extended MDS to electronic excited states described by RT-TDHF. By using two-dimensional spectroscopy for excited states, we can obtain time evolution of electronic excited-state coupling. STFT and MDS with RT-TDHF/TDDFT calculations would be effective analyzing methods for electron dynamics associated with the excited states.

III. Efficient time evolution

A time evolution method based on Chebyshev recurrence relation (CRR) for time-dependent Schrödinger equation was developed and succeeded in decreasing computational cost of nuclear wave packet dynamics [7,8]. In this study, we developed CRR for time-dependent equation with anti-Hermitian operator, such as quantum Liouville equation. We applied this method to equation of motion in terms of density matrix in RT-TDHF/TDDFT.

[1] K. Yabana and G. F. Bertsch, *Phys. Rev. B* **54**, 4484 (1996). [2] K. Yabana, T. Nakatsukasa, J.-I. Iwata, and G. F. Bertsch, *Phys. Status Solidi B* **243**, 1121 (2006). [3] C. Y. Yam, S. Yokojima, and G. H. Chen, *J. Chem. Phys.* **119**, 8794 (2003). [4] T. Akama and H. Nakai, *J. Chem. Phys.* **132**, 054104 (2010). [5] Y. Tanimura and S. Mukamel, *J. Chem. Phys.* **99**, 9496 (1993). [6] T. Yagasaki and S. Saito, *J. Chem. Phys.* **128**, 154521 (2008). [7] S. K. Gray and G. G. Balint-Kurti, *J. Chem. Phys.* **108**, 950 (1998). [8] G. G. Balint-Kurti, *Theor. Chem. Acc.* **127**, 1 (2010).

Theoretical study on chemical reactions including non-adiabatic electron dynamics under laser fields.

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I. Objectives: The goal of the present study is to find a way to create and control electronic states for novel chemical reactions by applying laser fields and/or so-designed reaction fields. Inspired by the remarkable advances in the experimental measurements of ultrafast dynamics including electron dynamics in molecules [1,2], we develop a theory of nonadiabatic electron wavepacket dynamics as a tool to achieve the goal.

II. Degenerate electronic systems: Degenerate electronic systems are ubiquitous and play important roles in nature [3]. Chemical reactions driven by a dense manifold of degenerate electronic states proceed with a complicate electronic-state mixing by continuous nonadiabatic interactions. For instance, highly coherent electron dynamics causes a significant fluctuation of the charge distribution and a time-dependent variation of electronic polarization. In this way, such systems can provide a highly active chemical reaction field.

III. Boron cluster: Electronic wave functions of boron clusters away from the equilibrium geometries are very sensitive to the changes of molecular structure. The electronic characters of constituent boron atoms are well represented by the valence electron deficiency and small radii of valence orbitals, which allows for many applications in the experimental studies [4,5]. These properties yield high degrees of degeneracy of bonding character in the excited states of boron clusters, which emerges an active chemical reaction field that is dynamically modulated by persistent nonadiabatic transitions in the dense manifold.

IV. Contents of presentation: Toward laser control of chemical reaction, we apply the path-branching representation to describe the non-Born-Oppenheimer (NBO) electron dynamics. This approach makes it possible to treat nonadiabatic dynamics in optical fields that in turn induces additional nonadiabatic transitions [6-11]. Electronic wave packets evolve in time quantum mechanically along branching NBO paths. After showing its performance in a prediction scheme for an optimal laser pulse towards an aimed electronic state, we present and discuss the following illustrative examples; (a) a remarkable nonadiabatic charge transfer in (Na+Cl) [10], (b) activation of electronic states during complicated nonadiabatic dynamics ($H_2@B_{12}$) in structure isomerization dynamics, and (c) laser control of non-adiabatic bifurcation of reactive or non-reactive (energetically inelastic collision) dynamics of $B_{12}+H_2$ [12].

[1] *Attosecond Physics*, (Eds.) L. Plaja, R. Torres and A. Zaier (2013) Springer

[2] *Quantum Dynamic Imaging*, (Eds.) A. D. Bandrauk and M. Ivanov (2011) Springer

[3] *Adv. Chem. Phys., The Role of Degenerate States in Chemistry* (Vol. 124), (Eds.) M. Baer and G. D. Billing (2003) John Wiley & Sons.

[4] *Boron Science*, Ed. N. S. Hosmane (2012) CRC Press

[5] R. B. King, *Chem. Rev.* **101**, 1119 (2001)

[6] T. Yonehara, K. Hanasaki and K. Takatsuka, *Chem. Rev.* **112**, 499 (2012)

[7] T. Yonehara and K. Takatsuka, *J. Chem. Phys.* **132**, 244102 (2010)

[8] K. Takatsuka and T. Yonehara, *Phys. Chem. Chem. Phys.* **13**, 4987 (2011)

[9] T. Yonehara and K. Takatsuka, *J. Chem. Phys.* **128**, 154104 (2008)

[10] K. Takatsuka and T. Yonehara, *Adv. Chem. Phys.* **144**, 93 (2010)

[11] T. Yonehara and K. Takatsuka, *Chem. Phys.* **366**, 115 (2009)

[12] T. Yonehara and K. Takatsuka, *J. Chem. Phys.* **137**, 22A520 (2012)

Theoretical study of magnetism of Mn clusters using general spin orbital DFT

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I. Introduction

Magnetism of small manganese clusters has not been understood due to the fragilities of the bondings [1-4]. To begin with, the magnetism of Mn dimer, i.e. the local magnetic interaction of the Mn clusters, had been the controversy issue among theoretical and experimental studies until several years ago, because many density functional calculations indicated that the ground-state of Mn_2 is a high-spin state and the ESR results for Mn_2 in a rare-gas matrix showed the singlet signal [2-4]. The multireference perturbation theory (MRPT) suggested that the experimental results seem to be correct [2]. We also showed that the ground-state of Mn_2 is the singlet spin state if we choose an appropriate functional [4], settling the issue completely. On the basis of these previous researches, we picked out the Hartree-Fock PBE functional, which reproduces the MRMP2 results for both chemical bonding properties and the magnetic interaction of Mn_2 , and applied it to small Mn clusters [5].

II. Results and discussion

The first step is the optimization of the geometries of the Mn clusters (Mn_3 - Mn_7). We started from the most stable structures of the Lennard-Jones model for the clusters on the basis of the fact that the bond-order of Mn_2 is less than 0.1 with either HFPBE or MRMP2, indicating the chemical bonding of Mn_2 is not the covalent type, but the van der Waals type [4]. We optimized further the geometries for highest spin states of these clusters. Using these optimized structures, we applied the general spin orbital versions of DFT with the HFPBE functional. We obtained the spin structures of the low-spin states as shown in the figure 1, being agreement with the Stern-Gerlach experimental results [1]. The details will be discussed on that day.

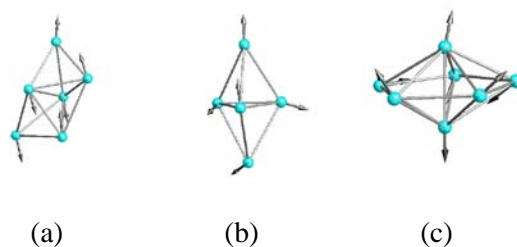


Figure 1 Spin structures of Mn_5 - Mn_7

- [1] M. B. Knickelbein Phys. Rev. **B 70** (2004) 014424.
- [2] B. Wang, Z. Chen: Chem. Phys. Lett. **387** (2004) 395; S. Yamamoto, et al. J. Chem. Phys. **124** (2006) 124302.
- [3] A. Baumann, R. J. Van Zee, S. V. Bhat, and W. Weltner: J. Chem. Phys. **78** (1983) 190.
- [4] S. Yamanaka, et al. Int. J. Quantum Chem. **107** (2007) 3178.
- [5] S. Yamanaka et al. to be submitted.

Solid State Spectroscopic Properties of New Heterocycles: MS-CASPT and FMO Studies

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I. Introduction

Comprehensive experimental and computational studies are presented for the spectroscopic properties of novel 2-(2'-hydroxyphenyl)imidazo[1,2-a]-pyridine (HPIP) [1] and 2(1*H*)-pyridones [2]. Polymorph-dependent luminescence of HPIP, the Aggregation-Induced Emission Enhancement (AIEE) molecule, shows very weak fluorescence with a large Stoke's shift in apolar solvent which is ascribed to excited-state intramolecular proton transfer (ESIPT) emission. HPIP derivatives bearing cyano group at 6-position (6CN-HPIP) shows three packing-controlled luminescence (yellow, orange, red) in the solid state specific to the corresponding polymorphs. 2(1*H*)-pyridones are virtually non-fluorescence in solution while fluorescent in solid state.

II. Computational Details

The isolated HPIPs and 2(1*H*)-pyridones were investigated by DFT and MS-CASPT2. The potential energy surfaces in the ground (S_0) and excited (S_1) states were explored by means of CASSCF to find Conical Intersections, aiming to elucidate the origin of emission enhancement as well as possible mechanism for the packing-controlled luminescence color tuning of HPIP.

For the crystalline phase in the S_0 and S_1 state, the cluster models were extracted from the corresponding crystals and were treated by ONIOM and FMO-TDDFT. A central molecule was solely excited to S_1 and the surrounding molecules remained in S_0 (the frozen optimization).

III. Results

The FMO pair interaction analysis of the spectra of 2(1*H*)-pyridones indicate that (1) intermolecular hydrogen bonds provoke bathochromic shifts (2) electrostatic interactions induce hypsochromic shifts (3) crystal packing effects induce hypsochromic shifts in total from the maxima in vacuo.

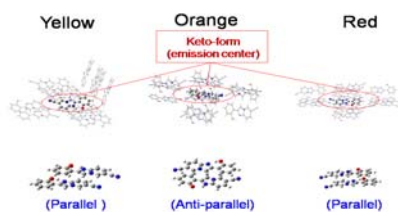


Fig. 1. Cluster models for 6CN-HPIPs computed by ONIOM and FMO-TDDFT

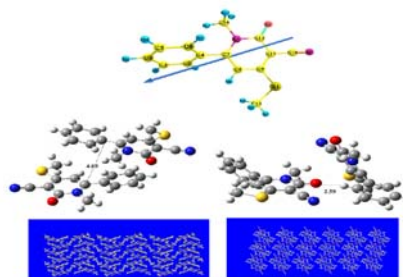


Fig. 2. Schematic images of 2(1*H*)-pyridone. Monomer, dimer, and crystal structures.

[1] Y.Shigemitsu, T.Mutai, H.Houjyou, K.Araki, *J.Phys.Chem.A*, **116** 12041-12048 (2012)

[2] Y.Shigemitsu, M.Hagimori, N.Mizuyama, B.-C.Wang, Y.Tominaga *Dyes and Pigments* 99(3), pp.940-949 (2013)

Quantum Computation of the properties of acrylamide

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I. Introduction

Acrylamides are very important for food chemistry [1, 2]. Intermolecular interaction potentials of the acrylamide dimer in 12 orientations have been calculated by using the second-order Møller-Plesset (MP2) perturbation theory. We have employed Pople's medium size basis sets [up to 6-311++G(3df,2p)] and Dunning's correlation consistent basis sets (up to aug-cc-pVTZ), and also carried out the Density Functional theory (DFT) calculations, then compared with the results of MP2.

II. Tables and Figures

Table 1. The bond length R and the binding energy E using a harmonic modeling near the equilibrium regions. The basis set used is 6-311++G**.

Method	R (Å)	E (kcal/mol)
MP2	4.209	-13.02
B3LYP	4.148	-14.00
wB97XD	4.107	-16.23
X3LYP	4.136	-14.73
M05	4.158	-15.13

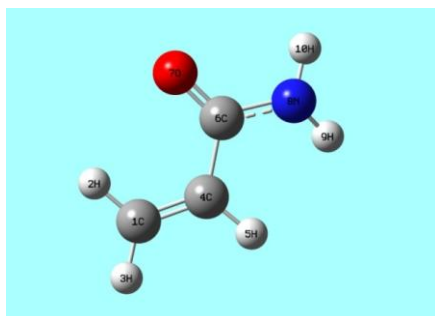


Fig. 1. The conformer of C_3H_5NO (syn)

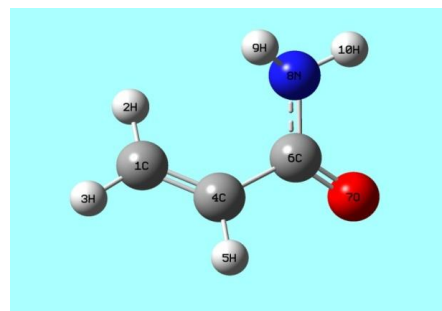


Fig. 2. The conformer of C_3H_5NO (skew)

III. References

- [1] W. L. Claeys, K. De Vleeschouwer and M. E. Hendrickx, *J. Agric. Food Chem.*, 2005, **53**, 9999–10005
- [2] FSA. *Food Standard Agency Study of Acrylamide in Food – Background Information & Research Findings*; Press briefing 17.05.02; Food Standard Agency: United Kingdom, 2002

Theoretical and UV Spectroscopic Considerations on the Proton-Transfer from Alcohols to Alkyl Pyridinimines

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The molecular interaction of alkyl pyridinimines with alcohols has been studied by UV spectroscopy and theoretical method.

The maximum absorption wavelength of the band around 350 nm became hypsochromically shifted toward 300 nm with longer alkyl groups of alcohols. The spectra of alcohol solutions with shorter alkyl groups of alcohols became similar to the spectrum in diluted sulfuric acid. Therefore, it is thought that alkyl pyridinimines receive the proton transferred from alcohol molecules without steric hindrance of the alkyl group of the pyridinimine, and are formed the cations.

From the calculated results of the hydrogen bond optimized model of 1EtPI/ ROH system and 1OcPI/ROH system, the value of the electron density on the imino group nitrogen tends to increase more negative value, when the alkyl chain of the ring nitrogen of the pyridinimine is short, and the alkyl chain of alcohol is long. The value of the electronic density of the imino group nitrogen tended to decrease a negative charge when alkyl chains were long of the pyridinimines and alcohols respectively, compared with the above calculation models. The above theoretical results suggest that 1RPI may become 1-alkyl-2-aminopyridinium cation in alcohol attended with the hydrogen bond complex, because when the alkyl chain is long, the effect of proton transfer becomes weak. The shoulder bands at 360 nm on 1RPI/ROH systems are supported by the calculated results as hydrogen bond complex.

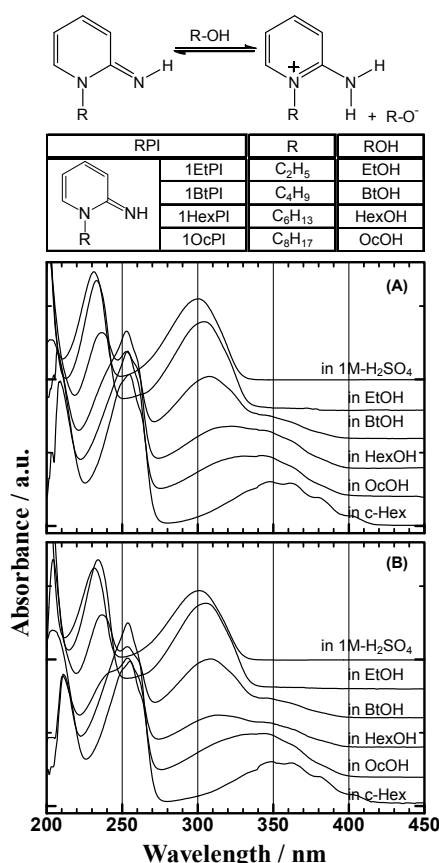


Fig.1 UV spectral results of 1EtPI and 1HexPI in various solvents at room temperature. (A) 1EtPI and (B) 1HexPI.

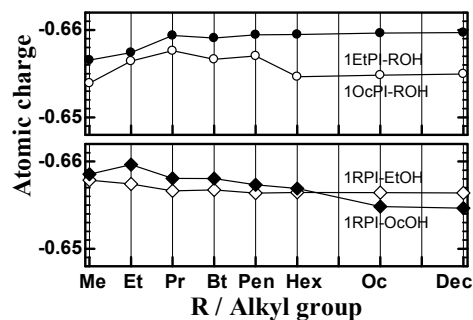


Fig.2 Alkyl group dependence of atomic charge of imino group N in RPI/ROH system for the lowest-energy structures. Calculated by B3LYP/6-31+G(d,p) method.

Essential Coordinates to Describe the Dynamics of Many-atom Systems

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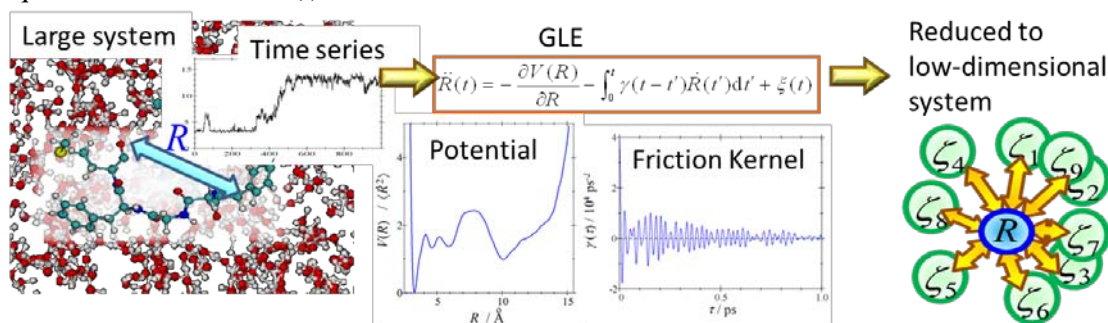
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The dynamics of realistic systems consists of the motions of a huge number of atoms that are contained in the system. In order to obtain insights into what is occurring in such systems, it is desirable to find a small number of variables that describe the essential part of given phenomena, rather than being involved in all the details. Here we present a method to extract a small number of essential coordinates to describe many-atom systems. After all-atom level simulations, which are enabled by the recent development of computational techniques, the present analysis is applied to the data and extracts a small number of dynamical variables to summarize the dynamics of the system. We investigate how the number of necessary coordinates changes with the time scale of the phenomenon in question.

We start our investigation by performing molecular dynamics (MD) simulations at all-atom level. As an example, we study the structural isomerization of a biological molecule Met-enkephalin in water. We monitor the time evolution of the end-to-end distance $R(t)$ obtained from the MD simulation. Then the equation of motion to describe the time evolution of $R(t)$ is derived in the form of the generalized Langevin equation (GLE). The friction term appearing in the GLE is an integration of the system velocity in the past. This “memory effect” arises from the dynamical interaction between the observed variable and the other degrees of freedom in the system (“environment”). The functional form of the friction term thus contains the information about how many and what kinds of dynamical modes exist in the environment. Starting from the GLE with the concrete functional form of the friction kernel derived from the MD simulation and introducing some effective variables that can be derived from the friction kernel, it is possible to obtain closed memory-less equations of motion for $R(t)$ and these effective variables. These effective variables can be interpreted as the environmental modes that couple to $R(t)$. In the case of Met-enkephalin, the dynamics of about 3000 atoms including the solvent was reduced to equations of motion of $R(t)$ and thirteen environmental variables.



Molecular Design for Light-Emitting Molecules

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The design principles for a highly-efficient light-emitting molecule are discussed from the view of vibronic couplings. We have recently proposed a concept of *vibronic coupling density* which enables us to control vibronic couplings [1]. Diagonal vibronic coupling density is defined by the product of the electron density difference between an excited state and the ground state and potential derivative. The potential derivative is defined by the derivative of an electronic-nuclear potential acting on a single electron with respect to a normal mode. The integral of the diagonal vibronic coupling density yields the diagonal vibronic coupling constant which gives rise to vibrational relaxation in the Franck-Condon state. Off-diagonal vibronic coupling density is defined by the product of the overlap density between two electronic states and the potential derivative. The integral of the off-diagonal vibronic coupling density gives the off-diagonal vibronic coupling constant which is the driving force of nonradiative transitions.

By using the vibronic coupling densities, we can analyse the origin of vibronic couplings in terms of electronic and vibrational structures. Moreover, we can control vibronic couplings in an excited state to develop a highly-efficient light-emitting molecule.

[1] Tohru Sato, Motoyuki Uejima, Naoya Iwahara, Naoki Haruta, Katsuyuki Shizu, Kazuyoshi Tanaka, *J. Phys. Conf. Ser.* **428**, 012010 1-19(2013).

Inner-shell ionized and excited states of carbon oxide and carbon sulfide compounds: open-shell reference (OR)-SAC/SAC-CI theoretical studies

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We developed open-shell reference symmetry adapted cluster (OR-SAC) and OR-SAC-configuration interaction (OR-SAC-CI) codes and applied to inner-shell core ionizations and singlet/triplet excitations of CO, CO₂, CS₂, and OCS. The OR-SAC/OR-SAC-CI calculations provided reasonable results judging from accordance with the corresponding experimental results. We suggested many electronic states other than those observed experimentally, and provided their nature assignments.

Table C1s and O1s core ionized and excited states for OCS calculated by OR-SAC-CI.

SAC-CI		Expt. ^a		Other Theor. ^a	
state	nature	ex. en. [eV]	$\Delta(E_S-E_T)$ [eV]	ex. en. [eV]	$\Delta(E_S-E_T)$ [eV]
<i>From C 1s core</i>					
1 ³ Π	C1s-π*	287.91	1.14	287.10	1.13
1 ¹ Π	C1s-π*	289.05		288.23	
1 ¹ Σ ⁺	C1s-σ*	291.91			
2 ¹ Σ ⁺	C1s-σ*	292.63			
3 ¹ Σ ⁺	C1s-3p _σ	293.52			
2 ¹ Π	C1s-3p _π	293.59			
4 ¹ Σ ⁺	C1s-σ*	294.39			
IP	C1s⁻¹	295.83		295.2	
<i>From O 1s core</i>					
1 ¹ Π	O1s-π*	533.76		533.7	
1 ¹ Σ ⁺	O1s-σ*	536.14			
2 ¹ Σ ⁺	O1s-σ*	537.37			
2 ¹ Π	O1s-3p _π	537.79			
3 ¹ Σ ⁺	O1s-3p _σ	537.81			
4 ¹ Σ ⁺	O1s-σ*	538.49			
3 ¹ Π	O1s-π*	538.71			
IP	O1s⁻¹	539.94		540.3	

^a Kroin et al., Phys. Rev. A 68, 012701 (2003)

Laser-Polarization Effects on Coherent Vibronic Excitation of Molecules with Quasi-Degenerate Electronic States

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I. Introduction

Laser pulses with a duration ranging from attoseconds to several femtoseconds instantaneously change molecular electronic states. Barth *et al.* have shown by a quantum simulation that π electrons of Mg porphyrin, which has a pair of doubly degenerate π -electronic excited states, can be rotated along its aromatic ring by a circularly polarized UV laser pulse [1]. On the other hand, we have demonstrated that transient rotation of π electrons in an aromatic molecule with quasi-degenerate π -electronic excited states can be induced along its ring by a linearly polarized UV laser pulse [2]. In this presentation, we report our recent results [3] on nonadiabatic couplings between ultrafast π -electron rotation and molecular vibration in an aromatic molecule irradiated by a laser pulse of arbitrary polarization.

II. Model

The model system 2,5-dichloropyrazine (DCP; Fig. 1) is of C_{2h} symmetry in its ground state and has optically allowed quasi-degenerate 1B_u excited states. The average excitation energy and energy gap of the two 1B_u states are 9.62 and 0.44 eV, respectively, at the CASSCF/6-31G* level. We performed nuclear wave packet simulations including nonadiabatic couplings between the two states on the potential energy surfaces with respect to the selected A_g normal modes, namely, breathing (Fig. 1a) and distortion (Fig. 1b) modes.

III. Results and Discussion

When DCP is excited by a laser pulse with the linear polarization vector \mathbf{e}_{in} or \mathbf{e}_{out} (Fig. 1c), the quasi-degenerate states are populated equally in both cases but the vibrational amplitude differs significantly (Fig. 2a). In contrast, the induced molecular vibration is almost the same for left (\mathbf{e}_{+1}) and right (\mathbf{e}_{-1}) circular polarizations (Fig. 2b). The rotational motion of π electrons is attenuated gradually by nonadiabatic couplings in all the four cases. The detailed analysis will be presented in the poster.

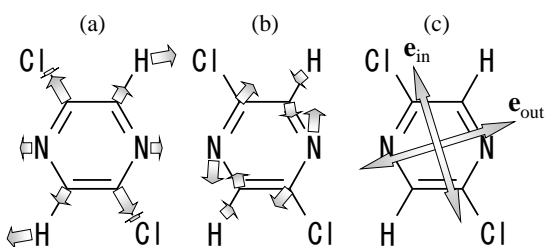


Fig. 1. Vibrational vectors of (a) the breathing and (b) distortion modes of DCP. (c) Directions of linear polarization vectors \mathbf{e}_{in} and \mathbf{e}_{out} .

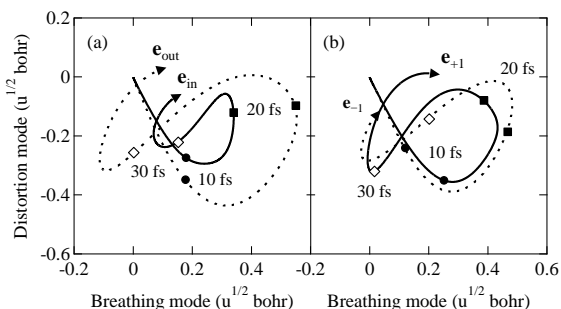


Fig. 2. Expectation value of the two-dimensional normal coordinates of DCP irradiated by (a) linearly and (b) circularly polarized UV laser pulses. The laser pulses fully decay at 7.26 fs.

[1] I. Barth *et al.*, Angew. Chem., Int. Ed. **45**, 2962 (2006); J. Am. Chem. Soc. **128**, 7043 (2006).

[2] M. Kanno *et al.*, Angew. Chem., Int. Ed. **45**, 7995 (2006); J. Chem. Phys. **127**, 204314 (2007).

[3] M. Kanno *et al.*, Phys. Rev. Lett. **104**, 108302 (2010); J. Phys. Chem. A **116**, 11260 (2012).

Protein Simulations by Generalized-Ensemble Molecular Dynamics Method

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I. Replica-permutation method

Efficient sampling in the conformational space is necessary to predict the native structures of proteins. The replica-exchange method (REM) is one of the most well-known methods among the generalized-ensemble algorithms. By exchanging the temperatures between the replicas, random walks of the replicas in the temperature space are realized. Accordingly, the simulation can escape from local-minimum states. We have recently proposed a better alternative to the REM, which we refer to as the replica-permutation method (RPM) [1]. In RPM not only exchanges between two replicas but also permutations among more than two replicas are performed, as shown in Fig. 1. Furthermore, instead of the Metropolis algorithm, the Suwa-Todo algorithm [2] is employed for replica-permutation trials to minimize its rejection ratio.

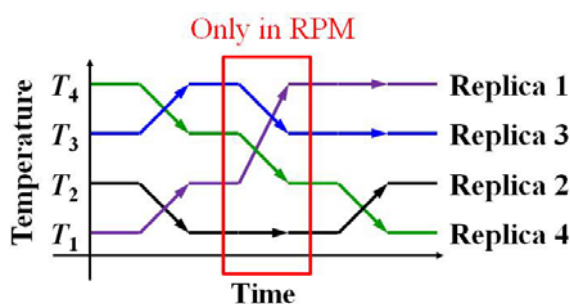


Fig. 1. An example of time series of temperatures in RPM

II. Pressure denaturation of protein

Next topic is pressure denaturation of proteins [3]. Pressure usually denatures proteins. However, some peptides have a more helical structure at high pressure than at atmospheric pressure. We chose an AK16 peptide (YGAAKAAAKAAAKA) from such peptides and studied the pressure dependence of the peptide by molecular dynamics simulations by the simulated tempering method for the isobaric-isothermal ensemble [4]. We calculated the fraction of helical structures and some structural properties at pressure values in the range from 0.1 MPa to 1.4 GPa. The partial molar volume change from the folded state to the unfolded state increases monotonically from a negative value to a positive value with pressure. The positive value of ΔV is consistent with experimental results. The radius of gyration of the folded state decreases with increasing pressure, which indicates that the helix structure shrinks with pressure. We revealed the molecular details of AK16 under high pressure conditions [5].

[1] S. G. Itoh and H. Okumura, J. Chem. Theory Comput. **9** (2013) 570.

[2] H. Suwa and S. Todo, Phys. Rev. Lett. **105** (2010) 120603.

[3] H. Okumura, Proteins **80** (2012) 2397.

[4] Y. Mori and Y. Okamoto, J. Phys. Soc. Jpn. **79** (2010) 074003.

[5] Y. Mori and H. Okumura, J. Phys. Chem. Lett. **4** (2013) 2079.

Theoretical studies on the electronic state of helical conformation with π conjugated systems

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I. Introduction

Interaction among aromatic units play an essential role in supramolecular chemistry. Polyaromatics have the π/π stacking interaction, which takes place intramolecularly and shows that two aromatic units preferentially interact in a parallel-displaced orientation, such as those in DNA and in the crystal packing of organic molecules^[1, 2]. Conjugated polymers such as polyaromatic molecules and polymeric metal complex have recently attracted much interest in the production of new materials with electroluminescent, optoelectronic and magnetic properties, solar cells, chemo-biosensors, and so forth. In this study, we focus two topics, *o*-phenylenes with unique inversion helical configurations and spin crossover complex shown a kind of polymeric metal complex in term of intra and/or intermolecular interaction and conformation change.

II Results

1 Helical inversion reaction pathways for *o*-phenylene oligomers

The stable configurations of *o*-phenylenes have helical tightly packed *n*-phenylenes with π/π stacking interactions. To investigate helical inversion pathways, we have studied theoretically the stable and transition-state geometries of tetrameric *o*-phenylenes (4-OP) using the density functional theory method. The pathway in which 4-OP converts from right- to left-handed geometry at once has activation energy, while a step-by-step reaction pathway through three different transition-states has much more lower activation energies. Therefore, one can conclude that the step-by-step inversion pathway is preferable for 4-OP^[3, 4].

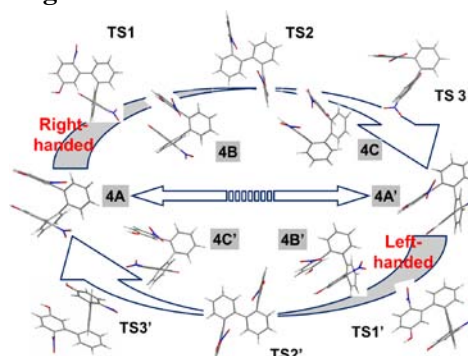


Figure 1 Possible of reaction pathways for 4-OP inversion reaction.

2 Modeling of size effects on various 2D shapes of spin-crossover nanoparticles

We performed of Monte Carlo simulations on two-dimensional core/shell square and rectangular lattice $L \times nL$ ($n = 1, 2$) for different sizes in order to study the effect of surface and size on the thermal behavior of spin-crossover nanoparticles. The surface effect is accounted for by constraining all the atoms situated in the boundary in the high-spin state as a result of the weak ligand-field prevailing in the coordination shell. The high-spin fraction is similar to behavior between square and rectangular lattice of spin-crossover nanoparticles, and in agreement with experimental data. Such a non-trivial change is explained as due to the competition between the negative pressures induced the high spin state surface and the bulk properties^[5, 6].

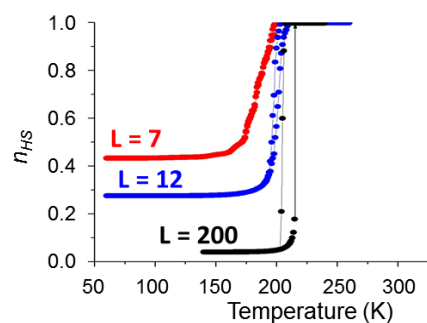


Figure 2 Calculated thermal variation of the HS fraction resulting from the size distributions on square lattice nano particles.

[1] E. Yajima *et al.*, *Chem. Rev.*, **109**, 6102 (2009) [2] Topics in Current Chemistry 234 Spin Crossover in Transition Metal Compounds II, III, (Springer) 2004 [3] E. Ohta *et al.*, *Nature Chemistry*, **3**, 68 (2010) [4] A. Muraoka, *Chem. Phys. Lett.*, **582**, 44 (2013) [5] A. Muraoka, J. Linares, K. Boukheddaden, F. Vallet, *Phys. Rev. B*, **84**, 054119 (2011) [6] A. Muraoka, *Materials Science Forum Journal*, S5C-P029, (2013)

Development of optimal control simulation with nonlinear interactions and its applications

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I. Introduction

Optimal control simulation provides a general and flexible tool for designing laser pulses that best achieve specified physical objectives. In this procedure, optimal pulses are designed by maximizing (or minimizing) the objective functionals that quantitatively describe the control achievement. Application of calculus of variations to the functionals leads to the nonlinear equations, called coupled-pulse design equations. Because intense laser pulses open up new dynamical phenomena in which nonlinear interactions induced by the laser pulses play an important role, it would be natural to extend the simulation to treat nonlinear interactions. In this presentation, we develop the methods to efficiently solve the coupled-pulse design equations with induced-dipole (nonlinear) interactions and apply them to molecular alignment/orientation control.

II. Theory

We outline our method through a case study of molecular alignment/orientation that enables molecular dynamics to be induced in a molecule-fixed frame. In this case, we consider the induced-dipole interactions up to the third order with respect to the laser field. The key idea is to divide the laser field into three identical components and then solve the pulse design

equations iteratively [1].

III. Results

Figure 1 shows the example of orientation control of CO molecules, in which a phase-locked two-color laser field is optimally designed. In (a), the envelope functions of the optimal pulse are shown. In (b), the degree of orientation and alignment are expressed as the expectation values of $\cos\theta$ and $\cos^2\theta$, respectively, where θ is the angle between the molecular axis and the polarization vector of the laser pulse. Fig. 1(c) shows the time dependence of the even (dotted line)- and odd (solid line)-numbered populations with the averaged rotational quantum number. This simulation clarifies the effectiveness of the alignment-enhanced molecular orientation mechanism.[1]

[1] K. Nakajima et al., J. Phys. Chem. A **116**, 11219 (2012).

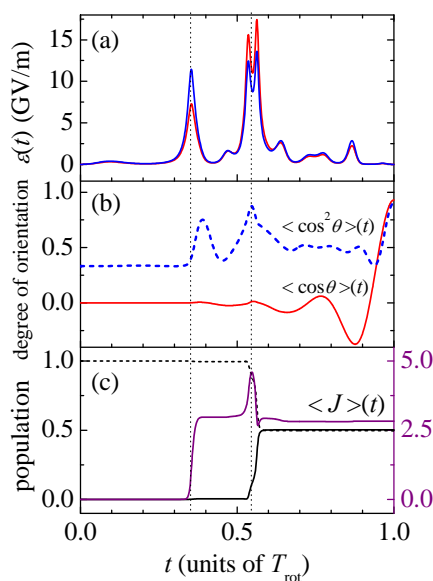


Fig. 1. Optimal control simulation of orienting CO molecules.

Exploring Theoretical Models for Water

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I. Molecule

The electronic state of water molecule in the ground state was studied with the variational quantum Monte Carlo method. In addition to a conventional form for the wave function expressed by the product of the Jastrow factor and the single Slater determinant, we have carried out the calculations with many Slater determinants [1]. Although the configuration interaction (CI) approach needs an extremely large number of expansion coefficients, the number of variational parameters can be reduced efficiently by using an idea of (molecular) orbital pair correlations [2], in which the high-dimensional coefficient tensor is expressed by a network of tensors that connects all orbitals with each other. While the number of the CI coefficients was 4900 for CAS(8,8) calculation, the degree of freedom for the variational parameters is reduced to 192. We have thus improved the energy value over the single determinant calculation.

II. Cluster

Ab initio path integral Monte Carlo and molecular dynamics simulations have been performed for water trimer system [3,4] in which the electron correlation effects have been taken into account up to the MP3 level. Geometrical structures and molecular interactions in hydrogen-bonded systems have thus been analyzed in light of the interplays among the nuclear quantum, thermal, and electron correlation effects. The fragment molecular orbital method has also been employed to enable the simulations for larger systems [3], for which the incorporation of periodic boundary condition has been made as well [5].

III. Liquid

We have employed the classical density functional theory [6] combined with the reference interaction site model to calculate the radial distribution functions (RDFs) of liquid water [7]. The density expansion for the Helmholtz free energy functional is retained up to the third order in order to take into account the effects of the bridge functions beyond the hypernetted-chain (HNC) approximation. The ternary direct correlation functions in the expression of the bridge functions are then given by a factorization approximation in terms of the site-site pair correlation functions. We have thus obtained the RDFs in which a poor description by the HNC approximation for the second peak of the O-O RDF at room temperature has been remedied.

[1] S. Tanaka, J. Phys. Soc. Jpn. 82 (2013) 075001. [2] K.H. Marti, B. Bauer, M. Reiher, M. Troyer and F. Verstraete, New J. Phys. 12 (2010) 103008. [3] T. Fujita, H. Watanabe and S. Tanaka, J. Phys. Soc. Jpn. 78 (2009) 104723. [4] T. Fujita, S. Tanaka, T. Fujiwara, M. Kusa, Y. Mochizuki and M. Shiga, Comput. Theor. Chem. 997 (2012) 7. [5] T. Fujita, T. Nakano and S. Tanaka, Chem. Phys. Lett. 506 (2011) 112. [6] J.P. Donley, J.G. Curro and J.D. McCoy, J. Chem. Phys. 101 (1994) 3205. [7] S. Tanaka and M. Nakano, Chem. Phys. Lett. 572 (2013) 38.

Molecular Informatics by Electronic-Structure Simulations

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Electronic-structure methods are applied to numerically describe molecules for classification and database search for molecular design and discovery. Practical electronic-structure calculations are now available thanks to elaborative development of molecular theories, numerical algorithms, software, and computer resources. Similar to other technologies, such impressive advance of Quantum Chemistry can be a good driving force providing new possibilities of the field. In this presentation, we will discuss about the usefulness of molecular informatics by the electronic-structure calculation. Our particular focuses are on photochemistry for in-vivo imaging and renewable energy generation (related to chemistry of excited states), and on drug discovery through molecular-similarity search (related to chemistry of intermolecular interaction). It will be shown that rich and insightful information are now available when we think of the electronic-structure calculation as an excellent descriptor of molecules.

A Theoretical Study on Proton-Conduction Mechanism for Perovskite-Type Compounds

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Abstract

Hybrid Khon-Sham calculations were performed to clarify the proton-conduction mechanism for BaZrO₃ perovskite. From chemical bonding rule, it was found that covalent bonding is formed between conductive hydrogen and oxygen. The calculated activation energy for proton-conduction was much larger than the experimental ones. It is because O-H covalent bonding formation affects the low-frequency real part in AC impedance spectra. It was concluded that the higher proton-conductivity in wet condition is derived from “proton pumping effect”. In this presentation, the calculation results of not only BaZrO₃ but also SrTiO₃ will be shown.

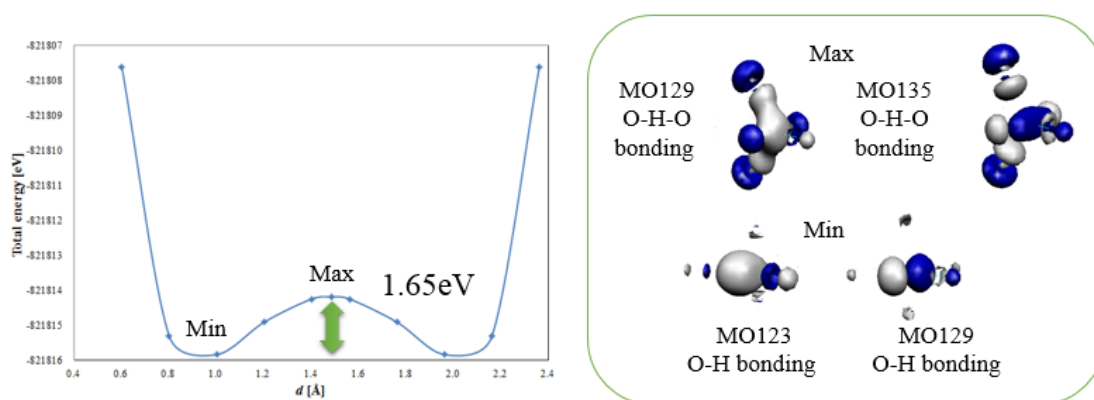


Figure The calculated potential energy curve along diagonal line, and molecular orbitals (MOs) for Ba₂Zr₄O₄H model

References

- [1]T. Onishi, Adv. Quant. Chem. 64, 31-81 (2012)
- [2]T. Onishi, and T. Helgaker, Int. J. Quant. Chem. 112, 201-207 (2012)
- [3]T. Onishi, and T. Helgaker, Int. J. Quant. Chem. 113, 599-604 (2013)
- [4]T. Onishi, and T. Helgaker, Prog. Theor. Phys. Chem. B27, 233-248 (2013)

Level Structure of Excited States and Two-Photon Absorption Properties of Cyclic Paraphenylene Compounds

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Two-photon absorption (TPA) properties of cycloparaphenylenes (CPP) with different ring sizes have been studied experimentally and theoretically. The TPA spectra of CPPs with several ring sizes shown in Figure 1 were measured by the femtosecond Z-scan method. It was found that TPA cross sections of these compounds are considerably large as pure hydrocarbons without any donor or acceptor substituents, and are increased with increasing ring size. The increase is hold even at the level of TPA cross section per one benzene ring as $\sigma^{(2)}/n = 39$, 55, and 71 GM for [9]-, [12]-, and [14]CPP, respectively. In this study, the TPA properties of the CPPs have been theoretically investigated by the TDDFT methods. All the excited state properties were calculated by the TDDFT/B3LYP method using the DALTON 2011 program [1] for the geometries optimized for the ground states. The one-photon absorption (OPA) and TPA spectra were calculated by the methods reported previously [2].

Due to high symmetry of the molecular structures of the compounds, several characteristic level structures can be found in the excited states. For example, the lowest excited state, which corresponds to the HOMO-LUMO transition, is both OPA and TPA forbidden. The lowest OPA allowed excited state can be assigned to transitions as degenerate HOMO-1, HOMO-2 \rightarrow LUMO and HOMO \rightarrow degenerate LUMO+1, LUMO+2.

Two strong TPA peaks were experimentally observed around 560-600 nm. Based on the result of the calculations, the peak observed at the longer wavelength is assigned to the transitions as degenerate HOMO-1, HOMO-2 \rightarrow degenerate LUMO+1, LUMO+2. On the other hand, the peak at the shorter wavelength is assigned to the transitions as HOMO \rightarrow degenerate LUMO+3, LUMO+4 and degenerate HOMO-3, HOMO-4 \rightarrow LUMO. The difference between the transition energy of the two peaks is decreased with increasing ring size, which accounts for the experimental observations. It is found that the orbital degeneracy due to high symmetry of the molecular structures can be the origin of the strong TPA intensities of these compounds.

[1] C. Angeli, K. L. Bak, V. Bakken, et al., DALTON 2011.

[2] K. Ohta, S. Yamada, K. Kamada, A. D. Slepko, F. A. Hegmann, R. R. Tykwinski, L. D. Shirtcliff, M. M. Haley, P. Sałek, F. Gel'mukhanov and H. Ågren, *J. Phys. Chem A*, **115**, 105 (2011).

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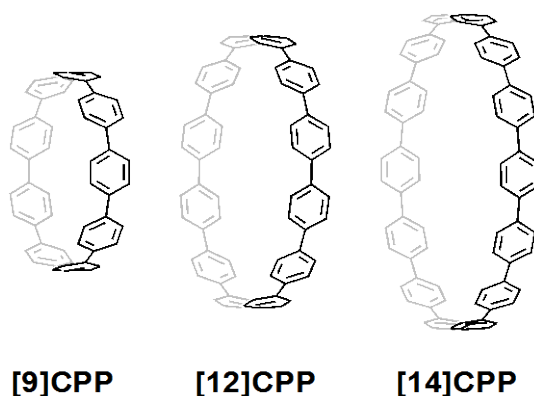


Figure 1. Structures of cycloparaphenylenes studied in this work.