Abstracts of Poster Presentations, Sep. 3

Exact two-component relativistic theory for NMR parameters

<u>Qiming Sun</u>, Wenjian Liu, Yunlong Xiao ¹College of Chemistry and Molecular Engineering, Peking University

Abstract

The calculation of Nuclear magnetic resonance (NMR) shielding constants demands fully relativistic treatments since they are sensitive to the electronic structure in the vicinity of the nucleus. Following the exact two-component (X2C) relativistic theories for electronic structure [1–5], a simple X2C theory for NMR shielding constants is proposed [6]. With the so-called magnetically balanced (MB) basis sets [7–10], a matrix decoupling condition is introduced to reduce the fourcomponent formalism down to the two-component one. The inclusions of GIAO via the MB-GIAO scheme [11] and the Gaunt term for current-current interaction are available. In the X2C approximation, the dia- and para-magnetic terms, which are identical to the corresponding four-component ones, arise naturally. The extra computational effort is inevitable since the coupled-perturbed equations are required not only for the molecular orbitals but also for the decoupling procedure. However, the efficiency can be gained by introducing the concept of "from atoms to molecule". Both the exact and approximate schemes will be examined at the DFT level.

References

- [1] W. Kutzelnigg and W. Liu J. Chem. Phys. 2009, 123, 241102.
- [2] D. Peng, W. Liu, Y. Xiao and L. Cheng J. Chem. Phys. 2007, 127, 104106.
- [3] W. Liu and W. Kutzelnigg J. Chem. Phys. 2007, 124, 114107.
- [4] W. Liu and D. Peng J. Chem. Phys. 2009, 131, 031104.
- [5] W. Liu Mol. Phys. 2010, 108, 1679.
- [6] Q. Sun, W. Liu, Y. Xiao, and L. Cheng J. Chem. Phys. 2009, 131, 081101.
- [7] Y. Xiao, D. Peng, and W. Liu J. Chem. Phys. 2007, 126, 081101.
- [8] Y. Xiao, W. Liu, L. Cheng and D. Peng J. Chem. Phys. 2007, 126, 214101.
- [9] W. Kutzelnigg and W. Liu J. Chem. Phys. 2009, 131, 044129.
- [10] L. Cheng, Y. Xiao, and W. Liu J. Chem. Phys. 2009, 130, 144102.
- [11] L. Cheng, Y. Xiao, and W. Liu J. Chem. Phys. 2009, 131, 244113.

Quantization of Chemical Reaction: The Dynamic Correlation Diagram Method Free from Noncrossing Rule

<u>Hiroyuki Nohira</u>,¹ Toshiyuki Nohira² ¹ Professor Emeritus from Saitama University, Japan ² Graduate School of Energy Science, Kyoto University, Japan

Both Fukui's frontier orbital (FO) theory [1] and Woodward-Hoffmann's orbital symmetry conservation (W-H) theory [2] are based on the molecular orbital (MO) theory. However, there are some obvious inconsistencies between the two theories in explaining the electron movement [3]. The process of chemical reactions has been explained by the potential surface analysis based on the time-independent Schrödinger equation. However, this approach is not always appropriate for describing unsteady states, because the variable of reaction coordinate should be time t by its very nature. When considering the time-scale of chemical reactions for molecules, there is inherent uncertainty in the energy levels for the midway state of chemical reactions owing to the Heisenberg uncertainty principle [Fig. 1]. The states which can be accurately described by quantum mechanics exist discontinuously in chemical reactions. Such quantization of chemical reactions solves all noncrossing problems. We also show that such an essential fact leads to new concepts and theories in chemical reactions such as stable molecule, elementary reaction, minimum deformation of orbital phases, and the universally applicable "dynamic correlation diagram method" unifying FO theory and W-H theory [4].

The original Schrödinger equation $i\hbar \frac{\partial \Psi(r,t)}{\partial t} = \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(r,t) \right\} \Psi(r,t) \quad \Box$

Born-Oppenheimer approximation
1) Separation of the variable *r* from *t*2) Assumption of stationary states
The resulting time independent equation

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right\}\Psi(r) = E\Psi(r)$$



Fig. 1. A schematic representation of the potential energy surface and time course for an elementary reaction.

- [1] Fukui, K. Acc. Chem. Res. 1971, 4, 57-64.
- [2] Woodward, R. B., Hoffmann, R. *The Conservation of Orbital Symmetry,* Verlag-Academic, Weinheim, Germany, **1970**.
- [3] Nohira, H., Tetrahedron Lett. 1974, 2573-2576.
- [4] Nohira, H. The 41st IUPAC World Congress, S05O03, 2007, Torino, Italy.

Additional variational condition in the ROHF method ensuring a fulfillment of Koopmans' theorem

Boris N. Plakhutin

Laboratory of Quantum Chemistry, G.K.Boreskov Institute of Catalysis, Russian Academy of Sciences, Novosibirsk 630090, Russia.

A general formulation of Koopmans' theorem (KT) is derived in the ROHF method for molecular and atomic systems with arbitrary orbital occupancies and total electronic spin. The key point of the formulation is the new variational condition introduced in the ROHF method in addition to the familiar variational principle for the total energy.

The new condition ensures the stationarity of the ionized energy (ionization potential or electron affinity) defined in Koopmans' approximation with respect to a variation of orbitals within the ionized electronic shell. Taken together, the variational principle and the new condition define the special (*canonical*) form of the ROHF Hamiltonian whose eigenvalues (orbital energies) satisfy KT for the whole energy spectrum.

The talk will focus on an intimate relation between the variational conditions underlying the present (canonical) ROHF method and the variational conditions in the limited CI approach, and on a practical applicability of the new theory.

		<i>I</i> _{2s} , KT	I_{2s} , experim.	<i>I</i> _{2<i>p</i>} , KT	I_{2p} , experim.
Li	${}^{2}S$, $2s^{1}$	5.342	5.3918		
Be	${}^{1}S$, $2s^{2}$	8.415	9.32270		
В	${}^{2}P$, $2p^{1}$	12.222	12.93	8.432	8.2981
С	${}^{3}P$, $2p^{2}$	16.082	16.59	11.792	11.260
Ν	${}^{4}S$, $2p^{3}$	20.118	20.33	15.445	14.53414
0	${}^{3}P$, $2p^{4}$	29.576	28.48	14.452	13.618
F	^{2}P , $2p^{5}$	40.365	37.86	18.621	17.423

KT estimates [4] of the valence ionization potentials of the second row open-shell atoms. Basis set aug-cc-pV6Z. All values in eV.

- B.N. Plakhutin, E.V. Gorelik, and N.N. Breslavskaya, J. Chem. Phys. 125, 204110 (2006).
- 2. B.N. Plakhutin and E.R. Davidson, J. Phys. Chem. A. 113, 12386 (2009).
- 3. E.R. Davidson and B.N. Plakhutin, J. Chem. Phys. 132, 184110 (2010).
- 4. B.N. Plakhutin, submitted.

The electronic properties of organic dyes porphyrin-thiophene-perylene and its derivatives modified by varying thiophene linker

<u>Tatiya Chokbunpiam</u>,^{1,2} Patchanita Thamyongkit,³ Oraphan Saengsawang,² Supot Hannongbua^{2,4}

¹ Petrochemical and Polymer Science Program, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand

² Computational Chemistry Unit Cell (CCUC), Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand

³ Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand

⁴ Center of Excellence for Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, 10330, Thailand.

Abstract

In this work, quantum chemical calculation was applied to investigate a new series of potential light-harvesting compounds consisting of porphyrin molecule linked to perylene unit via a oligothiophenic bridge (Por-*n*Thio-Per). The number (n) of thiophene ring was varied from 0 to 10 rings. Electronic properties of these compounds were studied using density functional theory (DFT) and time-dependent DFT approaches. The results revealed that Por-3Thio-Per compound can be a new promising compound which acts as light harvesting in organic dye solar cell. Due to, this compound display sufficient performance in terms of band energy, molecular orbital coefficient and UV-visible spectra covered a broader range without disturbing characteristic spectra of chromophor.



Figure 1. Molecular structure of Por-*n*Thio-Per (n = 0-10).

Reference

- [1] M. Gräzel, J. Photochem. Photobiol.A, 2004, 164, 3-14.
- [2] H. Hoppe and N. S. Sariciftci, J. Mater. Res., 2004, 19(7), pp. 1924-1944.

FRANCK-CONDON FACTORS FOR DIATOMIC MOLECULES FOR AN ARBITRARY ANHARMONIC POTENTIAL

L. SANDOVAL¹, I.URDANETA², and A. PALMA²

¹Facultad de Ciencias de la Computación, Benemérita Universidad Autónoma de Puebla. Puebla, Pue. 72570 (lourdes.sandoval55@gmail.com)
²Instituto de Física, Benemérita Universidad Autónoma de Puebla. Puebla, Pue. 72570 (palma@sirio.ifuap.buap.mx), (urdaneta@sirio.ifuap.buap.mx)

Abstract

In this work we develop a harmonic approximation of the Franck-Condon Factors (FCF) for any anharmonic potential of diatomic molecules. The method is based on the Taylor series expansion of the potential and the second quantization formalism. Well known recurrence relations are used to calculate the FCF, which are incorporated in the hamiltonian. Keeping then only the quadratic terms, by the Bogoliubov-Tyablikov transformation the hamiltonian is found to be equivalent to an harmonic oscillator. The derivation is an alternative route to the Iterative Bogoliubov transformation (IBT), widely used to treat anharmonic potentials in a non-perturbative way. The FCF obtained by our method for the Morse potential are compared with numerical techniques like the RKR method and the Morse itself. Our results are in agreement with these numerical methods, being our technique entirely analytical and much simpler to use.

Faddeev Random Phase Approximation for Molecules

Matthias Degroote,¹ Dimitri Van Neck,¹ Carlo Barbieri² ¹Center for Molecular Modelling, Ghent University, Belgium ²University of Surrey, United Kingdom

The Faddeev Random Phase Approximation (FRPA) [1,2] is a Green's function method which couples collective degrees of freedom to the single particle motion by resumming an infinite number of Feynman diagrams. The Faddeev technique is applied to describe the two-particle-one-hole (2p1h) and two-hole-one-particle (2h1p) states in terms of Random Phase Approximation (RPA) phonons. This results in an equal treatment of the intermediary particle-particle (pp) and particle-hole (ph) channels. The poster will present the application of this method to molecules [3] and investigate the effects of adding fragmentation to the single particle propagator on the RPA instability arising in the dissociation limit.

[1] C. Barbieri and W. H. Dickhoff, Phys. Rev. C 63, 034313 (2001)

- [2] C. Barbieri, D. Van Neck and W. H. Dickhoff, Phys. Rev. A 76, 052503 (2007)
- [3] M. Degroote, D. Van Neck and C. Barbieri, Phys. Rev. A 83, 042517 (2011)

Development and applications of divide-and-conquer constrained self-consistent field method

Minoru Hoshino,¹ Yutaka Imamura,² Masato Kobayashi,^{2,3} Hiromi Nakai^{2,4,5}
 ¹ Nissan Chemical Industries, LTD., Japan
 ² School of Advanced Science and Engineering, Waseda University, Japan
 ³ Institute for Molecular Science, Japan
 ⁴ Research Institute for Science and Engineering, Waseda University, Japan

⁵ CREST, Japan Science and Technology Agency, Japan

I. Introduction

The evaluation of Marcus parameters¹ such as a reorganization energy and an electron coupling matrix is essential for the analysis of electron transfer (ET) processes in electronic materials and biological systems. Recently, Wu *et al.*² developed the constrained self-consistent field (CSCF) method to obtain the charge- and spin-localized diabatic states in the ET process within the framework of density functional theory and estimated the Marcus parameters including donor-acceptor interactions. The computational cost of the CSCF method scales as $O(n^{3-4})$, which is the same as that of the conventional SCF method, with the prefactor of the determination steps for Lagrange multipliers.

Nakai and coworkers^{3,4} have developed the divide-and-conquer (DC) method as a linear-scaling approach. The DC method can accelerate the diagonalization and construction of the Fock matrix and achieves linear-scaling computational cost for the SCF and correlated methods. This study has developed the hybrid approach between the DC and CSCF methods to deal with large-scale ET systems.

II. DC-CSCF theory

The DC method divides the entire system into small subsystems α composed of central and buffer regions. The total energy is described by

$$E^{\rm DC} = \frac{1}{2} \sum_{\alpha} \sum_{\sigma}^{\downarrow,\downarrow} \sum_{\mu\nu\in L(\alpha)} D^{\sigma\alpha}_{\mu\nu} \Big(H^{\rm core}_{\mu\nu} + F^{\sigma}_{\mu\nu} \Big).$$
(1)

The density matrix of the subsystem D^{α} is constructed from subsystem orbitals, the Fermi function f_{β} , and the partition matrix p^{α} :

$$D_{\mu\nu}^{\sigma\alpha} = p_{\mu\nu}^{\alpha} \sum_{i} f_{\beta} (\varepsilon_{\rm F}^{\sigma} - \varepsilon_{i}^{\sigma\alpha}) C_{\mu i}^{\sigma\alpha} C_{\nu i}^{\sigma\alpha^{*}}.$$
 (2)

The CSCF Lagrangian based on the DC expression is given by $\[\ \ \uparrow \downarrow \]$

$$W^{\rm DC} = E^{\rm DC} + \sum_{I} V_{I} \Biggl[\sum_{\alpha} \sum_{\sigma}^{\uparrow,\downarrow} \sum_{\mu\nu\in L(\alpha)} D^{\sigma\alpha}_{\mu\nu} \langle \phi_{\mu} | \hat{O}^{\sigma}_{I} | \phi_{\nu} \rangle - N^{\sigma}_{I} \Biggr].$$
(3)

The second term on the right-hand side in Eq. (3) represents the constraint conditions with the Lagrange multipliers V_I . The equations derived from the differentiations of the CSCF Lagrangian with respect to the orbitals and multipliers are solved self-consistently in the DC scheme.

The DC-CSCF method has been implemented to the DC part⁵ in the GAMESS program. Applications to the organic semiconductor materials will be reported in this presentation.

¹R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **811**, 265 (1985). ²Q. Wu and T. V. Voorhis, *Phys. Rev. A* **72**, 024502 (2005). ³T. Akama, M. Kobayashi, and H. Nakai, *J. Comput. Chem.* **28**, 2003 (2007). ⁴M. Kobayashi, T. Yoshikawa, and H. Nakai, *Chem. Phys. Lett.* **500**, 172 (2010). ⁵M. Kobayashi and H. Nakai, in *Linear-Scaling Techniques in Computational Chemistry and Physics: Methods and Applications*, edited by M.G. Papadopoulos, R. Zalesny, P.G. Mezey, and J. Leszczynski (Springer, 2011), pp. 97-127.

Gauge Function Optimization for Accurate Calculations of Magnetic Wavefunctions

Atsushi Kubo

Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502 Japan

In this poster, we will present some of the results discussed in our recent papers. [1,2] In the first paper, we showed that our computed current density for a H_2^+ ion in a very strong magnetic field (1 a.u.) did not satisfy the continuity equation, $\nabla \cdot \vec{J} = 0$. Epstein had noticed such violation of the conservation law and had tried to cure it[3]. We applied the Kennedy-Kobe (KK) variational principle to remove the divergence.[4] This method was only applied to an anisotropic harmonic oscillator, but has never been applied to real molecular systems.

In the second paper, we discussed about the difference between the gauge function optimization and the gauge invariant methods by Rebane[5] and by Lazzeretti and his coworkers[6]. The original paper was modified according to the suggestion of a reviewer to include the latter references. After the change, the manuscript became more clear. We thank the reviewer for helping us. The gauge invariant method adopts the random phase approximation, since the exchange term is nonlocal and is not gauge-invariant.[3a] On the contrary, we can combine the Hartree-Fock approximation with the gauge function optimization to remove the error. Moreover, in the gauge function optimization, the basis sets have to be optimized only for electron density, since a part of electron velocity field is described by the gauge function. Therefore, the size of the basis sets might be reduced.

We also investigated the case where the wavefunction had nodes. It has been known that the Rebane's equation is problematic at the nodes [6c]. The second paper showed that the KK equation can be solved without any problem. We confirm that the algorithm is correct, although we still do not know whether the method is effective or not. However, we believe that science has been developed from something unknown rather than the competition for a known subject.

[1] Atsushi Kubo, "Finite-element gauge function optimization for accurate current density calculations", Phys. Rev. A80, 032117 (2009).

[2] Atsushi Kubo, "Gauge Function Optimization 2: An accurately solvable model.", Int. J. Quantum Chem. accepted on 11 May 2011.

[3](a) S.T. Epstein, JCP 42, 2897 (1965); (b) JCP 58, 1592 (1973); (c) Isr. J. Chem. 19, 154 (1980).

[4] P.K. Kennedy and D.H. Kobe, Phys. Rev. A 30, 51 (1984).

[5] T.K. Rebane, Sov. Phys. JETP 11, 694 (1960).

[6](a) P. Lazzeretti, et al. Int. J. Quantum Chem. 60, 249 (1996). (b) M.P. Beccar Varela, et al. ibd. 77, 599 (2000). (c) S. Pelloni, et al., J. Phys. Chem. A 113, 14465 (2009).

Relativistic Corrections via Fourth-Order Direct Perturbation Theory

<u>Stella Stopkowicz^{a)}</u> and Jürgen Gauss ^{a)} a) Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany

Relativistic effects need to be considered in quantum-chemical calculations on systems including heavy elements or when aiming at high accuracy for molecules containing only lighter elements. For the latter purpose, consideration of relativistic effects via perturbation theory is an attractive option, and consequently such techniques, e.g., lowestorder direct perturbation theory (DPT2) [1] have evolved to standard tools for the calculation of relativistic corrections to energies and properties.

In this work, we extend the DPT treatment to the next order (DPT4) and demonstrate that the DPT4 energy correction can be obtained as a second derivative of the energy respect to the relativistic perturbation parameter. Accordingly, differentiation of a suitable Lagrangian, thereby taking into account all constraints on the wavefunction, provides a suitable expression for the fourth-order energy correction. The latter can be implemented using standard analytic second-derivative techniques. For closed-shell systems, the DPT4 corrections consist of higher-order scalar relativistic effects as well as spin-orbit corrections with the latter appearing here for the first time in the DPT series.

Relativistic corrections are reported for energies as well as for first-order electrical properties and compared to results from rigorous four-component benchmark calculations in order to judge the accuracy and the convergence behaviour of the DPT expansion.

W. Kutzelnigg, *Relativistic Electronic Structure Theory. Part I. Fundamentals*, (Elsevier, Amsterdam, 2002), p. 664, chapter 12

Analytic energy derivatives in relativistic quantum chemistry: Rigorous treatments of both scalar-relativistic and electroncorrelation effects

Lan Cheng and Jürgen Gauss

Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany

We report on the extension of analytic energy-derivative techniques [1] for quantumchemical computations on heavy-element containing systems. Scalar-relativistic effects are treated via spin-free relativistic theories including the spin-free Dirac-Coulomb (SFDC) approach [2, 3] in the four-component framework as well as the spin-free exact two-component (SFX2c) scheme [4, 5].

We present high-level coupled-cluster calculations of various molecular properties including electric-field gradient, equilibrium geometry, and vibrational frequency and demonstrate the general applicability of the scalar-relativistic coupled-cluster methods for systems containing elements from the first down to the fifth row of the periodic table. It is shown and should be emphasized that scalar-relativistic and electron-correlation effects need to be treated rigorously on the same footing for accurate theoretical descriptions, since their contributions are significant and at the same time strongly coupled together.

[1] I. Shavitt and R. J. Bartlett, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (Cambridge University Press, Cambridge, 2009), Chap. 11.

- [2] K. G. Dyall, J. Chem. Phys. 100, 2118 (1994)
- [3] L. Cheng and J. Gauss, J. Chem. Phys. 134, 244112 (2011)
- [4] K. G. Dyall, J. Chem. Phys. 115, 9136 (2001)
- [5] W. Liu and D. Peng, J. Chem. Phys. 131, 031104 (2009)

Solution of Time Dependent Schrödinger Equation by Quantum Walk

Shinji Hamada¹ <u>Masayuki Kawahata</u>¹ and Hideo Sekino¹ ¹ Toyohashi University of Technology, Japan

I. Abstract

Time dependent solution for quantum phenomena is most straightforwardly solved by Quantum Walk (QW) methods which is natural extension of random walk in classical statistics. Recently several applications have been performed for the prediction of internal freedom such as electron spin or optical chirality in the context of quantum computation. We discuss the potential problem of discrete representation QW in solving time-dependent Schrödinger equation and present some initial applications for free-electron and confined electron by potential.

As can be seen below, the solution with periodic condition is completely reproduced by discrete QW.



Solution of Time-dependent Schrödinger Equation with an initial condition of Gaussian distribution

Local unitary transformation in two-component relativistic scheme for large-scale molecular systems

Junji Seino,¹ Hiromi Nakai^{1,2,3}

 ¹Department of Chemistry and Biochemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, JAPAN
 ²Research Institute for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, JAPAN
 ³CREST, Japan Science and Technology Agency, 5 Sanban-cho, Chiyoda-ku, Tokyo 102-0075, JAPAN

Recently, Seino and Hada proposed an accurate two-component (TC) relativistic theory, infinite-order Douglas-Kroll (IODK) method for many-electron systems [1]. In this method, the one-electron Dirac Hamiltonian and electron-electron Coulomb interaction operator are transformed by the one-electron IODK unitary transformation originally introduced by Barysz, Sadlej, and Snijders (BSS) [2,3]. The total electronic energies numerically agree with those obtained with the four-component (4C) Dirac-Coulomb method even in super-heavy element. However, for large scale molecular systems, the calculation for TC relativistic Hamiltonian can be one of the most expensive parts in the total procedure due to the unitary transformation in whole molecular system.

In this study, we propose an efficient and accurate TC relativistic scheme based on local unitary transformation (LUT) [4]. This scheme utilizes the locality of unitary transformation, and therefore reduces the computational scaling from $O(N^3)$ to O(N). In addition, for linear-scaling Hartree-Fock (HF) by TC relativistic methods, we combine the generalized unrestricted HF (GUHF) with the divide-and-conquer (DC) method [5,6]. In this presentation, we will discuss the efficiency and accuracy of these TC relativistic calculations.

- [1] J. Seino and M. Hada, Chem. Phys. Lett. 461, 327 (2008).
- [2] M. Barysz, A. J. Sadlej, and J. G. Snijders, Int. J. Quant. Chem. 65, 225 (1997).
- [3] M. Barysz and A. J. Sadlej, J. Chem. Phys. 116, 2696 (2002).
- [4] J. Seino and H. Nakai, in preparation.
- [5] W. Yang and T. -S. Lee. J. Chem. Phys. 103, 5674 (1995).
- [6] M. Kobayashi and H. Nakai, J. Chem. Phys. 129, 044103 (2008).

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Thermoprogrammed reduction and thermoprogrammed desorption studies of metallic and oxidic catalysts

Vasile Georgescu,¹ Fanica Bacalum,² Luminita Mara³

¹Institute of Physical Chemistry "Ilie Murgulescu", Romanian Academy, Spl.

Independentei 202, Bucharest 060041, Romania(vgeorgescu@icf.ro)

² National Institute of Chemistry-ICECHIM, Spl. Independentei 202, Bucharest 060041, Romania,

³ National Research and Development Institute for Nonferrous and Rare Metals, 102 Biruintei Bvd., Pantelimon, Ilfov, Romania

I.Introduction

Metallic and oxidic catalysts are frequently used in heterogeneous oxidation and reduction, depollution and synthesis of organic compounds.

The investigations of these catalysts requires the determination of the active element and/or phase, as well as the influence of various factors on the active phase generation.

Among these, an important role is played by the preparation method (the precursors, the conditions of calcinations, etc.), the nature of the support as well as its interaction with various components, the extent of reduction, etc.

Temperature-programmed reduction (TPR) is developed technique used to chemically characterize of catalysts or catalytic precursors at different stages of the catalyst preparation sequence.

II.Experimental

During TPR, a hydrogen-containing gas mixture continuously perfuses the catalyst bed while the temperature of the bed is raised linearly with time. By measuring the consumption of hydrogen as a function of temperature, a so-called TPR profile is obtained.

The use of such profiles fingerprints of the chemical nature and environment of the catalytic component. Furtermore, the area under the TPR peak reflects the concentration of that component present on the catalyst surface.

Different pretreatments results in different catalytic precursors; the TPR profile is a record of the reduction of these precursors. It is likely that the precursor pool will contain a variety of species, each with its own characteristic reduction profile. The resulting TPR spectrum is a composite of these processes with some contribution likely from processes that do not involve changes in the oxidation state of the metal.

During the TPR process, the oxidation states of the supported metal cations decrease, resulting in a hydrogen consumption. This reduction process ceases after all the reducible metal cations are consumed..

III Conclusions

The TPR technique is extremely sensitive to the differences between catalysts prepared via different conditions and to the pretreatments of the catalyst prior to experimentation.

TPR is a temperature-dependent process and calculation equations consists of two components: an isothermal contribution and a temperature-programmed component.

Recent development of the analytic gradient in the fragment molecular orbital method

Takeshi Nagata,^{1,2} Dmitri G. Fedorov,² Kazuo Kitaura^{1,2} ¹Graduate School of Pharmaceutical Sciences, Kyoto University, 46-29 Yoshidashimo Adachi, Sakyo-ku, Kyoto 606-8501, Japan ²NRI, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

Recently, the analytic energy gradient has been shown to be complete at the RHF level in the framework of the fragment molecular orbital (FMO) method [1], by which the analytic FMO gradient is applicable to the accurate geometry optimization and the molecular dynamics simulation for large systems. In this study, we present the recent development of the analytic FMO gradient; the FMO gradient is extended to the MP2 level [2] and to consider the solvent effects. Both the explicit and implicit solvent effects are considered by the effective fragment potential (EFP) method [3,4] and the polarizable continuum model (PCM) [5,6], respectively. For the latter, a new FMO/PCM energy expression is proposed, giving a relatively accurate FMO/PCM energy compared to the previously published expressions [6] and making it easier to formulate and implement the gradient equations. The resulting FMO/PCM gradient was used to optimize the geometry of the Trp-cage miniprotein construct (PDB ID: 1L2Y) and the optimized geometry was compared with the first structure in the PDB file. The RMSD of 0.4136 Å shows that the optimized geometry well reproduces the PDB structure. We also present the FMO gradient in the electrostatic potential approximations, which aims for linear-scaling.

[1]. T. Nagata, K. Brorsen, D. G. Fedorov, K. Kitaura, and M. S. Gordon, J. Chem. Phys. **134**, 124115 (2011).

[2]. T. Nagata, D. G. Fedorov, K. Ishimura, K. Kitaura, J. Chem. Phys. (in press).

[3]. N. P. Day, H. J. Jensen, S. M. Gordon, and P. S.Webb, J. Chem. Phys. **105**, 1968 (1996).

[4]. T. Nagata, D. G. Fedorov, K. Kitaura, and M. S. Gordon, J. Chem. Phys. **131**, 024101 (2009).

[5]. J. Tomasi, B. Mennucci, R. Cammi, Chem Rev. 105, 2999 (2005).

[6]. D. G. Fedorov, K. Kitaura, H. Li, J. H. Jensen, and M. S. Gordon, J. Comput. Chem. **27**, 976 (2006).

A perturbation theory for friction of a large particle immersed in a binary solvent

Yuka Nakamura,¹ Akira Yoshimori,¹ Ryo Akiyama² ¹Department of Physics, Kyushu University, Japan ²Department of Chemistry, Kyushu University, Japan

I. Purpose

We have developed a new theory of a binary solvent to study effects of a distribution of solvent particles on friction. Here, we consider the friction from solvent particles to a large solute particle, such as a protein, moving in a solvent. When a solvent consists of two components, the distribution greatly depends on a particle number ratio of each solvent; hence we can examine effects of a distribution by changing the ratio. In fact, experiments on actomyosin motors in a binary solvent have shown effects of a distribution.

II. Theory

We employed a perturbation expansion by assuming that a solvent particle was much smaller than a solute particle. From the expansion, we derived hydrodynamic equations with new boundary conditions of the surface on a solute particle. By solving these equations analytically, we expressed the friction by the radial distribution functions of a binary solvent. These functions can be calculated from the microscopic interactions, therefore we can obtain the friction considering the interactions between solvent and solute particles.

III. Application

Using this theory, we calculated the friction of a hard-sphere system, varying the size ratio and mole fraction (Fig.1). The calculated results showed the large effects of a distribution on the friction even if a small amount of another component solvent (co-solvent) was added. For instance, the friction was 1.29 times as large as that of a one-component solvent when the mole fraction of a co-solvent was 0.0004 (The ratio of sizes was 50 : 1 : 4). Furthermore, the deviation from Stokes' law increased with a mole fraction of a co-solvent. These tendencies were stronger at a large size of a co-solvent than at a small size.



Fig.1 The friction *F* calculated by our theory. The vertical axis represents the deviation from Stokes' law (slip condition) on *F*. The size ratio of solute, solvent and co-solvent particles is 50 : 1 : X. X = 2, 3, 4 and 5.

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Spin-adapted open-shell TD-DFT

Zhendong Li and Wenjian Liu

Institute of Theoretical and Computational Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

Time-dependent density functional theory (TD-DFT) has emerged as a powerful tool for investigating electronic excitations of molecular systems. However, this holds only for closed-shell systems. As for open-shell systems of unpaired electrons, TD-DFT may fail miserably. On one hand, the results by UKS-based TD-DFT are often severely spin-contaminated and hence physically meaningless. On the other hand, the standard ROKS-based TD-DFT can only access those states due to singlet-coupled single excitations. The missed states due to triplet-coupled single excitations may even be lower in energy. The spin-adaption (SA) of TD-DFT sounds at first glance self-contradictory: The spin-adaption of single excitations require certain double and even triple excitations but the adiabatic approximation allows only single excitations. Here we show [1,2] that the way out of this dilemma is to invoke a tensor reference consisting of all the components of a high-spin multiplet. A minimal yet spin-complete single excitation configuration space can then readily be constructed by tensor products between single excitation tensor operators and the tensor reference. Further combined with the tensor equation-of-motion formalism, a very compact SA-TD-DFT for excitation energies can be obtained. Both the implementation and the computation of SA-TD-DFT are very much the same as the spin-contaminated UKS-TD-DFT. That is, the elimination of spin-contamination has been achieved for free. The idea of tensor-coupling is conceptually different from the traditional schemes that takes only one component of the multiplet as the reference and hence has to invoke ad hoc redefinitions of excitation operators/levels to generate those higher-rank excited configurations required by spin symmetry.

Reference:

1. Z. Li and W. Liu, J. Chem. Phys. 133, 064106-1-22 (2010).

2. Z. Li, W. Liu, Y. Zhang, and B. Suo, J. Chem. Phys. 134, 134101-1-22 (2011).

Assessment of density functional theory for calculations of magnetic interactions of manganese complexes

 <u>Shusuke Yamanaka</u>,¹ Keita Kanda,¹ Toru Saito,¹ Yasutaka Kitagawa,¹ Takashi Kawakami,¹ Masahiro Ehara,² Mitsutaka Okumura,¹ Haruki Nakamura, ³ Kizashi Yamaguchi⁴
 ¹Graduate School of Science, Osaka University, Japan ²Institute for Molecular Science, Japan ³Protein Institute, Osaka University, Japan
 ⁴TOYOTA Physical & Chemical Research Institute, Japan,

I. Introduction

Recently we have investigated manganese cluster in photosytem II [1], which catalyze the decomposition reaction of water. We rely on the newest and most reliable X-ray structure [2] and the optimized ones starting from the X-ray structure. However the stable spin states for some of them calculated by the B3LYP method are not consistent with the EPR experimental results of the native cluster [1]. We are now examining the modeling structure including various protonation types to the oxygens in-and-around the cluster. It is also possible that the B3LYP does yield incorrect magnetism of the manganese cluster. To confirm this, we implement of benchmark test of B3LYP, as well as other functionals, for calculations of magnetism of various manganese complexes [3].

II. Results

First we construct a test set consisting of 15 dinuclear manganese complexes, for which the X-ray diffraction and the magnetic susceptibility experiments have been The set of complexes include various oxidation patterns: Mn(II)₂ implemented. Mn(II)Mn(III), Mn(III)₂, Mn(III)Mn(IV), and Mn(IV)₂. Then we examine the basis set dependence of the calculational results of magnetism of the test set with using B3LYP functional to choose the appropriate basis set, with which the deviations of magnetic interactions from computational results of triple-zeta plus diffuse polarization basis are almost negligible. With employing this pruned basis set, we examined various exchange-correlation functionals, BHandHLYP, CAM-B3LYP, TPSSh, PBE0, PBEh35, HSEh1PBE, HSE1PBE, HSE2PBE, LC-wPBE, M06, M062-2X, M06-HF, HF, B3LYP*, for calculations of magnetism of the test set. The computational results will be discussed in relation to the experimental resuls, in particular with focusing on the dependency on the oxidation states and molecular structures.

References

[1] K. Kanda et al. CPL 506 (2011) 98; S. Yamanaka, et al. CPL in press; K. Kanda et al. Polyhedron submitted; S. Yamanaka et al. Advanced in Quantum Chemistry, submitted.
[2] Y. Umena, K. Kawakami, J-R. Shen, N. Kamiya, Nature 473 (2011) 55.

[3] S. Yamanaka et al., in preparation.

3PP-18

Computational Investigation on Adsorption and Dissociation of NH₃ Molecule on Fe(111) Surface

, Hsin-Tsung Chen,¹ and Yung-Chi Chen² Hui-Lung Chen^{2*}

¹ Department of Chemistry, Chung Yuan Christian University, Chungli 32023, Taiwan

² Department of Chemistry, Chinese Culture University, Taipei, 111, Taiwan

Abstract

Our calculations with spin-polarized density functional theory was carried out to characterize the adsorption and dissociation of NH₃ molecule on the Fe(111) surface. The molecular structures and adsorbate/substrate interaction energies of NH₃/Fe(111), NH₂/Fe(111), NH/Fe(111), N/Fe(111) and H/Fe(111) configurations were predicted. In these calculations, four adsorption sites, such as top (T), bridge (B), 3-fold-shallow (S) and 3-fold-deep (D) sites, of the Fe(111) surface were considered. It was shown that the barriers for the stepwise NH₃ dissociation reaction, NH_{3(g)} \rightarrow N_(a)+3H_(a), are 28.32 kcal/mol (for H₂N-H bond activation), 28.49 kcal/mol (for HN-H bond activation), and 25.34 kcal/mol (for N-H bond activation), respectively, and the entire process is 20.08 kcal/mol exothermic. To gain insights into the catalytic activity of the Fe(111) surface for the dehydrogenation of NH₃, the interaction nature between adsorbate and substrate is also analyzed by the detailed electronic analysis. This information with regard to the reaction mechanism, the catalytic activity of various surface sites, and the relevance of the surface structure would be otherwise difficult to achieve with experimental measurements, indicating that the periodic DFT calculations might play a significant role in the reasonable explication of NH₃ dissociation behavior in heterogeneous catalysis.

Keywords: Density-functional theory; Fe(111) surface; NH₃; dehydrogenation

Reference:

1. Ertl, G. Catal. Rev.-Sci. Eng. 1980, 21, 201.

2. Delbecq, F.; Zaera, F. J. Am. Chem. Soc. 2008, 130, 14924.

3. Chen, H.-L.; Chen, H.-T.; Ho, J.-J. Langmuir 2010, 26, 775.

4. Chen, H.-L.; Wu, S.-Y.; Chen, H.-T.; Chang, J.-G.; Ju, S.-P.; Tsai, C.; Hsu, L.-C. *Langmuir* **2010**, *26*, 7157.

*Corresponding author. E-mail: ch13@faculty.pccu.edu.tw

Spin-orbit TDDFT calculations with long-range correction

<u>Ayako Nakata</u>,¹ Takao Tsuneda,² Kimihiko Hirao³

¹Computational Materials Science Unit, National Institute for Materials Science, Japan ²Fuel Cell Nanomaterials Center, University of Yamanashi, Japan ³ RIKEN Advanced Institute for Computational Science, Japan

Relativistic time-dependent density functional theory (TDDFT) is a powerful tool to include both relativistic and correlation effects with low computational cost. However, TDDFT with conventional exchange functionals have severe problems in e.g. the reproducibility of charge transfer (CT) and Rydberg excitation energies and oscillator strengths. These problems are due to the lack of long-range exchange interactions in conventional exchange functionals. We have proposed long-range corrected (LC) DFT and have overcome these problems. Especially, LC-TDDFT succeeds in describing CT excitations with remarkable accuracy. CT excitations often play a major role in spin-forbidden transitions, such as phosphorescence, because the spin-orbit (SO) couplings are significant for excitations inducing the changes in electron distributions.

In this study, LC-DFT has been applied to a spin-orbit TDDFT to describe spin-forbidden transitions appropriately by TDDFT.

The LC method has been combined with the 2-component zeroth-order regular approximation (ZORA). In the LC scheme, the exchange energy is divided into long-range interaction and short-range interaction parts, which are represented by the Hartree-Fock (HF) exchange and exchange functional, respectively. The $\alpha - \alpha$, $\alpha - \beta$, $\beta - \alpha$, and $\beta - \beta$ long-range HF exchange energies have been evaluated in the SO-LC calculations. The short-range exchange functional has been treated in the noncollinear approach in the TDDFT calculations.

Table 1 shows the excitation energies and fine structures of a Rn atom calculated with LDA, BLYP, B3LYP, and LC-BLYP using the Gaussian basis function optimized in the relativistic calculations. LC-BLYP reproduces the spin-forbidden excitation energies

for which electrons	Table 1. $6p \rightarrow 7s$ excitation energies and fine structures of Rn [eV].					
are moved to widely-	State	LDA	BLYP	B3LYP	LC-BLYP	Exptl.
distributed orbitals.	Excitation	energy				-
Our results also	2	6.38	6.09	6.40	6.86	6.77
demonstrated that LC-	1	6.54	6.26	6.57	7.06	6.94
DFT accurately	0	9.69	9.31	9.73	10.47	10.66
reproduces ionization	1	9.75	9.39	9.79	10.54	10.79
energies of heavy	Fine struct	ure				
atoms based on the	2	0.00	0.00	0.00	0.00	0.00
Janak's theorem.	1	0.16	0.17	0.17	0.19	0.17
	0	3.31	3.22	3.33	3.61	3.89
	1	3.37	3.29	3.39	3.68	4.02

Comprehensive study of hybrid functionals applied to structural and electronic properties of semiconductors and insulators

Yu-ichiro Matsushita, Kazuma Nakamura, Atsushi Oshiyama

Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan CREST, JST, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan University of Tokyo

Local density approximation (LDA) and generalized gradient approximation (GGA) in density functional theory (DFT) has shown fantastic performance in understanding and even predicting material properties in spite of its relatively simple treatment of the exchange-correlation functional: e.g., for many materials, lattice constants and bulk moduli are reproduced within less than 1-2 % and several percent, respectively, deviations from experimental values in conventional approximation. Yet the approximations fail to describe some of the properties including ground-state magnetic ordering for some transition-metal oxides. The hybrid functionals combining LDA or GGA with the Hartree-Fock approximation (HFA) would be effective to break limitations of LDA and GGA. Recently, a success of application of Heyde-Scuseria-Ernzerhof (HSE) functional [1] to extended systems has been reported [2], but the numbers of such calculations and applications are still quite few.

In the present study, we present a comprehensive study about performance of several hybrid functionals, including the Perdew-Burke-Ernzerhof-free (PBE0) [3], HSE, and long-range corrected (LC) hybrid functional [4]. Our code was implemented in Tokyo Ab initio Program Package with plane-wave-basis set and norm-conserving pseudopotentials. For structural parameters, hybrid functionals generally give better agreements with experiments than GGA; in HSE functional, the lattice constants and the elastic constants are well described within 1.39 % and 5.4 % accuracy, respectively, with respect to experimental values. LC functional reproduces the lattice constants within 1.21 % and the elastic constants within 5.5 %. Figure1 compares theoretical band gaps based on GGA, HSE, and LC with the experiments, from which, while the



FIG.1: Comparison between theory and Expt.

GGA gaps are severely underestimated, the use of the hybrid functionals improves this underestimations [5].

References

- [1] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118, (2003) 8207.
- [2] J. Paier, M. Marsman, K.Hummer, G. Kresse, I.C.Gerber, and J.G.Angyan, J. Chem. Phys. 124, (2006) 154709.
- [3] J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. 105, (1996) 9982.
- [4] H. Iikura, T. Tsuneda, T. Yanai, and K. Hirao, J. Chem. Phys. 115, (2001) 3540.
- [5] Y. Matsushita, K. Nakamura, and A. Oshiyama, Phys. Rev. B in press.

Analytic derivatives of quartic-scaling doubly hybrid XYGJ-OS functional: Theory and applications

Hyunjun Ji,¹ Yihan Shao,² Igor Zhang,³ Xin Xu,³ William A. Goddard,^{1,4} Yousung Jung¹ ¹Graduate School of EEWS, KAIST, Republic of Korea ²Q-Chem Inc., USA ³Department of Chemistry, Fudan University, China ⁴Materials and Process Simulation Center, California Institute of Technology, USA

Abstract

Analytic first derivative expression of opposite-spin (OS)-PT2 corrected doubly hybrid XYGJ-OS functional[1] with non-SCF Kohn-Sham orbitals is derived and presented. The gradient as well as energy can be evaluated efficiently with quartic-scaling algorithm by the combination of Laplacian transform and auxiliary basis expansions[2]. The result is implemented into a quantum chemical software package, Q-Chem[3] 4.0 and tested for chemical applications.

[1] Zhang, I. Y.; Xu, X.; Goddard, W.; Jung, Y., under revision.

[2] Lochan, R.; Shao, Y.; Head-Gordon, M., J. Chem. Theory Comput.3, 988 (2007).

[3] Shao, Y. et al., Phys. Chem. Chem. Phys. 8, 3172 (2006).

Implementation and numerical assessment of local response dispersion method

Yasuhiro Ikabata,¹ Hiromi Nakai^{1,2,3}

¹Graduate School of Advanced Science and Engineering, Waseda University, Japan ²Research Institute for Science and Engineering, Waseda University, Japan ³JST-CREST, Japan Science and Technology Agency, Japan

Various types of dispersion correction methods have been developed to improve the description of weak interactions within the DFT framework. One of them is the local response dispersion (LRD) method [1,2], which computes dispersion energy directly from the ground-state electron density without fairly excess cost. The LRD method combined with the long-range corrected (LC-BOP) functional improves the potential energy curve of benzene dimer, as shown in Figure 1. This method has been integrated to the public edition of the GAMESS program package.

In this poster, we present the theoretical aspects of the LRD method, such as energy formulation, SCF implementation, analytical gradient, and TDDFT calculations. We also mention the numerical assessment of the LRD method not only for the closed-shell ground state but also for open-shell and excited states.



Figure 1. Potential energy curves of sandwich benzene dimer. [m,n] means the truncations of two-center and multicenter contributions after *m*th and *n*th orders, respectively. The aug-cc-pVTZ basis set is used in the LC-BOP+LRD calculation. The CCSD(T)/CBS curve is taken from Ref. [3].

T. Sato and H. Nakai, J. Chem. Phys., **131**, 224104 (2009).
 T. Sato and H. Nakai, J. Chem. Phys., **133**, 194101 (2010).
 C. D. Sherrill, T. Takatani, and E. G. Hohenstein, J. Phys. Chem. A, **113**, 10146 (2009).

Crossing between potential energy surfaces in 2-(pyridin-2-yl) furan-3-ol

Hossein Tavakol

Department of Chemistry, Faculty of Science, University of Zabol, Zabol, Iran.

Potential energy surfaces can be applied to presenting molecular dynamic motions such as rotations and changes in bond lengths and bond angles. Studies of molecular dynamics have been of interest in both computational and experimental research areas.^[1] Recently, dynamic phenomena such as rotations^[2] and tautomerism^[3] have been the subject of theoretical researches. In this line, potential energy surfaces (PESs) for dynamic motion have been studied by both computational and experimental methods.^[4]

In continuation of our previous researches about tautomerism^[5,6] and in order to investigate the possibility of diabatic crossing in PESs of organic molecules by theoretical methods, 2-(pyridin-2-yl)furan-3-ol and (2E)-2-(pyridin-2(1H)-ylidene) furan-3(2H)-one have been considered to study of their tautomerism interconversions, relative rotations of rings, OH bond rotations and possibility of crossing between those energy surfaces using DFT methods at the B3LYP/6-311++G** level of theory. The optimized structures of both tautomers and the transition state of tautomerism are completely planar. Study of tautomerism in PYFO shows that T1 tautomer is about 24.38 kJ/mol more stable than T2. The rate constants of tautomerism interconversion for converting T1 to T2 is 1.98×10^8 M⁻¹Sec⁻¹ and for converting T2 to T1 is 3.70×10^{12} M⁻¹Sec⁻¹ at room temperature that show the possibility of this tautomerism with high rate at ambient temperature. Rotation of OH bond in T1 shows two minimum (at 0° (global minimum) and 180° (local minimum)) and a transition state at 110° (and 265°) with 47.10 kJ/mol barrier energy. Relative rotation of rings shows global minimum at 0° for both tautomers and local minimum at 154° and 206° for T1 and 180° for T2. The barrier energy for ring rotation of T1 was observed at 90° and 270° with 63.69 kJ/mol heights and for T2 was observed at 120 with 170.86 kJ/mol height. Interestingly, the energy levels of ring rotations for T1 and T2 are the same and crossing between them was observed. Therefore, although these two potentials have not the same symmetries but because of the crossing between their energy level, crossing is not avoided.

References:

[1] 2. C. Wang, P. Zhang, J. Chem. Phys. 2010, 133, 134503.

[2] S. Wi, J. Spano, W.A. Ducker, J. Phys. Chem. C 2010, 114, 14986.

[3] A. Misra, S. Dalai, *THEOCHEM* **2007**, 807, 33.

[4] G. Granucci, G. Medders, A.M. Velasco, Chem. Phys. Lett. 2010, 500, 202.

[5] H. Tavakol, S. Arshadi, J. Mol. Model. 2009, 15, 807.

[6] H. Tavakol, Mol. Simul. 2010, 36, 391.

On the external source method for Kubo-transformed quantum correlation functions

Atsushi Horikoshi

Department of Natural Sciences, Tokyo City University, Japan

The Feynman path integral formulation of quantum mechanics represents a wellestablished route for the calculation of static properties of quantum many-body systems at finite temperature. However, it is computationally expensive to calculate dynamical quantities such as Kubo-transformed quantum correlation functions

$$C_{BA}^{\rm K}(t) = \int_0^\beta \frac{d\lambda}{\beta} \langle \hat{B}(-i\hbar\lambda)\hat{A}(t)\rangle_\beta.$$

Recently a new quantum dynamics method to calculate $C_{BA}^{\mathsf{K}}(t)$ has been proposed by Krishna and Voth [1]. This is an extended quantum dynamics perturbed by external sources [2]. In case that both of \hat{A} and \hat{B} depend on the position operator \hat{q} , the calculation procedure is summarized as follows: (1) Introduce an operator \hat{F} which satisfies $\hat{A} = \frac{d}{dq}\hat{F}$. (2) Introduce two external sources μ and ν which couple to the operators \hat{B} and \hat{F} , respectively. (3) Calculate the expectation value of the momentum operator \hat{p} , $p_{\mu\nu}(t) = \langle \hat{\rho}_{\mu}\hat{p}_{\nu}(t) \rangle$, where the density operator $\hat{\rho}_{\mu}$ is given by the Hamiltonian $\hat{H} + \mu \hat{B}$, and the time evolution of \hat{p} is driven by the Hamiltonian the transformed quantum correlation function using the approximate equation

$$C_{BA}^{\mathrm{K}}(t) \simeq \frac{1}{\beta} \left. \frac{\partial^3}{\partial \mu \partial \nu \partial t} \left. p_{\mu\nu}(t) \right|_{\mu,\nu=0} + \langle \hat{B} \rangle_{\beta} \langle \hat{A} \rangle_{\beta}.$$

This method is quite promising, because the path integral calculation of $p_{\mu\nu}(t)$ is expected to be less computationally demanding than that of $C_{BA}^{K}(t)$. It is still unclear, however, whether the method can be applied to general quantum systems, because the method is based on the approximate equation.

In this work [3] we derive an exact identity

$$C_{BA}^{\mathrm{K}}(t) = \frac{1}{\beta} \left. \frac{\partial^{3}}{\partial \mu \partial \nu \partial t} p_{\mu\nu}(t) \right|_{\mu,\nu=0} + \langle \hat{B} \rangle_{\beta} \langle \hat{A} \rangle_{\beta} + C_{BD}^{\mathrm{K}}(t) - \langle \hat{B} \rangle_{\beta} \langle \hat{D}(t) \rangle_{\beta},$$

where $\hat{D}(t) = -\frac{i}{\hbar} \left[\int_0^t ds \hat{F}(s), \frac{\partial \hat{V}}{\partial q}(t) \right]$. Omitting the operator $\hat{D}(t)$, we obtain the approximate equation given by Krishna and Voth. This approximation is valid in the short time region. We will present some results for model potential systems and clarify the properties of $p_{\mu\nu}(t)$ and $\hat{D}(t)$.

[1] V. Krishna and G. A. Voth, J. Phys. Chem. B110, 18953 (2006).

[2] H. Kleinert, Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets, World Scientific, Singapore, 2004.

[3] A. Horikoshi, in preparation.

Zero-dipole summation method for precisely estimating electrostatic interaction in molecular dynamics

Ikuo Fukuda,¹ Narutoshi Kamiya,² Haruki Nakamura² ¹Computational Science Research Program, RIKEN, Japan ²Institute for Protein Research, Osaka University, Japan

For computational studies of materials in a realistic manner, even in a classical point charge system, the appropriate treatment of the Coulombic interaction is important. However, due to its long-ranged nature and the existence of both positive and negative signatures of the potential function, it is difficult to handle the interaction in an effective manner, i.e., with high accuracy, low computational cost, freedom from artifacts, and ease of implementation.

We present a novel idea, zero-dipole summation, for evaluating the electrostatic energy of a classical particle system, and provide an algorithm for effectively utilizing the idea for molecular dynamics study [1]. The summation conceptually prevents the nonzero-charge and nonzero-dipole states artificially generated by a simple cutoff truncation. The resulting energy formula is nevertheless represented by a simple pairwise sum using a certain function, which enables effective application to high-performance computation with good scalability. We discuss heuristic derivation of the energy formula for an introductory understanding, explain a theoretical framework to justify the formula for a consistent description, and exhibit the numerical results, in comparison with the previously proposed scheme [2]. Accuracy of the energy function and the stability in MD simulation are investigated in crystal and liquid systems. In addition, we discuss the issue of treating bonding interactions for general molecule system, and provide the results of the application to the systems, including bulk water.

Our method is an extension of the charge neutralized summation developed by Wolf et al [3]. Furthermore, we found that the current method becomes a generalization of the pre-averaged potential method [4], which has been developed to tackle the artifact caused by the cubic symmetry in the periodicity assumption, e.g., used in lattice methods, applied to inherently non-periodic systems. Note that the pre-averaged potential method is based on a viewpoint of the isotropic property, which is different from the viewpoint of the electric neutrality in the current method. We discuss the relationships among these methods and the possibilities for their further applications.

[1] I. Fukuda et al., J. Chem. Phys. 134, 164107 (2011).

[2] I. Fukuda, Y. Yonezawa, and H. Nakamura, J. Phys. Soc. Jpn. 77, 114301 (2008).

[3] D. Wolf, P. Keblinski, S. R. Phillpot, and J. Eggebrecht, J. Chem. Phys. **110**, 8254 (1999).

[4] E. Yakub and C. Ronchi, J. Chem. Phys. 119, 11556 (2003).

Ab initio molecular dynamics approach to tunneling splitting in polyatomic molecules

<u>Yusuke Ootani</u>,¹ Tetsuya Taketsugu²

¹*RIKEN Advanced Institute for Computational Science* ²*Division of Chemistry, Graduate School of Science, Hokkaido University, Japan*

Nowadays, ab initio molecular dynamics (AIMD) has been widely used to investigate dynamical process of chemical reaction. AIMD does not require a predetermined potential function, and thus it can be applied to any polyatomic molecule in principle. In the AIMD approach, nuclear motions are evolved by integrating the Newton's equation of motion based on the energy gradient calculated point by point by ab initio methods. Thus, nuclear motion is treated by classical mechanics, and so some additional treatment is required to take into account nuclear quantum effects such as nonadiabatic transition and tunneling effects.

Recently, AIMD has been extended to excited-state reaction dynamics in which nonadiabatic transition plays an important role. Several approaches such as a surface hopping method, are successfully used to incorporate the nonadiabatic transition in a framework of classical trajectory simulation. On the other hand, there are few ways to tackle the tunneling effect and there have been no attempt to implement a semiclassical tunneling method to AIMD simulations.

In this work the semiclassical tunneling method of Makri and Miller [1] is implemented to our developed AIMD code as a practical tool to investigate the tunneling match of the tunneling

practical tool to investigate the tunneling effects in chemical reactions. Each time the turning point for tunneling is detected along the AIMD trajectory, the tunneling amplitude is evaluated on-the-fly through ab initio electronic structure calculation. The method is applied to umbrella inversion of ammonia and intramolecular hydrogen transfer in malonaldehyde. In the application to -

Table 1. Calculated tunneling splitting and experimental value (in cm⁻¹)

	Cal.	Exp.[2]
NH ₃	0.71	0.79
ND ₃	0.078	0.053
НОСН=СН-СНО	19.8	21.6
DOCH=CH-CHO	2.28	2.9

malonaldehyde, effects of multi-dimensionality are examined by assigning quantum zero-point energies only to significant vibrational modes and changing the amount of energy given to other degrees of freedom. The calculated tunneling splitting values are in good agreement with the corresponding experimental values for both molecules, as shown in Table 1.

[1] N. Makri and W. H. Miller J. Chem. Phys. 91, 4026 (1989).

[2] V. Spirko, J. Mol. Spectrosc. **101**, 30 (1983): S. L. Baughcum et al. J. Am. Chem. Soc. **106**, 2260 (1984).

Short-time Fourier transform analysis of electron dynamics described by real-time TDHF calculation

<u>Tomoko Akama</u>,¹ Akihiro Hiratsuka,¹ Yutaka Imamura,¹ Hiromi Nakai^{1,2,3} ¹School of Advanced Science and Engineering, Waseda University, Japan ²Research Institute for Science and Engineering, Waseda University, Japan ³CREST, Japan Science and Technology Agency, Japan

I. Introduction

The real-time time-dependent Hartree-Fock and time-dependent density functional theory (RT-TDHF/TDDFT) calculations have become useful tools not only for evaluating excitation spectra but also for describing electron dynamics. In preceding RT-TDHF/TDDFT studies, the frequency-domain properties were obtained by the Fourier transform technique and the electron dynamics was analyzed directly through time evolutions of molecular properties. In this study, we proposed an analysis of RT-TDHF calculations using the short-time Fourier transform (STFT) technique.

II. Short-time Fourier transform analysis of RT-TDHF calculation

In the RT-TDHF calculation, the TDHF equation is solved by the real-time propagation method to obtain the time-dependent induced polarization vector. STFT is a time-frequency analysis technique, transforming a time-domain property into a frequency-domain one with leaving time-domain information. The STFT analysis is applied to the induced polarization vector,

$$\delta \boldsymbol{P}(\omega,t) = \int_{-\infty}^{\infty} d\tau \, \delta \boldsymbol{P}(\tau) W(\tau-t) \, e^{-i\omega\tau} \,, \tag{1}$$

where W(t) is a window function that picks up a part of the signal in the time domain. Time evolution of excitation spectra is obtained as $\operatorname{Im}[\partial P(\omega, t)]$.

We carried out RT-TDHF/cc-pVDZ calculation and STFT analysis of formaldehyde dimer, in which two molecules, α and β , are vertically arranged. Figure shows the time evolution of the excitation peaks at 9.9 eV, mainly assigned to the π - π * excitations of

the molecules α and β . The intensities of these peaks oscillate. The phase of the oscillation of molecule β differed by about $\pi/2$ from that of molecule α . This shows that the induced polarization propagates from the π - π * excitation of the molecule α to that of β , through the intermolecular interaction. The STFT analysis of RT-TDHF calculation enables us to directly observe the electron dynamics associated with the excited states.

[1] T. Akama and H. Nakai, *J. Chem. Phys.* **132**, 054144 (2010).



Fig. Time evolution of peak intensities corresponding to π - π * excitations of molecules α and β .

Computational study on photo- and thermo-reactions between tetra-*tert*-butyl-substituted cyclobutadiene and tetrahedrane

Masato Sumita,¹ Kazuya Saito,² Yoshitaka Tateyama¹

 ¹WPI International Centre for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
 ²Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1, Tennodai, Tsukuba, Ibaraki 305-8571, Japan

We investigated the photo-chemical have reaction from tetra-tert-butylcyclobutadiene (TB-CBD) to tetra-tert-butyltetrahedrane (TB-THD) and its reverse thermo-chemical reaction processes in the ground state [1] by using CASSCF and MRMP2 computational methods. The initial step of the photochemical reaction is the HOMO-LUMO single-electron excitation $(1^{1}B_{1} \text{ state})$ and the rearrangement from TB-CBD to TB-THD occurs via the HOMO-LUMO double electron excited state $(2^1A_1$ state). After the transition from the $1^{1}B_{1}$ to the $2^{1}A_{1}$ state, most TB-CBD molecules only show photo-physical property without any reactions because the final point of the minimum-energy-path (MEP) calculation at the MRMP2//CASSCF level is the S_1/S_0 degeneracy space (DS_{ionic}), which results in turning back to TB-CBD in the S₀ state. However, on the way to the final point of the MEP, it is possible for some TB-CBD to transit at another S_1/S_0 degeneracy space (DS_{tetra}), which is related to the photoreaction from TB-CBD to TB-THD. The processes of the photoreaction from TB-DBD to

TB-THD are schematically summarized in Figure 1. On the other hand, two routes from TB-THD to TB-CBD were found in the S_0 state. is the route via One bicyclodiradical transition state. The other is the ionic transition state. In both reaction paths, only one TS is there in contrast to the plural step reaction suggested previously [2].



Figure 1. Schematic potential energy surfaces. TB-CBD isomerizes to TB-THD via the HOMO/LUMO double-electron excited state via the HOMO/LUMO single-electron excited state.

- [1] G. Maier, Angew. Chem. Int. Ed. Engl. 27 (1988) 309.
- [2] M. Sumita. K. Saito. Tetrahedron, 66 (2010) 5212.

Photophysical properties and vibrational structure of ladder-type penta *p*-phenylene and carbazole derivatives based on SAC-CI calculations

Potjaman Poolmee,¹ Masahiro Ehara,² Hiroshi Nakatsuji³

¹ Department of Chemistry, Faculty of Liberal Arts and Science, Kasetsart University, Kamphaeng Saen, Nakhon Pathom, Thailand
² Research Center of Computational Science, Institute for Molecular Science, 38-Nishigo-Naka, Myodaiji, Okazaki, Japan
³ Quantum Chemistry Research Institute, Goryo Oohara 1-36, Nishikyo-ku, Kyoto, Japan

The π -conjugated ladder-type molecules constitute an attractive field of organic photoactive materials. In this work, the photophysical properties of ladder-type penta *p*-phenylene (LPP) and carbazole derivatives (bisindenocarbazole and diindolocarbazole) have been theoretically investigated by using the symmetry-adapted cluster-configuration interaction (SAC-CI) method. The equilibrium geometries in the ground (S_0) and first excited (S_1) states were calculated to be planar and the excitation is delocalized over the molecules. The SAC-CI/DZP calculations have been applied to the absorption and emission spectra of these molecules. The absorption spectra were well reproduced in both peak positions and the shape of the absorption bands. The strong absorption is attributed to the HOMO \rightarrow LUMO (H \rightarrow L) transition, however, in carbazoles, the H-1 \rightarrow L transition is located below the H \rightarrow L transition. The vibrational structure in the S_0 - S_1 absorption band of LPP was analyzed by calculating the Franck-Condon (FC) factors based on the potential energy surfaces (PESs) along the normal coordinates that are relevant in the geometry change. The vibrational structure was well reproduced by the theoretical simulation. The C-C stretching mode dominantly contributes to the vibrational structure, while the breathing motion of molecular frame does not influence the structure. The emission energies calculated by the SAC-CI method also agree well with the experimental values. The vibrational structure in the fluorescence band was also examined by the FC analysis, for which theoretical spectrum is satisfactory for two carbazoles, while the 0-0 transition is overestimated in LPP. In diindolocarbazole, the S_2 state has large oscillator strength, while the S_1 state has small oscillator strength.

Probing the multiradical character and nonlinear optical properties of linear and cyclic polyacenes: a wrapping effect in open-shell polyacenes <u>Shabbir Muhammad</u>, Takuya Minami, Ryohei Kishi, Yasuteru Shigeta, Masayoshi Nakano

Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

I. Introduction

We have applied the broken-symmetry density functional theory method to the investigation of the second hyperpolarizabilities (γ) and multiradical characters (y_i) [1] of zigzag (Z) linear and cyclic polyacenes [2]. It has been found that linear [n]acenes when wrapped into their respective [n]cyclacenes show a significant change in their singlet diradical characters. For example, [5]acene by wrapping into [5]cyclacene changes its only primary diradical value of $y_0 = 0.407$ into two identical values of diradical characters, $y_0 = y_1 = 0.487$ for [5]cyclacenes. In contrast, wrapping of [6]acene into [6]cyclacene increases its primary diradical value from $y_0 = 0.540$ to $y_0 = 0.844$ with further emergence of two smaller identical values $y_1 = y_2 = 0.156$. These results show interesting insights into the relationship among the architectures, diradical characters and γ_{zzzz} values. Besides this, more pronounced but different effects on these properties have been observed by comparing zigzag graphenes to their respective wrapped nanotubes.

Systems	\mathcal{Y}_0	\mathcal{Y}_1	Yzzzz (a.u.)
Z-(5)acene	0.4078	0.0629	6.01E+03
Z-(6)acene	0.5409	0.1162	6.37E+03
Z-(7)acene	0.6441	0.1773	6.41E+03
Z-(8)acene	0.7256	0.2465	6.47E+03
Z-(9)acene	0.7941	0.3194	6.62E+03
Z-(10)acene	0.8455	0.3914	6.93E+03
Z-(5)cyclacene	0.4870	0.4870	2.89E+03
Z-(6)cyclacene	0.8447	0.1561	1.80E+03
Z-(7)cyclacene	0.6618	0.6618	2.83E+03
Z-(8)cyclacene	0.8508	0.2574	2.53E+03
Z-(9)cyclacene	0.8074	0.8074	3.00E+03
Z-(10)cyclacene	0.8519	0.3880	3.36E+03



[2] Anthony, J.E. *Angew. Chem. Int. Ed.* 2008, 47, 452-483

Table 1. Diradical characters (y_0, y_1) and γ_{zzzz} values for zigzag polyacenes

Reactivity of thiophenolate toward chalcogenadiazoles

N.P. Gritsan¹, <u>E.A. Suturina</u>¹, A.V. Zibarev²

¹Institute of Chemical Kinetics and Combustion of RAS, Institutskaya str. 3, Novosibirsk, 630090, Russia

²Institute of Organic Chemistry of RAS, Lavrentieva ave. 9, Novosibirsk, 630090, Russia

Thiophenolate anion (1) is known to reduce a series of chalcogenadiazoles to radical anions (π -RAs) [1]. Recently [2], it was discovered that reaction of 1 with 3,4-dicyano-1,2,5-selenadiazole (2) gives the product of hypercoordination at the Se center (3) isolated in the form of the salt [K(18-crown-6)][3] (4). The latter type of reactivity has never been observed previously. The X-ray structure of 4 revealed that the Se-S distance in the anion 3 (2.722 Å) is *ca*. 0.5 Å longer than the sum of the covalent radii, but *ca*. 1 Å shorter than the sum of van der Waals radii of Se and S [2].



To estimate the scope of this new reaction, thermodynamics and kinetics of the interaction between 1 and various 1,2,5-chalcogenadiazoles (chalcogen: S, Se, Te) were theoretically investigated at the DFT level using B3LYP, M06-2X and B97-D functionals. Calculations predict that hypercoordination of 1 with formation of the S-S bond is almost thermoneutral. The hypercoordinate products with the Se-S bond are thermodynamically more preferable. In turn, interaction of 1 with Te congener of 2 is predicted to lead to hypercoordinate anion featuring stronger Te-S bond than the Se-S bond in anion 3. Therefore, one can expect general character of the discussed hypercoordination in the case of heavier chalcogens. According to the QTAIM and NBO analysis, the Se-S bond in 3 is a donor-acceptor bond whose formation leads to transfer of ca. 40% of negative charge from 1 onto the heterocycle.

For various 1 / chalcogenadiazole reaction systems, thermodynamics and kinetics of electron transfer reaction were also theoretically studied to rationalize interchalcogen hypercoordination vs. reduction to π -RA dichotomy.

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[1] I.Yu. Bagryanskaya, Yu.V. Gatilov et al. *Eur. J. Inorg. Chem.* 2007, 4751.
[2] N.A. Semenov, E.A. Suturina et al. *J. Phys. Chem. A* 2011, DOI: 10.1021/jp2019523.

Molecular and Electronic Structures of the Super Reduced State of a Polyoxometalate (POM), $[Mo_{12}O_{40}P]^x$ (*x* = -3, -27)

<u>Yoshio Nishimoto</u>,¹ Hirofumi Yoshikawa,¹ Kunio Awaga,¹ Stephan Irle¹ ¹Graduate School of Science, Department of Chemistry, Nagoya University, Japan

Polyoxometalate (POM) clusters have a great potential as novel battery material with higher electronic capacity and stability. Its useful electrochemical properties in this regard were spectacularly demonstrated by Kawasaki *et al.* [1], and its stability under solid-state electrochemical redox conditions is of great importance for practical application. Its wide range of charge states is of great interest to theoretical chemists.

In our contribution, the molecular and electronic structures of a POM cluster, $[Mo_{12}O_{40}P]^x$ (x = 3-, 27-), were investigated using density functional theory (DFT). In the super-reduced state, which is achieved by reduction of POM³⁻ by formally 24 electrons, experimentalists found in the XAFS spectrum that the POM²⁷⁻ cluster has characteristic short (about 2.5 Å) Mo-Mo bonds and suffers characteristic geometrical changes of Mo-O bond lengths [2]. This observation was practically reproduced by our theoretical calculations at the RI-BP86-D/def-SVP level of theory, using lithium atoms as counter cations in order to stabilize the highly negative charge on the POM cluster. It was proven that the origin of observed short Mo-Mo bonds comes from the formation of triangular Mo-Mo sites, created under preservation of the original Mo skeleton via 'squeezing out' oxygen atoms from Mo-O-Mo bonds.

We note that our calculations were not only performed using ordinary geometry optimizations, but also employed the Born-Oppenheimer molecular dynamics (BOMD) technique. Starting with the structure of X-ray result, we first added 27 Li atoms in random positions. In Figure 1, the lower left structure was derived by an ordinary geometry optimization; on the other hand, the upper right structure was derived by quenching a BOMD NVT trajectory run at room temperature for 1.92 ps. Its resulting optimized geometry fits the experimental XAFS observations better, and is lower in energy by about 3 eV than the straightforwardly optimized geometry.

Finally, another important character of the POM cluster, the reverse process ($POM^{27-} \rightarrow POM^{3-}$), was also verified. On depriving 24 electrons via removal of the 27 Li atoms from the super-reduced state, it was confirmed that the molecular structure was reverted to the geometry of the 3- state in a straightforward geometry optimization.

[1] N. Kawasaki *et al. Angew. Chem.* 2011, *123*, 3533.
[2] H. Wang, H. Yoshikawa, K. Awaga *et al.*, in preparation.



Figure 1. Optimized Structures of POM²⁷⁻.

Electronic structure of transition metal systems from X-ray spectroscopy

Marcus Lundberg,^{1,2} Serena DeBeer,³ Uwe Bergmann,⁴ Samuel Wilson,² Britt Hedman,⁴ Keith O. Hodgson,^{2,4} Edward I. Solomon^{2,4}

¹Department of Physical and Analytical Chemistry, Uppsala University, Sweden ²Department of Chemistry, Stanford University, USA ³Department of Chemistry and Chemical Biology, Cornell University, USA ⁴SLAC National Accelerator Laboratory, USA

X-ray spectroscopy is a powerful probe of the electronic and geometric structure of transition metal enzymes and catalysts. A shortcoming of most methods is that the short lifetime of the core hole leads to a broadening that is larger than the energy difference between the electronic states of interest. This limitation can be overcome by scattering techniques, i.e., resonant inelastic X-ray scattering. In these experiments the energy transfer between the X-ray photon and the sample replaces the absorption energy in X-ray absorption spectroscopy (XAS) as a probe of the different energy levels. The improved energy resolution is due to the fact that the experiment does not directly observe a state with a deep core hole. We have experimentally studied scattering of hard X-rays, corresponding to a $2p \rightarrow 3d$ excitation (metal L-edge), to investigate metal-ligand bonding in iron model complexes and enzymes. As a first stage, we have interpreted the spectra using a parameterized valence bond configuration interaction (VBCI) model based on atomic multiplets, and show how the spectral information can be used to probe chemical bonding.



Figure 1. a) 1s2p RIXS plane of ferrocyanide. b) Experimental L-edge XAS spectrum compared to "L-edge-like" RIXS cut. c) VBCI multiplet simulations of L-edge and RIXS cut.

A theoretical study on proton conduction in nitrogen-doped SrTiO₃ perovskite

Taku Onishi,^{1,2} Trygve Helgaker³

¹Department of Chemistry for Materials, Graduate School of Enginering, Mie University, Japan ²The Centre of Ultimate Technology on Nano-Electronics, Mie University, Japan ³The Centre for Theoretical and Computational Chemistry (CTCC), Department of Chemistry, University of Oslo, Norway

I. Introduction

Proton-conductive materials have recently attracted much interest, driven by the search for efficient protonic electrolytes in solid oxide fuel cells (SOFCs). As is well known, $SrTiO_3$ perovskite of cubic structure shows proton conductivity at high temperatures. To enhance proton conductivity, Fe and Al doping at titanium site has been explored. In particular, very recently, Norby *et al.* investigated nitrogen doping in the proton conductive ZrO_2 . In this study, hybrid-DFT calculations have been performed to examine nitrogen doping at the oxygen site, as an alternative to Al and Fe doping at titanium site.

II. Result and discussion

Figure 1 shows the calculated potential energy curve in the Sr₂Ti₄O₃NH model, with local minima around oxygen and nitrogen, lowest around nitrogen. The activation energy from oxygen to nitrogen is 0.35eV, while the reverse barrier is 1.21eV, similar to the undoped barrier (1.16eV). Much hydrogen can consequently exist as part of the NH²⁻ thereby enhancing ion. proton conductivity by nitrogen doping.



Figure 1 The calculated potential energy curve in the Sr₂Ti₄O₃NH model

[1]T. Onishi, T. Helgaker, Int. J. Quant. Chem., in press.[2]J. M. Polfus, T. Norby, R. Haugsrud, Dalton Transactions 40, 132, 2011.

Application of the density matrix theory to the control of electronic ring current coupled to molecular vibrations in chiral molecule

<u>Hirobumi Mineo^{1,*},</u> M. Kanno², H. Kono², Y. Teranishi³, M. Yamaki⁴, S.D. Chao¹, S.H. Lin^{4,5} and Y. Fujimura^{2,5}

¹ Institute of Applied Mechanics, National Taiwan University, Taipei 106, Taiwan

² Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

 ³ Department of Physics, National Chiao Tung University, Hsinchu 300, Taiwan
 ⁴ Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan
 ⁵ Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan

In recent years quantum control of moelcular and nano or mesoscopic systems has been the subject of wide interest [1-5] for realization of the construction and design of quantum device applications in material science. Laser control of molecular ring systems has attracted a special attentions [6-8].

In this work we demonstrate how the linearly polarized laser pulse induces the electronic ring currents in a chiral molecule by the use of the density matrix method. The direction of the electronic ring currents are controlled by the polarization of the laser pulse through pumping to the quasi-degenerate two excited states. In the present study we consider the bi-phenol molecule which consists of the two phenols connected by a single chemical bond, and both phenols form a distorted angle.

[1] M. Nest, F. Remacle, and R.D. Levine, New J. Phys. 10, 025019 (2008).

[2] K. P. Singh et al., Phys. Rev. Lett. 104, 023001 (2010).

[3] A. Bandruk, S. Chelkowski, and H.S. Nguyen, Int. J. Quantum Chem. 100, 834 (2004).

[4] P. Krause, T. Klamroth, and P. Saalfrank, J. Chem. Phys. 123, 074105 (2005).

[5] T. Ihn et al, Europhysics News 36, 78 (2005).

[6] I. Barth, J. Manz, Y. Shigeta, and K. Yagi, J. Am. Chem. Soc. 128, 7043 (2006).

[7] I. Barth and J. Manz, Angew. Chem. Int. Ed., 45, 2962 (2006).

[8] M. Kanno, H. Kono, Y. Fujimura, and S.H. Lin, Phys. Rev. Lett. 104, 108302 (2010).

^{*} E-mail: mineo@gate.sinica.edu.tw
Inverse heavy-atom effect in conjugated carbenes, silylenes, aldehydes and ketones

<u>Mojmír Kývala</u>, Jakub Chalupský Institute of Organic Chemistry and Biochemistry, Czech Republic

I. Introduction

It is well known that the presence of an atom of high atomic number (Z), which is either part of, or external to, a molecule can significantly enhance the probability of spin-forbidden transitions between electronic states of the molecule. As these transitions, e.g. phosphorescence or intersystem crossing, involve electronic states of different spin multiplicities, the enhancement, for which the name "heavy-atom effect" came into use, may easily be attributed to the increase in spin-orbit coupling (SOC) between the states [1].

However, in a few cases an opposite, so-called *inverse* heavy-atom effect, was observed or calculated. It was rationalized in terms of a decomposition of the Cartesian vector of SOC between two nonrelativistic electronic states of a molecule into a sum of contributions of atoms or pairs of localized orbitals. While the length of a contribution is supposed to be always normal (complying with the empirical Z^2 rule), its direction and orientation may be essentially arbitrary.

II. Results

We adopted the suggested explication and incorporated it in the model of 2 electrons in the 2 nearly nonbonding molecular orbitals of a biradical, as well as to the model of 4 electrons in the 3 frontier molecular orbitals (π , n and π^*) of the carbonyl group. Combining apparent physical arguments with our computational experience, we devised a set of simple orbital-based *rules* with the aid of which the sense (positive or negative) and to a limited extent also the size of the heavy-atom effect on SOC between the 2 lowest closed-shell singlets S₀, S₂ and the lowest triplet T₁ of planar conjugated carbenes and silylenes as well as between the 3 lowest singlets S₀, ¹(n, π^*), ¹(π , π^*) and the 2 lowest triplets ³(n, π^*), ³(π , π^*) of planar conjugated aldehydes and ketones (or N-heterocycles) can smoothly be predicted.

The reliability of the predictions is verified through quasirelativistic *ab initio* calculations of the vectors of SOC between S_0 (S_2) and T_1 in many carbenes and silvlenes, and among S_0 , ${}^1(n, \pi^*)$, ${}^1(\pi, \pi^*)$, ${}^3(n, \pi^*)$ and ${}^3(\pi, \pi^*)$ in many aldehydes and ketones (and several pyridines), using the full DKH1 spin–orbit Hamiltonian and state specific DKH2 CASSCF or MRCIS wave functions. For a few selected molecules (preferably those which should exhibit strong inverse heavy-atom effect) observable properties like zero-field splitting, integrated intensity of singlet–triplet absorption or phosphorescence radiative lifetime are also calculated using double-group (spin–orbit and spin–spin) MRCIS or quasidegenerate perturbation theory.

[1] A. D. McNaught, A. Wilkinson, eds., IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"), Blackwell Scientific Publications, Oxford, 1997

3PP-37

Analysis of the effect of intermolecular interactions on dielectric properties in hydrogen-bonded material 5-bromo-9-hydroxyphenalenone

Hiroki Otaki,1 Koji Ando1

¹Department of Chemistry, Graduate School of Science, Kyoto University, Japan

It is well known that many of the hydrogen-bonded materials undergo phase transitions associated with proton (deuteron) ordering. 5-Bromo-9-hydroxyphenalenone (BrH-PLN), which belongs to the zero-dimensional hydrogen-bonded system, exhibits paraelectric (PE) – antiferroelectric (AFE) phase transition in the deuterated compound [1]. However, a preliminary calculation of an isolated monomer has shown that the magnitude of molecular electronic dipole moment is too small to reproduce the experimental transition temperature (~ 40 K).

We here focus on the effect of intermolecular interactions on the dielectric properties of BrHPLN. By means of density functional theory (DFT) with plane-wave basis sets and the Fragment Molecular Orbital (FMO) methods, we have found that $C-H \cdots O$ type intermolecular hydrogen bonding and π - π stacking interactions affect the molecular dipole moment significantly. We also propose a Monte Carlo method with the correction of the induced dipole moment, reflecting the results of the FMO calculation at all possible nearest neighbor trimer configurations. We shall show that the Monte Carlo simulation with the correction results in better agreement with the experiments [2].

Acknowledgement

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Figure 1: Schematic (a) molecular and (b) crystal structure of BrHPLN.



Figure 2: Dielectric constant calculated by Monte Carlo simulation with/without the correction of the dipole moment.

[1] T. Mochida, A. Izuoka, T. Sugawara, Y. Moritomo and Y. Tokura, J. Chem. Phys., 101, 7971 (1994).
[2] H. O. Lin, and K. A. L. Phys. Chem. Chem. 12, 10710 (2011).

[2] H. Otaki and K. Ando, Phys. Chem. Chem. Phys., 13, 10719 (2011).

Electronic states of GdF assigned in jj-coupling scheme

Shigeyoshi Yamamoto,¹ Hiroshi Tatewaki²

¹School of International Liberal Studies, Chukyo University, 101-2 Yagoto-Honmachi, Showa-ku, Nagoya 466-8666, Japan ²Graduate School of Natural Sciences, Nagoya City University, Aichi 467-8501, Japan

I. Introduction

The electronic states of the GdF molecule [1] have been investigated with the 4-component relativistic configuration interaction (CI) method. The wave functions are represented in the *jj*-coupling scheme. However, *LS*-coupling scheme is popular and the notation of electronic state is standardized. For example, the GdF ground state is written as $^{7}\Sigma_{7/2}^{-}$. The configuration of the Gd part in GdF is written as $(4f)^{7}$ (6s)². However for molecules containing heavy elements such as lanthanides, *jj*-coupling scheme is dominant. Besides the *jj*-coupling scheme is usually adopted in the 4-component relativistic theory. We have assigned all the electronic states of GdF below 3.0 eV. For this assignment, we have proposed a terminology [2] for families or states based on the *jj*-coupling scheme.

II. Excited states assigned with *f*-shell Omega decomposition method

The wave functions are classified by the projection (Ω) of the total angular momentum onto the molecular axis. A series of states which start from the highest Ω and decrease one by one until 0 or 1/2 can be found. We called it *family*. We call the highest Ω state *root*. The family members can be considered to be derived from the root.

There are c.a. 100 states below 3.0 eV for GdF. These states have been classified into families by the excitation energy and the *f*-shell Omega components weight which is defined as follows.

weight(
$$\Omega_f$$
) = $\sum_{i \in \Omega_f} C_i^2$ (1)

Here, Ω_f denotes the angular momentum generated from the seven electrons of the (4*f*) molecular spinors, and C_i is a CI coefficient of the *i*-th Slater determinant. The multiconfigurational CI wave function can be represented compactly with the *f*-shell Omega weights.

[1] S. Yamamoto and H. Tatewaki, J. Chem. Phys. 129, 244505 (2008).
[2] S. Yamamoto and H. Tatewaki, J. Chem. Phys. 134, 164310 (2011).

NMR shieldings of an excimer

<u>Michiko Atsumi¹</u>, Daniel Roca-Sanjuán¹, Hans Jørgen Aagaard Jensen², Trygve Helgaker³, and Roland Lindh¹

¹ Department of Physical and Analytical Chemistry, Quantum Chemistry, Uppsala University, Sweden

 ² Department of Physics and Chemistry, University of Southern Denmark, Denmark
 ³ Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, Norway

Multiconfigurational self-consistent field (MCSCF) methods have been used to study the nuclear shieldings at the lowest excited singlet state of nucleobase excimers (excited dimers). The optimized structure of excimers were reported by Roca-Sanjuán et al.[1] by complete active space self-consistent field (CASSCF)/complete active space plus second-order perturbation theory (CASPT2) level of theory.

Since there are no experimental results of nuclear constants in excited state excimer, the primary calculation has been carried out for the nuclear shieldings of uracil at ground state. Using the same method, excimer results for the ground state and two lowest excited states were also obtained. The state-average CASSCF calculations and geometry optimizations were done by Molcas 7. A preliminary version of Dalton 2011 was employed for state-specific CASSCF and nuclear shielding calculations. The atomic natural orbital (ANO) type basis set has been used for all atoms.

[1] D. Roca-Sanjuán, G. Olaso-González, I. González-Ramírez, L. Serrano-Andrés and M. Merchán *J. Am. Chem. Soc.*, **2008**, *130* (32), 10768

Zero-field splitting tensors of nitroxide-based biradicals: A theoretical study

Kenji Sugisaki,¹ Kazuo Tovota,¹ Kazunobu Sato,¹ Daisuke Shiomi,¹ Shuichi Suzuki,¹ Keiji Okada,¹ Masahiro Kitagawa,² Takeji Takui¹

¹Department of Chemistry, Graduate School of Science, Osaka City University, Japan ²Department of System Innovation, Graduate School of Engineering Science, Osaka University, Japan

Nitroxide radicals have been widely investigated both experimentally and theoretically owing to their rich variety of applications in chemistry, biochemistry, and materials science. In nitroxide radicals the unpaired electron is almost localized on the oxygen and nitrogen atoms, giving rise to strong spin-orbit couplings. Theoretical investigations of the zero-field splitting (ZFS) tensors (D tensors) of nitroxide-based biradicals are important because the spin-orbit coupling appears as the second-order contribution to the D tensor in perturbation theory starting from non-relativistic Schrödinger equation. In this work, the spin-orbit and spin-spin terms of the D tensors $(\mathbf{D}^{SO} \text{ and } \mathbf{D}^{SS} \text{ tensors, respectively})$ of nitroxide-based biradicals 1–3 (Figure 1) are investigated by the state-of-the-art quantum chemical calculations.

The Molecular geometries have been optimized at the UBP86/6-31G* level for the lowest triplet state, and the \mathbf{D}^{SO} tensors calculated by a hybrid CASSCF/MRMP2 approach [1–3],



which has recently proposed by us. The \mathbf{D}^{SS} tensors have been computed by using McWeeny–Mizuno's equation with the ROBP86/cc-pVDZ spin density [2–3].

The experimental and theoretical ZFS parameters $D (D = D_{ZZ} - (D_{XX} + D_{YY})/2)$ are summarized in Table 1. For 1 and 2, our calculation can reproduce the experimental D value within 10% of error. For 3, the calculations significantly overestimate the absolute value of D. Since the spin-orbit contribution to D in 3 is ca. 14%, most of errors in the

calculations are possibly	Table 1. Theoretical and experimental D values.				
from the \mathbf{D}^{SS} term. The	Molecule	$D^{\rm SS}/{\rm cm}^{-1}$	$D^{\rm SO}/{\rm cm}^{-1}$	$D^{\rm SS+SO}/\rm cm^{-1}$	$ D(\text{Exptl.}) /\text{cm}^{-1}$
dependence pf the dihedral	1	-0.0337	+0.0063	-0.0376	0.0394
angle on the D tensors will	2	-0.0590	+0.0151	-0.0668	0.0639
also be discussed.	3	-0.0342	-0.0035	+0.0353	0.0250

[1] Sugisaki, K. et al. Chem. Phys. Lett. 2009, 477, 369–373.

[2] Sugisaki, K. et al. ChemPhysChem 2010, 11, 3146-3151.

[3] Sugisaki, K. et al. Phys. Chem. Chem. Phys. 2011, 13, 6970-6980.

Density functional theory calculations of iodine cluster anions: structures, chemical bonding nature, and vibrational spectra

<u>Miho Otsuka¹</u>, Hirotoshi Mori², Hitomi Kikuchi¹, Keiko Takano¹ ¹Graduate School of Humanities and Sciences, Ochanomizu University, Japan ²Division of Advanced Sciences, Ocha-dai Academic Production, Ochanomizu University, Japan

I. Introduction

The tendency of iodines to form stable polyiodide anions is well known. A scientifically interesting feature is their bond property. The idea of a three-center four-electron (3c-4e) bond to explain the linear electron-rich three-center bond feature in I₃⁻ was confirmed with density functional theory (DFT) calculations [1, 2]. The object of the present study is to elucidate the chemical properties of larger iodine clusters, I_n^- (n = 3, 5, 7), in detail.

II. Method

All available equilibrium structures were surveyed using the global reaction route mapping (GRRM) technique [3] with UB3LYP/LANL2DZ level of theory. Then, the surveyed structures were refined using MCPtzp+ basis, a larger basis set with a model core potential [4], to obtain enough accuracy for discussion on chemical bonding nature. Natural bond orbital (NBO) analysis was applied to analyze the chemical bonds [5] and Raman spectra were also predicted for comparison with experiments.

III. Results and discussion [6]

It was found that all the stable minima of I_n^- have a single or a branched chain structure (Figure 1). There were no energy minima for cyclic structures. NBO analysis suggested that I_n^- consist of I_2 and linear I_3^- units containing 3c-4e bonds. DFT calculations showed that I_n^- (n = 5, 7) have two types of Raman scattering, in regions 140-190 cm⁻¹ and 110-120 cm⁻¹, which are assigned to the vibrations of I_2 and I_3^- units, respectively. A comparison of theoretically predicted Raman spectra with experimental results [7] revealed the existence of I_n^- (n = 5, 7) isomers with 3c-4e bonds.

 G. A. Landrum et al. J. Chem. Soc., Dalton Trans., 1997, 3605. [2] M. L. Munzarova et al. J. Am. Chem. Soc., Sect. A 1972, A28, 574. [3] S. Maeda et al. Chem. Phys. Lett. 2003, 381, 177. [4] E. Miyoshi et al. J. Chem. Phys., 2005, 122, 074104. [5] A. E. Reed et al. Chem. Rev. 1988, 88, 899. [6] M. Otsuka et al. Comput. Theor. Chem., submitted. [7] P. H. Svensson et al. Eur. J. Inorg. Chem., 2000, 1275.



Figure 1 Structure of stable isomers of I_n^- (n = 3, 5, 7)

A computational method for infrared reflection absorption spectroscopy

<u>Takeshi Iwasa</u>,^{1,2} Kazuki Horiuchi,² Masaya Shikishima,² Yuji Noguchi,² Shuhei Nagaoka,² and Atsushi Nakajima^{1,2}

¹ JST, ERATO, Nakajima Designer Nanocluster Assembly Project, 3-2-1 Sakado, Takatsu-ku, Kawasaki, 213-0012, Japan

² Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Infrared reflection absorption spectroscopy (IRAS) has been widely used to investigate geometric structures and orientations of molecules at a surface, where the selection rule is different from that in gas phase. The electric field at a surface mainly lies along the surface normal due to the interference between the induced and reflected light, and thus IRAS peak intensities depend on the molecular orientation. We present a computational method for IRAS spectrum and a numerical demonstration using Ti(aniline) deposited onto an alkanethiol self-assembled monolayer (CH-SAM) surface.

Geometric structures of Ti(aniline)- C_3H_8 from singlet to quintet states are optimized at the B3LYP/def2-TZVP level of theory. The molecular orientation is determined by fitting C_3H_8 to CH-SAM whose orientation is taken to be 15° from the surface normal. k-th IRAS peak for these configurations is computed using the next formula.

$$I_k \sim \left| \left(\frac{\partial \vec{\mu}}{\partial Q_k} \right) \cdot \vec{n} \right|^2 = \left| \left(\sum_{i=1}^{3N} c_{k,i} \frac{\partial \vec{\mu}}{\partial b_i} \right) \cdot \vec{n} \right|^2 \tag{1}$$

where $\vec{\mu}$ is the dipole moment, Q_k is the k-th normal coordinate, \vec{n} is the unit vector of the surface normal, $c_{k,i}$ is the transformation matrix from the atomic displacements b_i to Q_k . The numerical derivatives $\partial \vec{\mu} / \partial b_i$ and vibrational frequencies are obtained using a locally modified version of SNF 4.0¹. We adopt $|b_i| = 0.01$ a.u. and the scaling factor of 0.977.

As an example, we show (a)IR and (b)IRAS spectra for the triplet state in Fig. 1. The peak intensity at 1500 and 1405 cm⁻¹, for instance, decreases and increases, respectively, as a result of the orientation. The projection of $\partial \vec{\mu} / \partial Q_k$ to the surface normal enables us to directly compare the IRAS spectrum with experimental results. We will present the IR and IRAS spectra for the other spin states and comparisons with the experiment to determine the geometric and electronic structures of the Ti(aniline) deposited onto the CH-SAM.





Figure 1: IR and IRAS spectra for the triplet state.

Photoinduced charge-transfer and normal-cleavage reaction of Mg⁺-Benzene complex

Kota Daigoku¹

¹Division of Chemistry, Center for Natural Sciences, College of Liberal Arts and Sciences, Kitasato University, Japan

The magnesium-benzene complex in gas phase provides simple model systems for the cation- π interaction. For the Mg⁺-benzene complex, the experimental result of the photoinduced dissociation reaction shows that the dominant product is not charge-transfer products, Mg⁰ and benzene⁺, but normal-cleavage reaction products, Mg⁺ and benzene¹. However this selective reaction mechanism is not well understood. We investigated the potential energy curves of Mg⁺-benzene complex in the ground and low-lying excited states at the RASPT2 methods.

The starting points of the dissociation reaction are the 1 ${}^{2}E_{1}(3p_{x,y} \in 3s)$ and 2 ${}^{2}A_{1}(3p_{z} \in 3s)$ states according to the experiment and theoretical calculations. The energy curve of the 1 ${}^{2}E_{1}$ state shows the vibrational predissociation and conical intersection in the Frank-Condon region. The former is correlated to the charge transfer (3s $\in \pi$) state and the later is crossing with the 1 ${}^{2}E_{2}$ ($\pi^{*} \in 3s$) state. The transition through the conical intersection will occur prior to the predissociation reaction because of the 1 ${}^{2}E_{2}$ state via the conical intersection will occur prior to the 1 ${}^{2}E_{1}$ state, the transition to the 1 ${}^{2}E_{2}$ state. After the nonradiative transition to the 1 ${}^{2}E_{2}$ state via the conical intersection will occur prior to the 1 ${}^{2}E_{2}$ state via these conical intersections, the curve crossing in the short Mg-benzene distance region will make the ground-state channel open.



Figure 1. Potential energy curves of Mg⁺-benzene complex along the Mg-benzene distance calculated at RASPT2 level.

[1] X. Yang, K. Gao, H. Liu, S. Yang, J. Chem. Phys. 112, 10236 (2000).

Theoretical study on the molecular structures of X-, α- and β-types of lithium phthalocyanine dimer

<u>Michinori Sumimoto</u>,¹ Yukio Kawashima,² Daisuke Yokogawa,³ Kenji Hori,¹ Hitoshi Fujimoto⁴

 ¹Graduate School of Science and Engineering, Yamaguchi University, Japan
 ²Department of Research Superstar Program, Organization for the Promotion of Advanced Research, Kyushu University, Japan
 ³Institute for Protein Research, Osaka University, Japan
 ⁴Department of Chemistry, Faculty of Science, Kumamoto University, Japan

It is very important to select a suitable functional for the calculation target using the density functional theory (DFT) method. In particular, special care should be taken for weakly bound systems with non-covalent interactions, which require an accurate assessment of the long-range interaction. Marom and co-workers [1] recently suggested an approach to treat the long-range interaction in DFT calculations for weakly bound systems, and applied it to weakly-bound metal phthalocyanine (MPc) dimers with the closed-shell electron system.

We reported the results of theoretical calculations on the potential energy curves (PECs), geometry optimizations, and electronic structures for three dimers of LiPc and MgPc using three types of functional systems, PBE1PBE, B3LYP, and M06 [2]. We discussed how the dispersive interaction affects the geometric and electronic structures of the LiPc and MgPc dimers. The calculated results provide a clear understanding of the computational method for both open- and closed-shell MPc dimers: the PBE1PBE and B3LYP functional systems cannot evaluate a weak dispersion interaction appropriately. In contrast, the M06 functional can estimate a weak dispersion interaction well in both the

open- and closed-shell MPc dimers. However, the results should be examined with caution against overestimation of the relative stabilities. Basis set superposition error (BSSE) corrections play an important role for the quantitative analysis, but the calculation results without BSSE corrections may be enough for the qualitative discussion of the relative stability.

N. Marom, A. Tkatchenko, M. Scheffler, L. Kronik, J. Chem. Theory Comput. 2010, 6, 81.
 M. Sumimoto, Y. Kawashima, D. Yokogawa, K. Hori, H. Fujimoto, J. Comput. Chem. 2011, in press.



Figure 1. PECs for the α -, β -, and X-type LiPc dimers, which were obtained by single point calculations with the PBE1PBE, B3LYP, and M06 functional systems while varying the Li-Li distance. The red and black colors show the PECs with and without BSSE corrections, respectively.

Ab initio Studies of Aromatic Excimers Using Multiconfiguration **Quasi-Degenerate Perturbation Theory**

Soichi Shirai,^{1,2} Suehiro Iwata,³ Takao Tani,^{1,2} Shinji Inagaki^{1,2} ¹Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan ²JST-CREST, Kawaguchi, Saitama 332-0012, Japan ³Tovota Physical and Chemical Research Institute, Nagakute, Aichi 480-1192, Japan

I. Introduction

Aromatic excimers have been both experimentally and theoretically investigated in the field of photophysics and photochemistry because of their unique properties. However, there have been limited ab initio studies even today. In this study, we theoretically investigate the electronic states of excimers of benzene, naphthalene, anthracene, pyrene and perylene (Figure 1) using the multiconfiguration quasi-degenerate perturbation theory (MCQDPT) for systematical understandings [1].

II. Computational Details

The reference configuration space for MCQDPT was carefully designed for an appropriate description of the target electronic states with a tractable computational cost. Assuming eclipsed parallel arrangements of the aromatic dimers, the potential energy curves for the ground and excimer states (the lowest La-derived excited states) were computed as a function of the intermolecular distance, r(R-R) from 2.7 to 10.0 Å.

III. Results and Discussion

The calculated monomer absorption energies and excimer fluorescence energies are in good agreement with the experimental values (Table 1). Detailed analysis of the wave function confirms the mixing of the exciton resonance (ER) and the charge resonance (CR) states, which are responsible for the attractive nature of two monomers in the excited state. In the excimers, ER and CR states are found to contribute almost equally to the wave function. Therefore, the order of binding energy, $D_{\rm e}$ is consistent with the orders of monomer transition dipole moment and "Ionization Potential - Electron Affinity". These results suggest that the electronic states of these aromatic excimers are appropriately described and systematically understood by using MCQDPT.

	and references therein) for the selected spectroscopic parameters for the lowest L_a -derived excited state.						
	Dimor	r _e	D _e	Flu. (eV)		Abs. (eV)	
	Diffe	(Å)	(eV)	Calc.	Exptl.	Calc.	Exptl.
	(Benzene) ₂	3.00	0.44	3.96	3.94	4.82	4.79
Figure 1. Aromatic excimers	$(Naphthalene)_2$	3.05	1.00	3.17	3.13	4.41	4.45
	(Anthracene) ₂	3.15	1.02	2.28	2.30	3.23	3.27
treated in this study.	(Pyrene) ₂	3.16	1.49	2.42	2.59	3.66	3.70
	$(Perylene)_2$	3.21	1.65	1.69	1.94	2.82	2.86

Table 1. Calculated and experimental values (see ref. [1]

[1] Shirai, S.; Iwata, S.; Tani, T.; Inagaki, S. J. Phys. Chem. A. in press (DOI: 10.1021/jp201130k).

Applying residual minimization method to GIAO-CPHF equation convergence for calculation of nuclear magnetic shielding tensors

<u>Toshihiko Abe</u>,¹ Toshiyuki Hirano,¹ Hirotaka Tanimura,¹ Fumitoshi Sato¹ ¹Institute of Industrial Science, The University of Tokyo, Japan

I. Introduction

A new method to robustly solve the coupled perturbed Hartree-Fock (CPHF) equation for calculation of nuclear magnetic shielding tensors is proposed. The DIIS method is widely adopted, where it solves the equation projected onto the iterative subspace[1]. On the other hand, the proposed method seeks the solution in the iterative subspace by the residual minimization method[2] to minimize the residual defined in the whole orbital space. Compared to general residual minimization methods (ex.[3]), the proposed one showed the good convergence.

II. Method

The GIAO-based CPHF equation is represented by projection onto the occupied and the vacant orbitals as follows[4].

$$\mathbf{P}^{(1,0)} = -\frac{1}{2} \mathbf{P}^{(0)} \mathbf{S}^{(1,0)} \mathbf{P}^{(0)} + 2 \sum_{K}^{occ} \sum_{L}^{vac} \frac{\mathbf{c}_{K}^{+} (\mathbf{F}^{(1,0)} - \epsilon_{K} \mathbf{S}^{(1,0)}) \mathbf{c}_{L}}{\epsilon_{K} - \epsilon_{L}} \times (\mathbf{c}_{K} \mathbf{c}_{L}^{+} - \mathbf{c}_{L} \mathbf{c}_{K}^{+}), \qquad (1)$$

where \mathbf{c}_{K} and $\mathbf{P}^{(0)}$ are the LCAO coefficients and the density matrix that satisfy the HF equation, respectively. $\mathbf{P}^{(1,0)}$ and $\mathbf{F}^{(1,0)}$ are the first order perturbed density and Fock matrix with respect to the external magnetic field, respectively. The $\mathbf{P}^{(1,0)}$ is given by solving the CPHF equation. Since $\mathbf{F}^{(1,0)}$ depends on $\mathbf{P}^{(1,0)}$, by expanding all the coefficients the CPHF appears as $\mathbf{H}\mathbf{u} = \mathbf{b}$, where \mathbf{u} is the vector representation of $\mathbf{P}^{(1,0)}$. **H** is a supermatrix and usually solved by iterative calculation.

The proposed method uses the linear combination of vectors in the iterative subspace $\mathbf{u} = \sum_{l}^{L} k_l \mathbf{u}_l$ and minimizes the 2-norm of the residual $\|\mathbf{R}\|^2 = \|\mathbf{b} - \mathbf{H}\mathbf{u}\|^2 = \sum_{l,m=1}^{L} k_l k_m (\mathbf{H}\mathbf{u}_l) \cdot (\mathbf{H}\mathbf{u}_m) - 2 \sum_{l=1}^{L} k_l (\mathbf{H}\mathbf{u}_l) \cdot \mathbf{b} + \|\mathbf{b}\|^2$; that is,

$$\frac{\partial \|\mathbf{R}\|^2}{\partial k_m} = \sum_{l=1}^L 2k_l (\mathbf{H}\mathbf{u}_m) \cdot (\mathbf{H}\mathbf{u}_l) - 2(\mathbf{H}\mathbf{u}_m) \cdot \mathbf{b} = 0.$$
(2)

Therefore we solve $\sum_{l=1}^{L} k_l(\mathbf{H}\mathbf{u}_m) \cdot (\mathbf{H}\mathbf{u}_l) = (\mathbf{H}\mathbf{u}_m) \cdot \mathbf{b}$, which is an *L*th-order linear equation.

III. Results

In the figure, the computational results of a nitrogen molecule were shown as the norm of the difference of $\mathbf{P}^{(1,0)}$ to the number of iterations. The simple damping and method 3 showed good convergence. In principle, the residual is not increased by the method 3, so that the method 3 might prevent divergence when the simple damping cannot provide a stable derivative density matrix.



• Simple damping

- Simple residual minimization (Method 1)
- Residual minimization with adjusting the damping factor (Method 2)
- Method 2 + normalization (Method 3)
- 1] P. Pulay, Adv. Chem. Phys., 69, 241, 1987.
- A. Tamura, K. Kikuchi and T. Takahashi, J. Comp. Phys., 137, 247, 1997.
 Y. Saad and M.H. Schultz, SIAM J. Sci. Stat. Comput., 7, 856,
- [3] Y. Saad and M.H. Schultz, SIAM J. Sci. Stat. Comput., 7, 856, 1986.
 [4] M. A. Freiter, and P. Hillman and A. Arrawal, J. Chem. Phys.
- [4] M. A. Freitag, and B. Hillman and A. Agrawal, J. Chem. Phys., 120, 1197, 2004.

A theoretical study on the photodissociation of HNO $_3$ involving S $_2$, S $_1$ and S $_0$ states

Hongyan Xiao,¹ Satoshi Maeda,^{1,2} Keiji Morokuma^{1,3}

 ¹Fukui Institute for Fundamental Chemistry, Kyoto University, Japan
 ²The Hakubi Center, Kyoto University, Japan
 ³Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, United States

Nitric acid (HNO₃) molecule plays an important role in atmospheric chemistry. Depending on the irradiation wavelength, the photodissociation of nitric acid has rich photochemical decay channels. The common conclusion in experiments (J. Phys. Chem. 1993, 97, 9924; J. Chem. Phys. 1994, 100, 8040; Chin. J. Chem. Phys. 2009, 22, 191) is that at or near 248 nm the dissociation $OH(X^2\Pi) + NO_2(\tilde{A}^2B_2)$ on $2^1A''$ state (the second excited state, S_2) is dominant, while at larger wavelength the dissociation OH(X $^{2}\Pi$) + NO₂($\tilde{X}^{2}A_{1}$) on 1¹A" state (the first excited state, S₁) is the primary pathway. With an increase in photon energy, the minor $O(^{1}D)$ product was observed at 222 nm (J. Chem. Phys. 1992, 96, 5887). In this work, we investigated the photodissociation mechanism of HNO₃ based on CASPT2 calculations using a systemic reaction path search method. Our results indicated that upon photoexcitation with energy higher than 248 nm, elimination $OH(X^2\Pi) + NO_2(\tilde{A}^2B_2)$ on S₂ potential energy surface (PES) should be dominant, while at energy below this, fission $OH(X^2\Pi) + NO_2(\tilde{X}^2A_1)$ on S_1 PES is the primary pathway. In addition, the dissociation pathway to $O(^{1}D)$ on S₂ PES has been found. Our results in general agree with and provide theoretical basis for the experimental results.



Figure. Photodissociation HNO₃ from $S_2 \rightarrow S_0$ by 3S-CASPT2(12,8)/6-31+G*(kJ/mol)

Theoretical Study of Luminescent Vapochromic Complexes Including AuCu₂(NHC)₂ Core

<u>Shinya Tsukamoto</u>, Shigeyoshi Sakaki^{*} Fukui Institute for Fundamental Chemistry, Kyoto University, Japan

I. Introduction: Metallophilic interaction by d^{10} - d^{10} metal contact exhibits interesting luminescent behavior in many cases. Though a lot of compounds have been synthesized to date, a complex including AuCu₂ core has been limited. Recently, new vapochromic compounds which contain a AuCu₂ core were synthesized. They exhibit different luminescent color when they are exposed to vapor (Scheme1). In this work, we theoretically investigated their ground and excited states, coordinations of MeCN and MeOH, and elucidated the reason why their emission spectra depend on gas molecule. The bonding nature between Au(I) and Cu(I) will be also discussed.



II. Method: The geometry optimization was carried out by DFT method with B3PW91 functional. For Au and Cu atoms, triple-zeta basis sets of Stuttgart group with 2f polarization functions were employed. For other atoms, 6-31G(d) basis sets were used, where one diffuse function was added to O atom. The emission peak was evaluated as the S₀-T₁ energy difference with the T₁ geometry.

III. Results and Discussion: The Au-Cu distances of 1 and 2 are 4.742 and 3.174 Å, respectively, in the S₀ ground state, suggesting that gas molecule coordinate with Cu center influences the Au-Cu contact. Their optimized structures of the T₁ state are not symmetrical; the Au-Cu distances are 4.983, 4.588 Å in 1 and 2.634, 2.609 Å in 2. The T₁ state of 1 was assigned to Cu d→Py π*. Its calculated emission energy (2.93 eV) agrees with the experimental one (2.68 eV). On the other hand, the T₁ state of 2 was assigned to Au d→Au-Cu bonding MO (Fig 1), indicating that the Au-Cu bond is formed in the T₁ state. This is consistent with the shorter Au-Cu



distance in the T_1 state. The calculated emission energy (2.27 eV) agrees well with experimental value (2.47 eV). Detailed discussion including **3** will be presented in the poster session.

Fig.1 SOMO of $\mathbf{2}$ in the T₁ state

Reference: [1] Strasser, C. E. et al. J.Am. Chem. Soc 132, 10009, 2010.

Intersystem crossing in spin-crossover complexes

<u>Gergely Juhász</u>, Yoshihito Shiota, Kazunari Yoshizawa Institute for Materials Chemistry and Engineering and International Research Center for Molecular Systems, Kyushu University, Japan

I. Introduction

Coordination complexes featuring bistability of spin- and electronic states are potential building blocks for switchable molecular materials. The geometry distortion of the molecule associated with such spin-transition, however, can be extremely complex and raise a major challenge for the theoretical description of the switching process. We demonstrate a new approach, searching the Minimum Energy Crossing Points (MECPs) on the low-energy energy surfaces in spin-crossover complexes.

II. Method

The calculation of equilibrium geometries, potential energy surfaces (PESs) in the lowest energy spin-states, and the MECPS between them has been performed using Gaussian 09, Gammes and ORCA programs at B3LYP* / 6-311+G(d,p) level of theory.

III. Results and discussion

For the initial tests, we chose well-characterized spin crossover systems: $[Fe(II)(2-pic)_3]^{2+}$, $[Fe(III)(acpa)_2]^+$, and $[Fe(III)(pap)_2]^+$. Due to the flexibility of the 2-pic ligand, the Fe(II) system is close to the ideal octahedral ligand environment, where the low-spin (S=0) to high-spin (S=2) transition is accompanied with an approximate Δr =0.21 Å bond Fe-N length change. This distortion can be described well along an approximately total-symmetric breathing mode, and the calculated MECP of the S=0 and 2 states can be well approximated along this normal mode. On the other hand, when the S=1 intermediates spin state shows a strong Jahn-Teller effect, therefore axial distortions are also important to describe the geometry.



The Fe(III) systems with {FeN₄O₂} chromophores suffer an asymmetric distortion during the spin transition, as the bond distance change for Fe-N bonds is in order of $\Delta r=0.18$ -0.25 Å, while for the Fe-O bonds, it is smaller than $\Delta r=0.4$ Å. Careful analysis of the equilibrium and MECP geometries was possible with the new approach, and the distortions of the coordination environment and the ligands were directly observed.

Theoretical study on two-photon absorption properties of two-dimensionally extended π -conjugated systems

Koji Ohta,¹ Satoru Yamada,¹ Kenji Kamada,¹ Aaron D. Slepkov,² Frank A. Hegmann,² Rik R. Tykwinski,³ Laura D. Shirtcliff,⁴ Michael M. Haley,⁴ Pawel Sałek,⁵ Faris Gel'mukhanov,⁵ Hans Ågren⁵

¹Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Japan

²Department of Physics, University of Alberta, Canada

³Institut für Organische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg,

Germany

⁴Department of Chemistry and Materials Science Institute, University of Oregon, USA ⁵Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, Sweden

Previously, we have measured two-photon spectra absorption (TPA) of а pair of two-dimensionally conjugated quadrupolar donor/acceptor (D/A)chromophores, **TPEB** [tetrakis(phenylethynyl)benzene] $(\mathbf{R}^1,$ R^2 , R^3 . R^4 =Donor(D) or Acceptor(A) in Figure 1) by the



femtosecond Z-scan method [1] and found that these Figure 1. Molecular compounds display large TPA cross sections. In this structure of TPEBs.

study, to clarify the mechanisms of the TPA process, the TPA properties have been theoretically investigated by the TDDFT methods [2]. All the excited state properties were calculated by the TDDFT/B3LYP method using the DALTON 2.0 program. The one-photon absorption (OPA) and TPA spectra were simulated by the methods reported previously [3]. In the experimental spectra of the noncentrosymmetric TPEBs $(R^1=R^3\neq R^2=R^4)$ and $R^1=R^2\neq R^3=R^4$, the shape of the OPA and TPA spectra differs considerably from each other, even though the TPA transitions should occur to the same excited states where the OPA transitions occur because of the noncentrosymmetry of these molecules. For example, the largest OPA band appears around 3.8-3.9 eV, but the corresponding TPA bands do not appear in the spectra. Calculations for the TPEBs reveal that this discrepancy results from the destructive interference between the different transition paths in TPA.

[1] A. D. Slepkov, F. A. Hegmann, R. R. Tykwinski, K. Kamada, K. Ohta, J. A. Marsden, E. L. Spitler, J. J. Miller, and M. M. Haley, *Opt. Lett.* **31**, 3315 (2006).

[2] K. Ohta, S. Yamada, K. Kamada, A. D. Slepkov, 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).

[3] K. Ohta and K. Kamada, *J. Chem. Phys.* **124**, 124303 (2006); K. Ohta, L. Antonov, S. Yamada, and K. Kamada, *J. Chem. Phys.* **126**, 084504 (2007).

Structures and Binding Properties of Noble Gas Compounds: NgBeO and NgBeOBH₃ (Ng = He, Ne, Ar)

<u>Hitomi Suto</u>,¹ Hirotoshi Mori,² Keiko Takano¹

¹Graduate School of Humanities and Sciences, Ochanomizu University, Japan ² Division of Advanced Sciences, Ochanomizu University, Japan

I. Introduction

After the first experimental observation of a novel neutral xenon compound, XePtF₆ [1], noble gas containing molecules had kept considerable chemical interests and had been extensively studied from both experimental and theoretical point of views. Among the studies, the existence of neutral He containing systems is still in question, since no such a system has been observed experimentally. Frenking *et al.* and Takayanagi *et al.* predicted the presence of the neutral light noble gas compounds, NgBeO (Ng = He, Ne, Ar), using the MP4 and CASPT2 levels of *ab initio* electronic structure calculations, respectively [2,3]. In this study, we tried to have a further chemical insight to predict the existence of the neutral noble gas compounds.

II. Computational details

The electronic structures of BeO, NgBeO and NgBeO-BH₃ (Ng = He, Ne, Ar) were studied by CCSD(T), CASPT2, CASPT3 and MRSDCI levels of theory, which are implemented in the MOLPRO program package. In the multi-reference calculations, 6 electrons were distributed in 7 active orbitals. Two types of basis sets, aug-cc-pVQZ and aug-cc-pCVQZ, were used. All core electrons were frozen for the aug-cc-pVQZ basis, meanwhile, Be(1s) core electrons were frozen and correlated with valence electrons for the aug-cc-pCVQZ basis.

	Tabl	le 1 Be-O bond l	ength with the CA	SPT3 level of the	ory [Å]
Table I lists the		aug-cc-pVQZ ^{a)}	aug-cc-pCVQZ ^{a)}	aug-cc-pCVQZ ^{b)}	exp.
obtained by CASPT3	BeO	1.3356	1.3353	1.3306	1.3308
levels of theory.	He-BeO	1.3302	1.3300	1.3256	
Compared with the	Ne-BeO	1.3315	1.3312	1.3268	
experimental results,	Ar-BeO	1.3335	1.3332	1.3289	
.1 1 1 1 .					

III. Results and Discussion

the calculation taking ______a) with frozen core b) without frozen core into account the core-valence correlation effect from Be(1s) showed extremely high accuracy for BeO. This result indicates that not only Be(2s) but also Be(1s) plays an important role for the BeO bonding, presumably due to the bond polarity ascribed to electronegativity of O. As for the NgBeO (Ng = He, Ne, Ar), the role of Be(1s) would be more important because noble gases may affect the Be(1s) as well as the Be(2s). Essential factors for the stabilization by binding of noble gases will be discussed in details with the results of NgBeOBH₃.

[1] Bartlett, N. Proc. Chem. Soc., 218(1962)

[2] Frenking, G.; Koch, W.; Jurgen, G.; Cremer, D. J. Am. Chem. Soc. 110, 8007(1988)

[3] Takayanagi, T.; Motegi, H.; Taketsugu, Y.; Taketsugu, T. Chem. Phys. Lett. 454, 1(2008)

Theoretical Study of Inverted Sandwich Type Dinuclear Complexes of ethylene and dinitrogen molecules

Masayuki Nakagaki,[¶] Yusaku I. Kurokawa,[§] and Shigeyoshi Sakaki[¶] [¶]*Fukui Institute for Fundamental Chemistry, Kyoto University, Japan* [§]*Ouantum Chemistry Research Institute, Japan*

I. Introduction

Inverted sandwich type complexes (ISTCs) of dinuclear three-coordinate chromium(I) with DDP ligand, (DDPH = $2-{(2,6-diisopropylphenyl)amino}pent-2-ene)$, were synthesized by Tsai et al.¹ and Monillas et al.² Interestingly, the effective magnetic moment significantly depends on the metal and sandwiched organic molecule. In this study, we investigated the electronic structure of the ISTCs of ethylene and dinitrogen molecules.

II. Computational Details

We replaced the DDP ligands with AIP (AIPH = 1-amino-3-imino- prop-1-ene; SCHEME 1) for brevity. Geometry optimization was carried out for each spin states by the DFT method with B3LYP functional. The total energies were evaluated by the DFT, CASSCF, and MRMP2 methods. The active space consists of the d-orbitals of two metals and π^* orbital(s) of ethylene and dinitrogen molecules.

III. Results and Discussion

The geometrical parameters optimized by the B3LYP method agree with experimental value. Table 1 shows the relative energies of various spin states of $(\mu$ -C₂H₄) [M(AIP)]₂. Though the high spin state is stable in the B3LYP computational results, the singlet or triplet states are stable in the MRMP2. The effective magnetic moment (μ_{eff}) of $(\mu$ -C₂H₄) [Cr(AIP)]₂ estimated by MRMP2 is 1.8 μ _B. This value is smaller than the experimental value (4.2 μ_B), indicating that the MR-MP2-calculated stability of the quintet state is underestimated. On the other hand, the μ_{eff} (2.6 μ_B) of $(\mu-N_2)[Cr(AIP)]_2$ is close to the experimental value (3.9 μ_B). We will present discussion about the relation between spin multiplicity and bonding nature.

	TABLE 1. Relative energies of spin states of $(\mu_2-\eta^2:\eta^2-C_2H_4)$ [M(AIP)] ₂ (M=Sc-Cr) calculated by MRMP2 and B3LYP (in parentheses) method (in kcal/mol)					
H I I I I I I I I I I I I I I I I I I I		Sc	Ti	V	Cr	
R'	11tet				14.2	(30.9)
	9tet			63.3 (27.0)	8.7	(0.0)
R	7tet		27.8 (44.7)	5.2 (0.0)	3.7	(66.6)
DDP: R=Me, R'=2,6- ⁱ Pr ₂ C ₆ H ₃	5tet	74.4 (34.3)	2.4 (0.0)	2.4(46.1)	2.8	(51.2)
AIP: R=H, R'=H	3let	2.1 (0.0)	0.0 (35.2)	1.9(25.3)	0.0 ((117.1)
SCHME1: $(\mu_2 - \eta^2 : \eta^2 - C_2 H_4) [M(AIP)]_2$	1 let	0.0 (18.3)	2.3 (27.0)	0.0(64.7)	0.1 (100.4)

[1] Y.-C. Tsai et al., J. Am. Chem. Soc. 2007, 129, 8066.

[2] W. H. Monillas et al., J. Am. Chem. Soc. 2007, 129, 8090.

Theoretical Study of the Mechanism of Valence Tautomerism in Cobalt Complexes

Yoshihito Shiota,¹ Daisuke Sato,¹ Gergely Juhász,^{1,2} Kazunari Yoshizawa^{1,2}

¹ Institute for Materials Chemistry and Engineering, Kyushu University, Japan

² International Research Center for Molecular Systems, Kyushu University, Japan

I. Introduction

Valence tautomeric (VT) complexes have attracted much attention recently because of their possible application as new molecular devices like memory or display devices. VT complexes show a ligand-metal electron transfer coupled with a spin change on the central metal ion, which can be switched by external stimuli like light, heat, or pressure. We use a model for the cobalt bis(quinone) complex [Co^{III}(3,5-dbcat)(3,5-dbsq)(bpy)] (cat: catecholate, sq: semiquinon, and bpy: 2,2'-bipyridine), which was first reported by Buchanan and Pierpont in 1980. The complex is in the Co^{III-LS} form (LS: low-spin doublet state) below 273 K, and the population of the Co^{III-HS} form (HS: high-spin sextet state) starts with increasing temperature.

II. Method of calculation

Energy calculations for the $[Co^{II-HS}(sq)_2(bpy)]$ and $[Co^{III-LS}(sq)(cat)(bpy)]$ complexes in the doublet, quartet, and sextet spin states were carried out by using the B3LYP* functional (with 15% Hartree–Fock exchange) implemented in the program packages Gaussian 03 and GAMESS. For the Co atom, the (14s9p5d)/[9s5p3d] primitive set of Wachters-Hay with one polarization f-function ($\alpha = 1.117$) and for the H, C, N, and O, the 6-311G** basis set were used.

III. Results and discussions

Valence tautomerism is studied in $[Co^{II-HS}(sq)_2(bpy)]/[Co^{III-LS}(sq)(cat)(bpy)]$ mononuclear cobalt complex by using DFT methods. Calculations at the B3LYP* level of theory reproduce well the energy gap between the Co^{III-HS} and Co^{III-LS} forms, giving an energy gap of 4.4 kcal/mol, which is comparable to an experimental value of 8.9 kcal/mol. Potential energy surfaces and crossing seams of the electronic states of the doublet, quartet, and sextet spin states are calculated along minimum energy paths connecting the energy minima corresponding to the different spin states. Calculated minimum energy crossing points (MECPs) are located 8.8 kcal/mol in the doublet/sextet surface, 10.2 kcal/mol in the doublet/quartet surface, and 8.4 kcal/mol in the quartet/sextet surface relative to the doublet ground state. Considering the energy of the three spin states and the crossing points, the one-step relaxation between the Co^{III-HS} and Co^{III-LS} forms is the most probable. This research shows that mapping MECPs can be a useful strategy to analyze the potential energy surfaces of systems with complex deformation modes.

[1] D. Sato, Y. Shiota, G. Juhász, and K. Yoshizawa, J. Phys. Chem. A 2010, 114, 12928-12935.

Density functional study of NO binding to Co-center in N_2S_2 coordination environment

<u>Yuko Wasada-Tsutsui</u>,¹ Zhang Zizheng,¹ Hiroaki Wasada,² Tomohiro Hashimoto,² Takuma Yano,¹ Tomohiko Inomata,¹ Yasuhiro Funahashi,¹ Tomohiro Ozawa,¹Hideki Masuda¹ ¹Nagoya Institute of Technology, Gokiso-cho Showa-ku, Nagoya 466-8555, Japan ²Faculty of Regional Studies, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan

Diatomic molecules with 14, 15, and 16 valence electrons, such as CO, NO, and O_2 molecules and ions, binding to metals at active sites of enzymes, play an important role in biological processes. There are many calculations for binding energies of these molecules to Fe-center of heme to investigate their different affinities. A NO molecule, known as a noninnocent ligand, behaves as NO⁺, NO, or NO⁻ in coordination compounds and has high NO affinity to later member of the transition metals.

Fe and Co cations centered at the active site of nitrile hydratase (NHase) have a unique coordination environment constructed from N and S donor atoms. It is expected that this coordination environment should help the metal center in sensitizing NO molecules as well as in catalyzing a hydration process of nitriles. High sensitivity to NO is expected for Co-type NHase analogue. A binding energy is a convenient probe of affinity to the Co-center in NHase.

In this work, we studied NO binding mode to Co-centered N_2S_2 complexes of NHase analogues using density functional method. We calculated binding energies of the some typical small molecules of the spectrochemical series to two complexes having different number of amido-type N atom (Figure 1) in order to elucidate effects of electron donation and charge on the NO selectivity. The calculation shows that the binding energies of a NO molecule are larger than those of a NH₃ molecule, especially those to the coordination environment having more amido-type N atoms.

We also examine binding energies to $[Co(NH_2)_k(HS)_l(NH_3)_m(H_2S)_n]^{(3-k-l)+}$ (*k*+*l*+*m*+*n*=4) modeled on NHase analogues to explain NO selectivity based on electronic structure theory.



Figure 1. Co-centered N_2S_2 complexes of NHase analogues

DFT study of the properties and formation mechanism of 2-hydroxyterephthalate dianion

<u>Nobuaki Tanaka</u>, Shigeo Itoh, Hiromasa Nishikiori Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, Japan

Blue fluorescence of 2-hydroxyterephthalate dianion (HTP) has been utilized as a probe of OH radical generation in aqueous solution where the HTP is generated by the reaction of terephthalate dianion with OH radical. This method is widely used in the radiochemical, sonochemical and photocatalytic reaction. In this study we will focus on the structure and formation mechanism of HTP.

The molecular structure of HTP in water was optimized using density functional theory, that is, the B3LYP and M06-2X functionals. On the $C_{ring}C_{ring}OH$ torsion potential energy curve of HTP two minima were found corresponding to the planar intramolecular hydrogen bonding and the nonplanar nonhydrogen bonding forms. Vertical excitations energies were calculated by time-dependent density functional theory and compared with the experimental data.

The addition reaction of the OH radical to terephthalate dianion is also considered. All possible reaction sites were included.

Theoretical Interpretation of the Photophysical Properties of [n]Cycloparaphenylenes

Cristopher Camacho Yasutomo Segawa Kenichiro Itami Stephan Irle Department of Chemistry, Nagoya University, Nagoya 464-8601, Japan

The photophysical properties of cycloparaphenylenes are studied and analyzed by means of time-dependent density functional theory (TD-DFT) as well as molecular dynamic simulations in conjunction with the time-dependent self-consistent charge density-functional tight binding [1] (TD-SCC-DFTB) and TD-DFT methods. TD-DFT energetics employ the CAM-B3LYP exchange-correlation functional [2] with the def-SV(P) basis set [3]. The features observed in the absorption and emission spectra of [n]CPPs are studied and assigned. A doubly degenerate E state is responsible for the strong absorption observed in the UV-vis spectra; while its distorted Jahn-Teller components are responsible for the strong emissions recorded in the fluorescence spectra. It is also found that dynamic effects play an important role in the proper description of the features observed in the emission spectra of [n]CPPs.



[1] T. A. Niehaus, S. Suhai, F. Della Sala, P. Lugli, M. Elstner, G. Seifert, and Th. Frauenheim, *Phys. Rev. B*, **63**, 085108 (2001).

- [2] T. Yanai, D. P. Tew, and N. C. Handy, Chem. Phys. Lett., 393, 51 (2004).
- [3] A. Schaefer, H. Horn, and R. Ahlrichs, J. Chem. Phys., 97, 2571 (1992).

NMR calculations of transition metal complexes containing M≡P triple bond

<u>Terutaka Yoshizawa</u>, Shigeyoshi Sakaki Fukui Institute for Fundamental Chemistry, Kyoto University, Japan

I. Introduction

Transition-metal complexes containing a multiple bond with non-transition metal elements (e.g. P, Si) have attracted much attention not only due to their exotic nature arising from their unusual bonding characteristics but also due to their interesting electronic and photophysical properties. To understand well them, their electronic structure and bonding nature should be investigated well. NMR chemical shifts can provide important information about the electronic structure and bonding nature, and NMR chemical shifts of $[(i-PrPh''N)_3Mo\equiv P]$, $[(i-PrPh''N)_3W\equiv P]$, and $[(R'Ph''N)_3Nb\equiv P]^-$ (*i*-Pr = CMe₂H, Ph'' = 3,5-Me₂C₆H₃, and R' = (CH₃)₃CCH₂) including the M \equiv P triple bond, where we employed density functional theory and relativistic Hamiltonian (second-order Douglas–Kroll–Hess method).

II. Computaional details

We substituted *i*-Pr, Ph", and R' of the real complexes for H in order to reduce the CPU time. Geometries of the PMo(NH₂)₃, PW(NH₂)₃, and PNb(NH₂)³⁻ were fully optimized with the B3LYP functional. LANL2DZ was employed for M and 6-31+G(3df,3pd) for the other atoms. The chemical shift δ (P) was evaluated with the B3LYP, where well-tempered basis set and Sapporo-TZP with diffuse functions were employed for W and the other atoms, respectively.

III. Results

Optimized geometries agree with experimental ones (Fig. 1). NMR chemical shifts $\delta(P)$ for three model complexes and experimental values are shown in Table 1. The calculated $\delta(P)$ values are not bad, considering that rather small model was employed. It is noted that experimental $\delta(P)$ values decrease in the order Mo > W > Nb, and the decreasing trend is

reproduced well by the calculations. We will discuss scalar relativistic and spin-orbit effects for the $\delta(P)$ values and the relation between the M=P triple bond and $\delta(P)$.



Fig.1 PMo(NH₂)₃.

Table 1. Calculated NMR chemical
shifts $\delta(\mathbf{P})$ and experimental values
(ppm) for the model complexes.

Model	$\delta(\mathbf{P})^{\mathrm{a,b}}$	Exptl.
PMo(NH ₂) ₃	1503 (1570)	1256
PW(NH ₂) ₃	1142 (1353)	1021
		949.2
$PNb(NH_2)_3^-$	1126 (1198)	1019.8
		1110.2

^aH₃PO₄ was taken as a standard. ^bScalar relativistic Hamiltonian was used. The values in parentheses are estimated with non-relativistic Hamiltonian.

Calculation of magnetic constants *D* in Zero-Field Splitting by *ab initio* methods

<u>Takashi Kawakami</u>, Keiji Kinoshita, Akira Ito, Yasutaka Kitagawa, Shusuke Yamanaka, Kizashi Yamaguchi, Mitsutaka Okumura *Graduate School of Science, Osaka University, Japan*

The magnetic anisotropy is an important property of radicals. The magnetic anisotropy Hamiltonian can be expressed as

$$H = D(S_z^2 - S^2) / 3 + E(S_x^2 - S_y^2)$$

where D and E are axial and transverse zero-field splitting (ZFS) parameters. This interaction is due to spin-spin coupling (SS) and second-order spin-order coupling (SOC).

For theoretical treatments of ZFS parameters, previously Pederson and co-workers have developed a method calculating the ZFS parameters with the DFT methods. In the series of our studies, we developed new *ab initio* MO program package ("Q" by Ryo Takeda in our group). The Pederson's treatments are also included in this program. Thus, several *ab initio* MO methods can be applied to calculating zero-field splitting parameters caused by mainly spin-orbit coupling. We examine the behavior and tendency of the method by applying it to some basic molecules such as small molecules (ex. carbene), pure organic molecular magnets, single-molecular magnets (SMM), etc.[1-4] It shows the method has good accuracy. We suggest applicable region of the method.

In addition, Neese has also developed another calculation scheme with coupled-perturbed equation. This method is involved in their program package "ORCA". Thus, we also evaluated ZFS parameters by Neese's methods.

[1] R. Takeda, M. Shoji, S. Yamanaka, K. Yamaguchi, Polyhedron, 24 (2005) 2238.

[2] R. Takeda, K. Koizumi, M. Shoji, S. Yamanaka, M. Okumura, K. Yamaguchi, *Polyhedron*, **26** (2007) 2309.

[3] R. Takeda, S. Yamanaka, K. Yamaguchi, *Int. J. Quant. Chem.*, **102** (2005) 80.
[4] R. Takeda, S. Yamanaka, M. Shoji, K. Yamaguchi, *Int. J. Quant. Chem.*, **107** (2007) 1328.

Multiple core ionizations and their relaxation process induced by X-ray free-electron laser irradiation

<u>Yutaka Imamura</u>,¹ Takaki Hatsui²

¹School of Advanced Science and Engineering, Waseda University, Japan ² XFEL Research and Development Division, RIKEN, Japan

Introduction X-ray free-electron laser (XFEL) facilities have enabled to produce laser pulses strong enough to fully ionize the molecules in short-wavelength regime. Multiple photoionization of core electrons by XFELs then produces molecules with holes in any orbitals. XFELs thus provide a new opportunity to investigate the excited states of multiply ionized molecules such as ionized states with multiple holes in inner-valence orbitals. In this paper we have studied theoretically multiply ionized states of aromatic molecules and subsequent valence excitations.

<u>**Result & Discussion**</u> Multiply ionized states and their valence excitations of two aromatic molecules such as aniline and pyridine molecules are investigated. Multiply ionized states are calculated by the Δ SCF method based on density functional theory (DFT) with the B3LYP exchange-correlation functional. The valence excitations are calculated by time-dependent density functional theory/Tamm-Dancoff approximation (TDDFT/TDA).

The single and double ionizations of N1s electrons are examined. Let us discuss effects on orbital energies by the ionizations. For both molecules, the π orbitals around HOMO are relatively stabilized by the ionizations. The σ^* (Rydberg) orbitals around LUMO are significantly stabilized in comparison with the π and π^* orbitals for the ionized states of aniline. This is attributed to the fact that the ionizations occur at the N atom and its stabilization is large for the σ^* (Rydberg) orbitals localized around the N atom. On the other hand, this is not the case of pyridine because the N atom is a part of the six-member ring and provides a different picture of the orbitals. Therefore, the HOMO-LUMO gap for aniline is reduced because of the significant stabilization of the σ^* LUMO, whereas that for pyridine is not affected significantly.

Next we examine valence excitations for the multiply ionized states. As is predicted from the HOMO-LUMO gap for pyridine, the excitation energies do not change considerably. On the other hand, those for aniline drastically red shift and demonstrate the possibility that the doubly ionized state of aniline molecule can absorb visible light. The systematic investigation against other molecules and experiments for visible light absorption will be discussed in the poster presentation.

Characteristic Fluxional Behavior and Bonding Nature of Hydrogen-bridged Bis(silylene) Complexes

<u>Nozomi Takagi</u>¹, Yuto Odagiri², Hisako Hashimoto², Hiromi Tobita², Shigeyoshi Sakaki^{1*}

¹Fukui Institute for Fundamental Chemistry, Kyoto University, Japan ²Department of Chemistry, Graduate School of Science, Tohoku University, Japan

Hydrogen-bridged bis(silylene)tungsten complexes (1 - 3)in Scheme 1) are of considerable interest, because these complexes are considered as a model of the transition state in H/D exchange of methane and silane by Cp_2MR (M = Ln; R = H, CH₃, SiH₃) [1]. The variable temperature ¹H NMR spectra dynamic behavior involving site-exchanges show of substituents (R^1 to R^4). Interestingly, only in **3** two different types of processes, the cis/trans-exchange (Process I) and the *trans/trans*-exchange (Process II), were observed simultaneously independently and depending on the temperature, though only Process I was observed in 1 and 2.



 $[\]begin{array}{l} {\bf 1}: {\bf R}^1 = {\bf H}, \, {\bf R}^2 = t {\bf B} {\bf u}, \, {\bf R}^3 = {\bf R}^4 = {\bf M} {\bf e} \\ {\bf 2}: {\bf R}^1 = {\bf R}^3 = {\bf R}^4 = {\bf M} {\bf e}, \, {\bf R}^2 = t {\bf B} {\bf u} \\ {\bf 3}: {\bf R}^1 = {\bf R}^3 = {\bf M} {\bf e}, \, {\bf R}^2 = {\bf R}^4 = t {\bf B} {\bf u} \end{array}$

Scheme 1



Here, we investigated the mechanism of the dynamic behavior by density functional theory and post-Hartree-Fock calculations. Our calculations indicate that in the Process I the 1,3-Me migration occurs easier than the W=silylene rotation : see Scheme 2 for these steps. In the Process II, the hydrogen-bridged bis(silylene) unit rotates with the smaller activation barrier than that of Process I (Scheme 3). This result agrees well the experimental fact that the Process II takes place at lower temperature



than the Process I. The details of the reaction features as well as the characteristic bonding features of the three-center interaction of Si-H-Si, the W-Si double bonding nature, and the rather short Si-Si distance will be presented.

^{[1] (}a) L. Perrin, L. Maron, O. Eisenstein, *Inorg. Chem.*, 2002, 41, 4355. (b) L. Maron, L. Perrin, O. Eisenstein, *Dalton. Trans.*, 2003, 4313. (c) L. Perrin, O. Eisenstein, L. Maron, *New J. Chem.*, 2007, 31, 549.

SAC-CI Study on Excitation Spectra of Doublet Molecules

Yasushi Honda, Tadamasa Shida, Hiroshi Nakatsuji Quantum Chemistry Research Institute (QCRI) CREST, Japan Science and Technolocy (JST) Agency

Shida, one of the authors, has developed a method for spectroscopy of radical molecules and succeeded in observations of excitation spectra for a large number of organic doublet radicals [1]. However, the natures of the spectral bands are still unknown or uncertain. In this study, we calculated excitation spectra of several organic cation and anion radicals using the Symmetry Adapted Cluster (SAC)/SAC-Configuration Interaction (SAC-CI) theory to obtain reliable interpretations of their spectral bands.

As the examples, the calculation results of the excitation spectra for cation radicals of polyenes $CH_2(CHCH)_nCH_2$ (n = 1-3) and tetracyanoquinodimethane (TCNQ) anion radical are shown below. The calculated spectra are in good agreement with the experimental ones.



Figure. Excitation spectra of polyene cation (left) and tetracyanoquinodimethan (TCNQ) anion (right) radicals calculated by SAC-CI together with their experimental ones.

The internal configuration inversion of Ortho-phenylene derivative

Azusa Muraoka,¹ Hiroshi Ushiyama,² Koichi Yamashita²

¹School of Science and Technology, Meiji University, Japan ² Department of Chemical system engineering, The University of Tokyo, Japan

I. Introduction

Poly-phenylene nanostructures are established in organic material chemistry. In sharp contrast to extensively studied *para* and *meta* connected analogues, however, *ortho* phenylene have been recognized as an elusive class of π -stacking compounds. Recent year, Ohta et al. demonstrated successful elaboration of multiple ortho phenylene system [1, 2]. We investigate the ortho phenylene derivative which included eight phenylene units and nitro group at the terminal positions. Although these conformation has the connection with tight angled aromatic units, ortho phenylene derivatives displayed a very fast helical inversion profile in solution [1]. As for the reasons for rapid inversion, we identify the dynamic aspect of π -stacking in relation to a theoretical notion that condensed π -clouds are repulsive to one another between neutral and cationic molecules. **II. Results and Discussions**

We related conformational transition of the helical geometry in neutral and cationic of ortho octa-phenylene derivative using *ab initio* MO calculations at the density functional theory at B3LYP level, and examined inter-planar rotational angles and distances between adjoining phenylene units and activation energy shown as Fig.1. We displayed that the ortho phenylene derivatives displayed a very fast helical inversion profile and described that it is activated in order to dynamically minimize a repulsive force operative between the condensed π -clouds. It is considered that the electron repulsion becomes weaker in molecules, leading to reduced interplanar distances between the co-facial phenylene units.



Fig.1 Geometry of neutral and cationic ortho phenylene derivative

[1] E. Ohta, H. Sato, S. Ando, A. Kosaka, T. Fukushima, D. Hashizume, M. Yamasaki, K. Hasegawa, A. Muraoka, H. Ushiyama, K. Yamashita, T. Aida, *Nature Chem.* **3**, 68 (2011); E. Yashima, *Nature Chem.* **3**, 12 (2011)

[2]J. He, J. L. Crase, S. H. Wadumethrige, K. Thakur, L. Dai, S. Zou, R. Rathore, C. S. Hartley *J. Am. Chem. Soc.*, **132**, 13848 (2010); C. S. Hartley, J. He, *J. Org. Chem.* **75**, 8627 (2010)

Time dependent quantum dynamical simulations of C_2 condensation under extreme conditions

Jacek Jakowski*

National Institute for Computational Sciences, JICS-ORNL, One Bethel Valley Road, Bldg 5100 ms 6173, Oak Ridge, TN 37831, USA

Stephan Irle

Institute for Advanced Research and Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan

Keiji Morokuma

Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 6006-8103, Japan

We report theoretical studies of initial phase of condensation of bulk C_2 into carbon nano-structures by means of Born-Oppenheimer and time-dependent quantum mechanical Liouville-von Neumann molecular dynamics employing density functional tight binding framework for electrons. We observe that the time-dependent quantum mechanical approach leads to faster formation of carbon nano-structures than analogous Born-Oppenheimer simulation. Our results suggest that the condensation of bulk carbon is non-adiabatic in its nature with the critical role of electronic stopping as in ion-irradiation of materials. Contrary to time-dependent quantum mechanical simulations, Born-Oppenheimer dynamics incorrectly predict that the short carbon chains obtained from initial reactive collisions between C_2 quickly evaporate, leading to much lower probability of secondary collisions and condensation. We also discuss some deficiencies in Born-Oppenheimer dynamics that leads to unphysical charge polarization and electron transfer.

^{*}Electronic address: jjakowsk@utk.edu

Theoretical study on angular momentum polarization of photofragment of ICI

Takahide Matsuoka¹, Oonishi Sayo¹, Satoshi Yabushita¹

¹School of Fundamental Science and Technology, Keio University, Japan

[Introduction] In a photoexcitation process, a linear molecule can be excited simultaneously to different electronic states after a mixed transition with parallel (//) and perpendicular (\perp) components. If these two excited states are led to an identical quantum state of the photodissociation products, their angular momentum polarization, which is a distribution of m_{J} , the fine structure levels, contains the coherent component, i.e. interference between the de Broglie waves for the different photodissociation processes, which reminisces Young's double slit model. Thus, the wavelength dependence of the angular momentum polarization contains the information of transition dipole moment (TDM), potential energy curve (PEC), and nonadiabatic coupling term (NACT). The objective of this study is to investigate the dynamics of photodissociation processes by evaluating angular momentum polarization parameter in theoretical methods, and comparing the results with experimental data to assess their accuracy.

[Theory and Method] Spin-orbit configuration interaction (SOCI) calculations were done for each electronic state with the COLUMBUS program package. For PEC, second-order CI calculations were performed and Davidson corrections were included. For first-order NACT, only the CI contribution was considered, and was calculated with the numerical differentiations (ΔR =0.005 bohr) of CI coefficients. First-order CI wavefunctions were employed for TDM. The dynamics calculations were done by the wavepacket method employing the Chebychev expansion method.

[Results and Conclusion] Within the region of 490 nm~560 nm wavelength, only two specific excited states (B0⁺ and A(1)) dominantly contribute to the first-rank polarization parameter. Hence the first-rank polarization parameter can be written as:

$$\operatorname{Im}\left[a_{1}^{(1)}(//,\perp)\right] \propto \sqrt{f(\mathbf{X}\to\mathbf{B}\to\mathbf{B})f(\mathbf{X}\to\mathbf{A}\to\mathbf{A})} \sin\left(\varphi_{\mathbf{B}0^{+}}-\varphi_{\mathbf{A}(1)}\right). \tag{1}$$

The parameter represents the orientation of the angular momentum of photofragment $Cl(^{2}P_{3/2})$ in a recoil direction of 45 degrees from light polarization vector. $f(X \rightarrow B \rightarrow B)$ for the // component represents the vertically excited wavepacket which has the contribution of TDM from the $X0^+$ state, and propagates adiabatically on the $B0^+$ state up $_{X0^+}$ to the asymptotic limit (see Fig. 1). In a similar manner, $f(X \rightarrow A \rightarrow A)$ for the \perp component represents the contribution from the Franck-Condon wavepacket on the A(1) state, which dissociates adiabatically on the same state. The phase part in eq. (1)_{Fig. 2}: Correlation scheme

is the phase difference of the de Broglie waves on the $B0^+$ and A(1) states at the dissociation limit. Since the de Broglie waves depend critically on the available energy, PEC, and NACT, a strong wavelength dependence of the parameter in general agreement = with experiment (Fig. 2), implies a high accuracy of = 0.0 ma the PECs.

[1] A. J. Alexander and T. P. Rakitzis, Mol. Phys. 103. 1665 (2005)







Fig. 1: First rank parameter. Circles: Expt. [1]. Blue curve: this work.

0.2 -

Quantum modeling the cooperative laser electron-γ-nuclear effects in spectra of molecular systems

<u>Alexander Glushkov</u>,^{1,2} Svetlana Malinovskaya,¹ Andrei Svinarenko¹ ¹Odessa OSENU University, P.O.Box 24a, Odessa-9, 65009, Ukraine ²ISAN, Russian Academy of Scinces, Troitsk, Moscow reg., 142090, Russia

A new class of problems has been arisen in the modern quantum optics and spectroscopy and connected with modelling of the co-operative laser-electron-nuclear phenomena in the atomic and molecular systems [1]. It includes a calculation of the probabilities and energies of the mixed γ -optical quantum transitions in molecules, intensities of the complicated γ -transitions due to the changing of the molecular excited states population under action of laser radiation, quantum calculation of the "laser-nuclear-molecule" systems [2]. Due to the emission or adsorption of the nuclear γ -quantum in molecular system there is changing the electron vibration-rotation molecular states. We developed new quantum approach to calculation of electron-nuclear γ transition spectra (set of vibration satellites) of nucleus in a molecule, based on relativistic density functional (DF) formalism and energy approach (S-matrix formalism of Gell-Mann and Low) [1]. Decay and excitation probability are linked with imaginary part of the atom (molecule) field system. Calculation results of electron-nuclear γ -transition spectra of the nucleus in some atomic, multiatomic systems are given. As illustration in fig.1a.b spectrum of emission and adsorption of nucleus ${}^{127}I$ (E_y=203keV) in molecule of H¹²⁷I is presented (the initial state of molecule: (a) $v_a=0, J_a=0$; b). $v_a=1, J_a=0$). Estimates are made for vibration-nuclear transition probabilities for number of molecules: diatomics, 3-atomic XY_2 (D_{$\propto h$}), 4-atomic XY_3 (D_{3h}), 5-atomic XY_4 (T_d), 7-atomic XY_6 (O_h) ones.



 A.Glushkov, O.Khetselius, S.Malinovskaya, *Europ.Phys.J.* 2008, 160. 195-204; *Molec.Phys.* 2008, 108, 1257; *Int.J.Quant. Chem.*2004, 99, 889-896; 2005, 104, 496-500; *Frontiers in Quantum Systems in Chemistry and Physics* (Springer). 2008, 18, 523-540.
 V.I.Gol'dansky, V.S.Letokhov, *JETP-Soviet Phys.* 1974, 78, 213-216; L.N.Ivanov, V.S.Letokhov, *ibid*, 1987,93,396-404; A.V.Glushkov, L.N.Ivanov, *Phys.Lett.A* 1992, 170, 33-38.

Raman scattering of the light on metastable levels of diatomics with an account for nuclear motion contribution

<u>Alexander Glushkov</u>,^{1,2} Olga Yu. Khetselius,¹ and Andrei Svinarenko¹ ¹Odessa OSENU University, P.O.Box 24a, Odessa-9, 65009, Ukraine ²ISAN, Russian Academy of Scinces, Troitsk, Moscow reg., 142090, Russia

Laser action on molecules leads to different non-linear processes, including the multi-photon ionization, excitation and dissociation, Raman scattering. The elementary two-photon processes are a linear coherent and a combinational scattering. The intensities and polarization of lines in these spectra are defined by polarizability and derivative on inter-nuclear distance. In this paper it is considered a process of Relay and Raman vibration scattering of the light on metastable levels of molecules (H₂, HD, D₂, Li₂, Rb₂, Cs₂). On the example of polarizability of metastable molecules it has been studied an effect of nuclear motion in processes of the second order of the perturbation theory [1]. New numerical method for construction of the Green electron functions for optical electrons and electron wave functions is developed within the pseudo-potential approach in the spheroid coordinates system that allows to take into account non-spherical character of molecular field.

We present the results of calculation of the molecular polarizability, its derivative on the inter-nuclear distance, a depolarization degree under Relay and Raman light scattering on the frequencies of the Rb, Nd lasers. Analysis of results of the calculation of a polarizability, its derivative on inter-nuclear distance, for example, for excited triple metastable $c^3\Pi_n$, states of the H₂, HD, D₂ molecules on the frequencies of the Rb (1,78eV) and Nd (1,18eV) lasers shows that the main contribution into the polarization of the cited metastable molecules is provided by changing the electron shell under action of the external electromagnetic field. An influence of the nuclear motion terms is in details considered too.

We have presented a relativistic generalization of the approach too. It is based on using the generalized dynamical nuclear model and the relativistic perturbation theory with account of the exchange-correlation effects [1].

[1] A.V. Glushkov, *Rus. J. Struct. Chem.* **1990**, 31, 9; **1992**, 32, 11; **1993**, 34, 3; *Rus. J. Phys.Chem.* **1992**,66, 589; **1992**, 66, 1259; *Int. Journ. of Quant. Chem.* **2005**, 104, 562; *J. Phys.CS.* **2006**, 35, 420.

[2] A.V.Glushkov, L.N.Ivanov, *Phys.Lett.A* 1992, 170, 33; A.V.Glushkov, O.Khetselius, S.V.Malinovskaya, *Molec.Phys.* 2008, 108, 1257; in *Frontiers in Quantum Systems in Chemistry and Physics, Progress in Theoretical Chemistry and Physics*, ed. by S. Wilson, P.J. Grout., J. Maruani, G. Delgado-Barrio, P. Piecuch (Springer, Berlin) 2008, 18, 505.

Electric Field Can Induce Heterogeneous Ice Nucleation

J. Yan and G. N. Patey

Abstract

Molecular dynamics simulations of confined water were carried out to study heterogeneous ice nucleation induced by an electric field under the freezing point. A very simple model, with an electric field that acts only within a very short distance of a surface was examined. We demonstrate that with this arrangement, ice nucleates readily at the surface, and grows outwardly into the bulk. It is found that proton disordered cubic ice, has grown onto the proton ordered ferroelectric layer, in a near seamless manner.

First Principles investigations on lithium – graphite interactions

<u>Alain Allouche</u> ¹*PIIM, CNRS & Université de Provence, Marseille, France*

The interaction of a lithium atom and a graphitic surface has many interests in many domains of energy production:

1) The future tokamak ITER aims to demonstrate that the nuclear fusion of deuterium and tritium nuclei is an energy source of the future. Unfortunately the highly energetic D/T plasma confined in this device seriously damages the materials cladding the inner walls of the tokamak, and this an essential issue for the ITER feasibility. Deposition of a lithium thin layer onto the graphitic elements was found to considerably decrease the carbonaceous materials erosion.

2) Hydrogen storage has been identified as a major challenge in the implementation of hydrogen as a fuel in vehicles. Graphite based materials are the most often proposed candidates for this purpose, and lithium strongly increases the H storage capacity.

3) Diffusion on and into the graphite surface precedes the formation of lithium – graphite intercalation compounds which can replace lithium metal electrodes in rechargeable Li-ion batteries.

From a quantum point of view, the lithium - graphite interaction can be atomic or ionic according to the situation. This contribution details DFT studies on the mechanisms of a single lithium atom interaction with the pristine or defective (0001) graphite surface. Because the Li(2s) energy level is so close to the graphite Fermi energy, there is a very subtle competition between hydrogen atom adsorption on carbon or Li atoms. Co-adsorbed atomic oxygen or atomic vacancies can displace this competition in one direction or the other.

We will also study the effects of lithiation and oxidation of graphite on of atomic hydrogen storage.

Computational studies of viral influenza A neuraminidase subtype N1

<u>Thanyada Rungrotmongkol</u>,^{1,2} Supot Hannongbua^{1,2}

¹Computational Chemistry Unit Cell, Department of Chemistry, Faculty of Science, Chulalongkorn University, Thailand ²Center of Innovative Nanotechnology, Chulalongkorn University, Thailand

While the seasonal influenza viruses spreading around the world cause the annual epidemics, the recent outbreaks of influenza A virus subtypes H5N1 and pandemic H1N1 (pH1N1) have raised a global human health concerns. We aimed at gaining insight into molecular details at neuraminidase (NA) of these two viruses. Interest is focused on drug's inhibitory activity against the wild-type and mutated N1 strains. Based on molecular dynamics approach in couple with linear interaction energy method, the pH1N1 NA was predicted to be susceptible to oseltamivir, with all important interactions being well conserved [1]. For both viruses [2,3], the known H274Y mutation conferred the high oseltamivir-resistance with decreased hydrophobicity, pocket size and vdW interactions at the bulky group. Instead, N294S was found to demonstrate medium drug-resistant level. Investigation was also extended to combinatorial chemistry drug design of NA inhibitors using the oseltamivir and pyrrolidine scaffolds [4,5]. From the large diversity combinatorial library, the small highly focused combinatorial subset of both designed analogs was proposed to contain NA inhibitors with considerably higher potencies toward the N1 enzyme than their parent inhibitors, oseltamivir and A-315675. A better understanding of molecular inhibition and source of drug resistance as well as a set of newly designed compounds is greatly useful as a rotational guide for synthetic and medicinal chemists to develop a new generation of anti-influenza drugs.

[1] T. Rungrotmongkol, P. Intharathep, M. Malaisree, N. Nunthaboot, N. Kaiyawet, P. Sompornpisut, S. Payungporn, Y. Poovorawan, S. Hannongbua, *Biochem. Biophys. Res. Commun.* **2009**; 385(3):390-394.

[2] T. Rungrotmongkol, T. Udommaneethanakit, M. Malaisree, N. Nunthaboot, P. Intharathep, P. Sompornpisut, S. Hannongbua, *Biophys. Chem.* **2009**; 145(1):29–36.

[3] T. Rungrotmongkol, M. Malaisree, N. Nunthaboot, P. Sompornpisut, S. Hannongbua, *Amino Acids* **2010**; 39(2):393-398.

[4] T. Rungrotmongkol, V. Frecer, W. De-Eknamkul, S. Hannongbua, and S. Miertus, *Antiviral Res.* **2009**; 82(1):51-8.

[5] T. Rungrotmongkol, T. Udommaneethanakit, V. Frecer, S. Miertus, *Comb. Chem. High Throughput Screen.* **2010**; 13(3):268-77.

Linearly conjugated chains exposed to an electric field: A closer look on the polarizabilities obtained with several quantum chemical methods

Peter A. Limacher,^{1,2} Hans P. Lüthi,¹ Paul W. Ayers² ¹Laboratory of Physical Chemistry, ETH Zürich, Switzerland ²Department of Chemistry, McMaster University, Canada

Conjugated molecular chains such as polyacetylene (alternating double and single bonds) or polyyne (alternating triple and single bonds) are materials of considerable interest to the chemical industry and material sciences as they exhibit large nonlinear optical effects when exposed to electric fields.

Unfortunately, the quantum chemical description of these systems, and in particular the calculation of polarizabilities and hyperpolarizabilities, is by no means trivial. It is well known, that conventional DFT fails to predict accurate values for these properties due to limitations in the exchange functional.[1] Especially for extended chains, this leads to a tremendous overestimation of the polarizabilities along the molecular propagation axis. The inclusion of pure HF-exchange in the recently developed longrange-corrected density functionals however, was successful in predicting more meaningful polarizabilities.[2][3]



In the meantime, it has been noted that also electron correlation has an unexpected effect on the polarizabilities of these systems: The initially positive contribution of electron correlation to the second hyperpolarizability of small systems is constantly diminishing when the chain length is extended and can even turn into a negative contribution for sufficiently large systems.[4][5]

- [2] H. Sekino, Y. Maeda, M. Kamiya, and K. Hirao, J. Chem. Phys. **126**, 014107 (2007).
- [3] P.A. Limacher, K.V. Mikkelsen, and H.P. Lüthi, J. Chem. Phys. 130, 194114 (2009).
- [4] Q. Li, L. Chen, Q. Li, and Z. Shuai, Chem. Phys. Lett. 457, 276 (2008).
- [5] P.A. Limacher, Q. Li, and H.P. Lüthi, J. Chem. Phys., in press.

^[1] S.J.A. van Gisbergen, P.R.T. Schipper, O.V. Gritsenko, E.J. Baerends, J.G. Snijders, B. Champagne, and B. Kirtman, Phys. Rev. Lett. 83, 694 (1999).

Molecular modeling of silver adsorption on α-quartz surface

<u>N.I.Vakula</u>¹, G.M. Kuramshina¹

¹Faculty of Chemistry, Moscow State University (M.V.Lomonosov), Moscow, 119991, Russia

Metal island films (MIFs) have many interesting properties and, particularly, a unique optical behavior. These films are effectively used as selective absorbers, optical polarizers, and data storage, etc. Using the optical behavior of MIFs opens up the possibility to produce low-cost photonic heterostructures.

In the present study, the new results on determining the suitable locations for incorporation of silver adatoms on the silica (001) surface has been performed. A series of searches has been carried out and all possible configurations have been optimized within first-principle calculations (DFT and QM/MM) with a goal to investigate the electronic structure and adsorption energy of silver atoms deposited on the silica (001) surface. An orthorhombic supercell with a slab of α -quartz has been used for modelling (001) surfaces (Fig.1). The initial configuration of the completely hydroxylated surface has been obtained by saturating the terminal oxygen atoms on both the top and bottom surfaces by hydrogen atoms.



Figure 1. Side view (a) and top view (b) of silica (001) surface used in calculations

All calculations have been performed with CP2K code¹. The technique based on the Quickstep² implementation of the density functional theory (DFT) method with Gaussian and plane waves (GPW³) scheme has been utilized. We have used the generalized gradient functional PBE and the Goedecker-Teter-Hutter⁴ pseudopotentials in conjunction with TZVP basis sets.

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¹Kohlmeyer. A.; Mundy. C. J.; Mohamed. F.; Schiffmann. F.; Tabacchi. G.; Forbert. H.; Kuo. W.; Hutter.

J.; Krack. M.; Iannuzzi. M.; McGrath. M.; Guidon. M.; Kuehne. T. D.; Laino. T.; VandeVondele. J.;

Weber. V. CP2K, 2004, http://cp2k.berlios.de

²VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. Comput. Phys.

Commun. 2005, 167, 103–128.

³Lippert, G.; Hutter, J.; Parrinello, M. Mol. Phys. 1997, 92, 477–487.

⁴Goedecker, S.; Teter, M.; Hutter, J. Phys. ReV. B 1996, 54, 1703–1710.
Theoretical study of [2+2] cycloaddition of cyclopentyne and ehtylene: Multireference and broken-symmetry approach

Toru Saito,¹ Yasutaka Kitagawa,¹ Mitsutaka Okumura,¹ Kizashi Yamaguchi² ¹Department of Chemistry, Graduate School of Science, Osaka University, Japan ²Center for Nanomaterial Design, Osaka University, Japan

Abstract

The [2+2] cycloaddition reaction of cyclopentyne and ethylene is examined by both the multireference (MR) and spin-unrestricted Hartree-Fock (UHF) based coupled cluster (CC) calculations. We focus on the competition between diradical stepwise and concerted mechanisms in the reaction. We have demonstrated that the spin contamination effect caused by the triplet state still remains at the UHF-CCSD(T)level [2-5]. To remove the spin contamination effect, an approximate spin-projection (AP) method is applied to the singlet solutions. The CC with the spin-unrestricted Brueckner determinant (UBD(T)) calculations were also performed because UHF-CCSD poorly describes the π conjugated organic species [6-8]. At the transition state, the calculated $\langle S^2 \rangle$ values for the singlet solutions are ~ 0.7 and ~ 0.1 obtained by UCCSD(T) and UBD(T), respectively, supporting that UBD(T) significantly suppresses the diradical character. Comparison of the activation barrier heights including thermal corrections between two mechanisms suggests that they are competitive and the difference is within 0.5 kcal/mol. The present results are consistent with the CR-CCSD(T) results of Kinal and Piecuch [9]. On the other hand, the stepwise pathway is favorable than the concerted pathway by 2.0 kcal/mol at the MkMRCCSD/cc-pVDZ level.

- [1] L. Fitjer et al. Tetrahedron Lett. 23, 1661 (1982).
- [2] T. Saito et al. Chem. Phys. Lett. 483, 168 (2009).
- [3] T. Saito et al. J. Phys. Chem. A 114, 7967 (2010).
- [4] T. Saito et al. J. Phys. Chem. A 114, 12116 (2010).
- [5] T. Saito et al. Theor. Chem. Acc., in press.
- [6] T. Saito et al. Chem. Phys. Lett. 498, 253 (2010).
- [7] T. Saito et al. Mol. Phys. 108, 2533 (2010).
- [8] T. Saito et al. Theor. Chem. Acc., in press.
- [9] A. Kinal, P. Piecuch, J. Phys. Chem. A 110, 367 (2006).

STRUCTURAL STUDY OF α -TETRAGONAL BORON BY COMPUTATIONAL METHOD

Jagadeesh.S, N.Uemura, K.Shirai*

Department of Theoretical Nanotechnology Nanoscience and Nanotechnology Center, ISIR, Osaka University, Japan

The crystalline boron exists as several polymorphs. Among them, the α tetragonal boron attracts attention from researchers due to its structural uniqueness, that is, a tetrahedral arrangement of icosahedra as seen in the following figure. In addition to four icosahedra, two interstitial boron (B) atoms are inserted. In the history of boron research, the α -tetragonal phase has been occupying a special position to shade the nature of the icosahedral bonding. Initially, it was thought that the crystal is composed of four B_{12} and two interstitial B atoms, being 50 B atoms in the cell. However, as the structural refinement was progressed, it became clear that pure B₅₀ structure alone was unstable. Impurities such as C or N atoms are incorporated in the crystal and only in this form α -tetragonal phase can be stabilized. A recent surprise is that, in spite of this metastable feature, pure B₅₀ form is reported in nanostructure boron, such as nanoribbon or nanobelt. There is no consensus regarding the stability of a-tetragonal phase in nanostructures. In this work, we investigated the formation of α -tetragonal phase and the electronic structure by first-principles pseudopotential method for bulk crystal. The enthalpy of formation (ΔH_f) of various defects with respect to pure α tetragonal phase revealed that the pure B₅₀ structure is unstable. As commonly observed in other boron crystals, the intericosahedra bond lengths are shorter than the intraicosahedra bond lengths. It means that the interstitial sites play a crucial role on the stability of crystal. Phonon calculation of the α -tetragonal boron confirmed the strong bonding between two icosahedra units. We observed the characteristic phenomenon, when the foreign atoms are incorporated in this structure. The phonon spectrum showed, the inter icosahedra bond strength enhanced by the foreign atoms like C, N and B.



The structure of α-tetragonal boron

* Corresponding author

Packing effects in organic donor-acceptor molecular heterojunctions

Mikiya Fujii, Koichi Yamashita

Department of Chemical System Engineering, The University of Tokyo, Tokyo 113-8656, Japan

I. Introduction

Organic semiconductors have been widely investigated for photovoltaic and light emitting devices. Especially, further improvements of more efficient organic solar cells (OSCs) are desired. Thus, we explored possibilities to make OSCs more efficient by adjusting the packing of molecular heterojunctions.

II. Computational methods

molecular We analyzed heterojunction that consists of а poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)diphenylenediamine) (TFB) and poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT). Geometrical optimization of TFB(monomer)/F8BT(monomer) complex was carried out with DFT-D/B3LYP/6-31G*. Excited states were also calculated with CIS/6-31G*. To analyze packing effects in charge transfer dynamics from TFB to F8BT, we rotated TFB around a principal axis. Then, we analyzed the charge transfer with a quantum master equation (QME) approach.

III. Results

A stable structure is shown in Fig. 1. From the excited states calculations, it is clarified that the packing strongly affects the energy level of the charge transfer state only (Fig.2). This packing dependency arises from a packing dependency of the exciton binding energy that is Coulomb interaction between an electron localized to F8BT and a hole localized to TFB. From the QME approach, it is confirmed that qualitative different electronic relaxation dynamics occurs in each different packing. Therefore, we conclude that the packing that is suitable for photovoltaic devices and the packing that is suitable for light emitting devices are different.



Fig1. A stable structure and molecular orbitals of TFB/F8BT complex. Upper and Lower molecules are F8BT and TFB, respectively. (a):HOMO. (b)LUMO



Fig. 2 Packing dependency of the excited states.

Theoretical Study of Interaction between Gas Molecule and Paddle-Wheel Unit of MOF

<u>Yuh Hijikata</u>, Shigeyoshi Sakaki^{*} *Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, Japan*

I. Introduction

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), which are constructed from organic linkers and metal ions, have attracted a lot of interests in their excellent abilities for gas storage and separation. Some of PCPs possess open metal sites (OMSs) which work as interaction sites for gas molecules. The paddle wheel unit is one of good examples, which is often used as building unit for many PCPs. We theoretically investigated the interaction energies (E_b) of several molecules with the paddle wheel unit, their bonding nature, and change of electronic structure.

II. Computational detail

In the paddle wheel unit, two metal ions are connected by organic linkers. The axial positions are OMSs, as shown Scheme 1. Structures were optimized by DFT method with M06L functional. E_b was evaluated with MP2 to MP4(SDTQ). In M=Cu, the difference of E_b between triplet and open shell singlet states were considered as shown in Scheme 2, while in M=Ni, singlet, triplet, and quintet state were investigated.



III. Results and discussion

The difference of E_b between open shell singlet $d_{\underline{s}}$ and triplet spin states was negligibly small in M=Cu. This is because L mainly interacts with Cu $4p_z$ orbital, while Cu d_{x2-y2} orbital little participates in the



interaction with L. As listed in Table 1, E_b increases in the order NO ~ N₂ < CO << CH₃CN < CH₃NC. This trend agrees with the trend of the charge transfer from L to Cu, except for CH₃CN and CO. This exceptional result is interpreted in terms of the negatively charged N of CH₃CN and positively charged C of CO. In Ni(II) complexes, the interaction of gas molecule induces change of spin multiplicity from triplet to quintet, interestingly. The change of spin state and comparison of E_b between Ni and Cu will be presented in the poster.

Table 1. E_b values of various gas molecules with the Cu(II) paddle-wheel complex in triplet state (R=H).

L	СО	CH ₃ CN	CH ₃ NC	NO	N_2
$E_b / \text{kcal} \cdot \text{mol}^{-1 a}$	6.5	12.5	14.9	4.0	4.1
r(Cu-L)	2.267	2.193	2.174	2.292	2.394
Charge transfer from L	0.213	0.125	0.222	-0.111	0.100

^{a)} The stabilization energy per one gas molecule. The MP2 method was employed. Counterpoise correction was made.

Electronic structures and molecular structures of polyynes

<u>Akira Imamura</u>,¹ Yuriko Aoki^{2,3}

¹Faculty of Engineering, Hiroshima Kokusai Gakuin University, Japan
²Faculty of Engineering Sciences, Kyushu University, Japan
³Group PRESTO, Japan Science and Technology Agency, Japan

I. Introduction

Recently, many interesting materials made from carbon atoms have been discovered such as carbon nanotubes, fullerenes and graphenes. In this paper, we studied electronic structures and molecular structure of polyynes with sp² carbons on both ends.

II. Molecules and method of calculations

Polyynes calculated were $H_2CC_nCH_2$ with various number of n. These molecules have two π systems which are perpendicular to each other and these π systems have their tendency to make double bond nature by Peierls instability but for different alternating bonds. In other words, these two π systems are competing to form the double bond formations. The calculations were carried out with Gaussian 03 with geometry optimization in 6-31G and 3-21G basis sets.

III. Results and Discussion

For $CH_2(C)_{38}CH_2$ and $CH_2(C)_{48}CH_2$, there have been found two metastable structures, one of which is the bond-alternating structure and another is nearly equi-bond structure. The former has small HOMO-LUMO gap while the latter has the relatively large gap although it is smaller in comparison with the value of polyyne with sp carbon atoms on both ends such as $H(C)_{40}H$ and $H(C)_{50}H$. The small HOMO-LUMO gap in bond-alternating structure is due to the fact that HOMO and MO's near to HOMO have relatively localized electronic distribution in both end regions and thus the weak interaction between the both regions leads to the small HOMO-LUMO gap. The stability is larger for the former especially in long polyynes. The calculated numerical values are listed in Table I. This result can be explained by using the perturbation theory published previously[1]. We will describe in detail at the poster session.

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molecule	structure	НОМО	LUMO	gap	Tot. Energy
$H_2C(C)_{38}CH_2$	Bond-alter	-0.1450	-0.1314	0.0135	-1515.2609
$H_2C(C)_{38}CH_2$	Equi-bond	-0.2410	-0.0581	0.1829	-1515.2101
$H_2C(C)_{48}CH_2$	Bond-alter	-0.1434	-0.1333	0.0101	-1893.5445
$H_2C(C)_{48}CH_2$	Equi-bond	-0.2389	-0.0620	0.1769	-1893.4261

Table I. HOMO-LUMO gap and total energy of polyynes with 6-31G (energy in a.u.)

IV. Conclusion

Interesting relationship between electronic structures and molecular structures of polyynes are found and discussed.

[1] Y.Aoki and A.Imamura, J. Chem. Phys., 103, 9726-9737(1995).

Structural dependence of the open-shell characters and second hyperpolarizabilities in one-dimensional systems composed of trigonal graphene nanoflake units

<u>Kyohei Yoneda</u>,¹ Hitoshi Fukui,¹ Takuya Minami,¹ Yasuteru Shigeta,¹ Takashi Kubo,² Edith Botek,³ Benoît Champagne,³ Masayoshi Nakano¹ ¹Graduate School of Engineering Science, Osaka University, Japan ²Graduate School of Science, Osaka University, Japan ³Facultés Universitaires Notre-Dame de la Paix, Belgium

I. Introduction

In our previous studies, we have theoretically found that the second hyerpolarizability (γ) [the microscopic origin of the third-order nonlinear optical (NLO) property] for open-shell singlet molecules shows a remarkable open-shell character dependence: the systems having intermediate open-shell characters tend to exhibit a

large enhancement of γ as compared to the closed-shell and pure open-shell systems [1]. We have studied graphene nanoflakes (GNFs) with several sizes and architectures as promising candidates of open-shell singlet NLO systems [2]. In this study, we investigate the structural dependence of the open-shell characters as well as of the γ values for several one-dimensional systems composed of the smallest trigonal GNF units (Fig. 1) [3].



Fig. 1. 1D systems composed of trigonal GNF units

II. Results and discussion

These systems show a wide range of open-shell characters, strongly depending on the linked form of trigonal GNF units, which is useful for controlling γ . In particular, in singlet alternately linked (AL) systems, having intermediate multiradical characters, γ is larger and increase supralinearly with the number of units (*N*) faster than in the non-alternately linked (NAL) systems, having a pure multiradical character (Fig. 2). These features provide a novel guideline for the molecular design of GNF based NLO materials.



M. Nakano et al., J. Phys. Chem. A 109, 885 (2005); Phys. Rev. Lett., 99, 033001 (2007).
M. Nakano et al., Chem. Phys. Lett. 467, 120 (2008); K. Yoneda et al., Chem. Phys. Lett. 480, 278 (2009); H. Nagai et al., Chem. Phys. Lett. 489, 212 (2010).
K. Yoneda et al., ChemPhysChem. 12, 1697 (2011).

An efficient light-harvesting system to excite optically-forbidden states of molecular aggregates

<u>Go Tei</u>, Masatoshi Nakatani, and Hajime Ishihara Graduate School of Engineering, Osaka Prefecture University, Japan

I. Introduction

Two types of ring-shaped pigment-protein complex, peripheral light harvesting complex (LH2) and core light-harvesting complex (LH1) are involved in the photosynthetic light-harvesting process of photosynthetic bacteria. The energy of sunlight absorbed by LH2 efficiently migrates to LH1, where the photosynthetic reaction center is located at the center of LH1. It is pointed that the geometrical structure of LH2, the characteristic ring shape, could positively function to achieve high efficient energy transfer in photosynthetic systems [1, 2]. On the other hand, it is proposed that, in particular resonant conditions, photon energies received by the metal structures forming a nano gap serving as an artificial light harvesting antenna can be concentrated into the target molecules in the vicinity of the nano gap without a large dissipation in the metals [3]. By employing a simple model, we show that such energy transparency can also occur between the optically allowed states of an antenna ring and the optically-forbidden states of a target ring, where antenna and target ring are the aggregate of point dipoles imitating the geometrical structure of LH2 and LH1, respectively.

II. Model and Results

We consider a model system consisting of target and antenna rings, which are modeled as the aggregate of point dipoles imitating the geometrical structure of LH1 and LH2, respectively. To investigate the population dynamics in the system, a method based on the nonlocal response theory and a Markovian quantum master equation is employed, which enables us to treat electric field and polarization of point dipoles self consistently. We found that, in particular resonant conditions, photon energies received by the optically-allowed states of the antenna ring can be concentrated into the optically-forbidden states of the target ring efficiently suppressing the relaxation in the antenna ring. It could be an example of efficient light-harvesting system to excite optically-forbidden states of molecular aggregates.

- [1] G. Tei et al, Physica Status Solidi (b), 248, 399 (2010)
- [2] M. Nakatani et al, Physica Status Solidi (b), 248, 448 (2010)
- [3] H. Ishihara et al., J. Photochem. Photobio. A (2011) in press

Theoretical Study on Electronic Structures of μ -oxo-Bridged Manganese Complex

<u>Nanami Seki</u>,¹ Akira Nakayama,² and Tetsuya Taketsugu² ¹Graduate School of Chemical Sciences and Engineering, Hokkaido University, Japan ²Graduate School of Science, Hokkaido University, Japan

The manganese complex has received much attention both theoretically and experimentally since manganese shows particularly rich redox property with several oxidizing states. In particular, the oxygen-evolving complex (OEC) in photosystem II (PSII), which is composed of a μ -oxo-bridged tetra-nuclear manganese cluster (Fig. 1), is known to oxidize water molecules into oxygen molecules efficiently [1], and its imitative complex (Fig. 2) also has the ability to evolve oxygen [2], so there is a growing interest in utilizing this kind of manganese complex as a catalyst in water splitting. In most theoretical studies on this type of metal complexes, density functional theory (DFT) methods have been employed to predict the structural and electronic properties and to investigate the reaction mechanism, with a reasonable cost. As to the relative energies of different spin states with open-shells of d-electrons, however, DFT methods are not considered to predict an accurate result [3].

In this work, we applied multi-configurational self-consistent field (MCSCF) method, as well as B3LYP (DFT) method, with Sapporo-DZP basis sets [4], to investigate the electronic structures of the highest/lowest spin



Figure 1. PSII oxygen-evolving complex (OEC)



Figure 2. OEC imitative complex Mn₂O₂(tpy)₂(H₂O)₂

states of several kinds of di- μ -oxo-bridged manganese dinuclear complex and to estimate the effective exchange integrals value (*J*) in detail, and discuss about the capabilities of the DFT method. In DFT calculations, the low-spin states are calculated by the broken-symmetry technique. More details and discussions are given in the poster session.

References

- [1] V.K. Yachandra, K. Sauer, and M.P. Klein, Chem. Rev. 96, 2927 (1996).
- [2] J. Limburg, J.S. Vrettos, L.M. Liable-Sands, A.L. Rheingold, R.H. Crabtree, and G.W. Brudvig, *Science* **283**, 1524 (1999).
- [3] E.M. Sproviero, J.A. Gascon, J.P. McEvoy, G.W. Brudvig, and V.S. Batista, *J. Inorg. Biochem.* **100**,786 (2006).
- [4] http://www.sci.hokudai.ac.jp/sapporo/