Abstracts of Invited and Contributed Talks, Sep. 3

From Density Functional Theory to Density Matrix Functional Theory

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Although DFT has been very successful, it also meets with important problems. The dissociation of electron pair bonds, and their weakening towards transition states, are problematic cases for (approximate) DFT. In the calculation of response properties with TDDFT, there are grave errors when one tries to construct excited state potential energy surfaces: upon stretching of bonds the excitation energy becomes totally wrong [1] the TDDFT method fails to describe doubly excited character [2], and fails for charge transfer transitions.

All these problems stem from the difficulty that functionals working with the local density and its derivatives have in recognizing the correlation of electrons along a lengthening bond [3]. The exact position of the other nucleus, and the onset of strong correlation effects, are however manifest in orbital information: the shape and energy for occupied and virtual Kohn-Sham orbitals, and the occupation numbers for the natural orbitals. We will discuss how orbital dependent functionals can be used to describe the strong correlation in the indicated cases, both in the DFT context (with virtual orbital dependent functionals [4]) and in density matrix functional theory [5,6,7].

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3A1-3I

Two-Point Weighted Density Approximations for the Kinetic Energy and Exchange-Correlation Energy

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Many of the problems in density-functional theory can be mitigated by carefully designing an exchange-correlation hole with the proper mathematical properties. This leads to generalized and extended versions of the venerable weighted density approximation (WDA). In this talk, I will show how well WDA can work for the kinetic energy, exchange energy, and exchange-correlation energy. One advantageous feature of the WDA is that it allows one to deal with fractionally occupied sites in a better way than conventional functionals. (For example, the H₂ dissociation problem is entirely solved.) The traditional criticism of WDA has been its high computational cost. These costs are mitigated by new algorithms using a new limited-memory quasi-Newton method that was designed especially for this application.

Linearity condition for orbital energy in density functional theory: Construction of orbital-specific hybrid functionals

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Introduction The recent development of more advanced hybrid functionals in density functional theory (DFT) overcome the several long-standing difficulties: dissociation curves; charge-transfer, Rydberg, and core excitations. Our group has also developed the orbital-specific (OS) hybrid functional that owns Hartree-Fock exchange (HFx) portions depending on orbital natures: core-valence-Rydberg (CVR)-B3LYP hybrid functional. However, these functionals often determined parameters by numerical assessment and, as a result, narrowed their applicability. This study attempts to determine the parameters so as to satisfy the physical constraint.

<u>*Theory*</u> The parameters included in hybrid functional, i.e., the HFx portions can be determined by the physical constraint: linearity condition for orbital energy (LCOE) [1]:

$$\frac{\partial^2 E}{\partial f_i^2} = \frac{\partial \varepsilon_i}{\partial f_i} = 0 \qquad (0 \le f_i \le 1)$$
(1)

where E, ε_i , and f_i represent the total energy, orbital energy and occupation number of the *i*th orbital. The LCOE enables to determine OS parameters based on a physical foundation and construct OS functionals.

<u>**Result & Discussion**</u> We calculate potential curves and bonding energies of He_2^+ using the cc-pCVTZ basis set for conventional and OS functionals. As shown in Fig. 1, the OS functionals, LC-BLYP and HF offer a reasonable description of bond dissociation although BLYP and B3LYP fail. The corresponding bonding energies are listed in Table

1. The deviations are shown in parentheses. The BLYP, B3LYP, and LC-BLYP functionals overestimate by more than 18 kcal/mol and HF underestimates by 11.7 kcal/mol. On the other Total energy [hartree] hand, the OS LC-BLYP and OS BLYP functionals accurately estimate bonding energies within 0.8 kcal/mol. Table 1 He_2^+ bonding energies This numerical in kcal/mol. BLYP 81.6 (27.0)assessment on He_2^+ 75.4 (20.8)B3LYP reveals that the LC-BLYP 72.6 (18.0)LCOE can play an HF 42.9 (-11.7) essential role in the OS LC-BLYP 55.3 (0.7)construction of DFT OS BLYP 55.4 (0.8)54.6 Exact --hybrid functionals.



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Density functional theory with fractional occupations

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We propose a density functional theory (DFT) with fractional occupations of the Kohn-Sham (KS) orbitals for the study of ground states of many-electron systems. This DFT, containing a free parameter which controls the orbital occupation numbers, can be reduced to KS-DFT with some fixed parameter. Utilizing the local spin density approximation (LSDA) to this DFT, improved results are obtained for systems dominated by either single-reference characters (e.g. reaction energies, equilibrium geometries) or multi-reference characters (e.g. bond-breaking processes of H₂ and N₂, twisted ethylene), when compared with KS-LSDA. Because of its very cheap computational cost (similar to KS-LSDA), this DFT is applied to the study of singlet-triplet energy gaps (ST gaps) of linear acenes (up to 74-acene). Our results are in good agreement with the available experimental results, and suggest that the decay of ST gaps with the acene length be monotonic, and the ST gap for the infinite chain be vanishingly small (smaller than 1 kcal/mol). Both physical arguments and numerical results for the choice of optimal parameter used in this DFT are presented.

3A2-1I

Cholesky Decomposition in Quantum Chemistry: A summary of the current status

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Abstract

This lecture is a brief presentation of the development of the Cholesky decomposition of two-electron integrals [1] and the implementation of the technique in contemporary ab initio methods as it stands today. The presentation will discuss the use of the method in standard wave function and density functional theory models, the development and implementation of the associated analytic gradients, and benchmark results with respect to accuracy and overall timings [2]. The lecture will present evidence why the CD technology is the optimal and most effective way to eliminate the need of precomputed RI auxiliary basis sets.

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Linear- and Sub-Linear Scaling Quantum-Chemical Methods

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The usefulness of the Laplace transformation for the formulation of linear-scaling methods is discussed for both response theories at Hartree-Fock (HF) and Density-Functional Theory (DFT) levels [1], and for the calculation of energies and energy gradients at the Møller-Plesset (MP2) level [2-4]. The transformation allows to entirely avoid the delocalized, canonical molecular orbital (MO) representation, which is crucial for the formulation of linear-scaling methods. In this way, only density or pseudo-density matrix-based quantities enter the formulations, so that sparsity can be exploited for electronically local molecular systems and linear scaling is attained. The largest system computed at the MP2 level is an RNA system comprising 1664 atoms and 19 182 basis functions [5].

Furthermore, we introduce a sub-linear scaling NMR method [6], that allows to compute NMR shieldings for selected nuclei only. This has important implications not only for the study of large molecules, but also for the simulation of solvent effects and molecular dynamics, since often just a few shieldings are of interest. Our theory relies on two major aspects both necessary to provide a sublinear scaling behavior: First, an alternative expression for the shielding tensor is derived, which involves the response density matrix with respect to the nuclear magnetic moment instead of the response to the external magnetic field. Second, as unphysical long-range contributions occur within the description of distributed gauge origin methods that do not influence the final expectation value, we present a reformulation suitable for truncation, so that an early onset of the sublinear-scaling behavior can be achieved. Applications to molecular systems with more than 1000 atoms will be shown.

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New developments and applications of the generalized energy-based fragmentation approach

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In this talk, I will present our recent developments and applications of the generalized energy-based fragmentation (GEBF) approach, which provide a fast and reliable theoretical tool for approximate *ab initio* calculations of very large molecules.[1-3] The essence of this method is to divide a large molecule into many fragments and obtain the approximate ground-state energy or properties of this molecule from the corresponding quantities of various "electronically embedded" subsystems. Very recently, an automatic algorithm for partitioning a large system has been accomplished, [4] which allows the applications of the GEBF approach to be available by non-expert users. With the newly implemented GEBF approach, one can compute energies, optimized structures, vibrational spectra, and some molecular properties of very large systems at various *ab initio* levels on ordinary PC workstations. The GEBF approach has been applied to investigate several interesting chemical problems in large systems, such as the driving forces of molecular self-assembling processes, [5] low-lying structures and stabilities of large water clusters, [6] and the structures, energies and enthalpies of helical structures for capped polyalanines with up to 40 residues.[7]

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3A3-1I

Cost-Effective Treatment of Relativistic Effects

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Relativistic effects need to be considered in quantum-chemical calculations when dealing with heavy-element compounds or when aiming at high accuracy. In the latter case these effects are even important for systems containing only light elements. In order to allow a routine treatment of relativistic effects, cost-effective as well as accurate schemes are needed which in particular are also applicable in the context of electron-correlation calculations. Two approaches will be pursued for this purpose in the following:

- direct perturbation theory (DPT) with a special emphasis on higher-order treatments;
- spin-free approaches based on a non-perturbative treatment of the scalarrelativistic effects. Spin-orbit coupling is here treated afterwards using perturbation theory.

In the lecture, the theoretical background of these schemes is discussed, and results for energies and molecular properties are given to judge the accuracy of the presented schemes.

Four-component relativistic multireference perturbation theory

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Multireference perturbation theory (MRPT) based on multiconfiguration (MC) reference functions has become a basic and practical tool for studying the electronic structures of molecules and the potential energy surfaces of chemical reactions. MRPT takes account of both static and dynamic electron correlations and thus can obtain accurate relative energies, including reaction, activation, and excitation energies, within a chemical accuracy (i.e., a few kcal/mol).

We have developed an MRPT using MC functions that we call "multiconfigurational quasidegenerate PT (MC-QDPT)".[1] It is a multiconfiguration basis *multi*-reference-state method based on van Vleck PT and includes multireference Møller–Plesset PT, a *single*-reference-state method based on Rayleigh–Schrödinger PT, as a special case. In particular, a version of MC-QDPT proposed later uses *general* multiconfiguration reference functions (GMC-QDPT or GMC-PT).[2] GMC-QDPT imposes no restriction on the reference space, so it is much more compact than complete active space (CAS)-based MRPT. In addition, since it can avoid unphysical multiple excitations, it is numerically stable.

Several years ago, we extended GMC-QDPT to a relativistic version with four-component general MC reference functions and applied it to the potential energy curves of I_2 and Sb_2 , and the excitation energies of CH_3I , etc.[3,4] These were the initial application of relativistic MRPT to molecular systems to the best of our knowledge.

In the presentation in ISTCP7, we present some applications to the excited states of several heavy-element complexes. The calculated excitation energies for $[PtCl_4]^{2^-}$, $[PtBr_4]^{2^-}$, and $[PtCl_6]^{2^-}$, for example, were in very good agreement with available experimental data. The maximum and average deviations were 0.18 and 0.08 eV, respectively, which were better than time-dependent density functional theory results. We also present an efficient simplified form of GMC-QDPT and a Kramers unrestricted simplified MCSCF method.

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IDEAS OF RELATIVISTIC QUANTUM CHEMISTRY

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Fundamental breakthroughs have recently been achieved in relativistic quantum chemistry for both electronic structure and magnetic properties:

(1) Electronic structure

For any quantum mechanical calculation one has to first choose an electronic Hamiltonian, the best of which must be something between the Dirac and Schrödinger equations. Here we propose an exact two-component (X2C) equation[1-6], which is conceptually simple, numerically accurate, and computationally efficient. In addition, it serves a seamless bridge between the Dirac and Schrödinger equations, in the sense that it allows for relativistic treatment of the heavy atoms and non-relativistic treatment of the light atoms in the molecule in a natural manner.

(2) Magnetic properties

Four-component relativistic theory of magnetic properties such as NMR shielding tensor is formally very simple: It consists only of a single term, the paramagnetism. Yet, it is plagued by two fundamental issues. Conceptually, the diamagnetism known from non-relativistic theory is "missing". Computationally, such a standard formulation is very demanding on basis functions of high angular momenta. Herewith we propose several strictly equivalent approaches [7-9] based on the generic ansatz of orbital decomposition [10, 11]. Not only does the diamagnetism arise naturally, but also is the computation simplified greatly. The X2C counterparts have also been formulated in a most general way [12].

The X2C Hamiltonian can be combined with know-how correlation methods so as to generate a new generation of relativistic many-body theories for the whole Periodic Table of elements.

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Recent development of the fragment molecular orbital method Dmitri G. Fedorov NRI, AIST, Japan

The fragment molecular orbital (FMO) method [1] enables large scale quantummechanical calculations of systems containing thousands of atoms, using conventional methods such as RHF, DFT or MP2. In FMO, the system is divided into fragments, and the total properties are computed from those of fragments and their pairs. Recent progress in the method development will be reviewed, including the fast geometry optimisation method FMO/FD [2], followed by a summary of recent applications [3]. More information about FMO including freely distributed software can be found in [4].



In FMO with frozen domain (FD), only the essential part of the system, polarizable buffer B including the active site A, is recomputed at each point in a geometry optimisation. The rest of the system, domain F, is computed only at the initial geometry. The complex of prostaglandin H(2) synthase-1 and ibuprofen, containing 19471 atoms at the B3LYP-D/6-31G* level for domain A and RHF/STO-3G for F was optimised in 32 h on 6 dual CPU quad-core 2.83 GHz Xeon nodes using GAMESS.

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Fragment molecular orbital calculations with ABINIT-MP(X)

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I. Introduction

The fragment molecular orbital (FMO) scheme proposed by Kitaura [1] has been one of promising recipes to treat large scale molecules such as proteins in a quantum mechanical manner with practical costs of computation through the natural parallelism. FMO-related methodological developments and associated applications have been achieved in diverse ways during this decade [2]. This presentation will cover various topics of FMO calculations performed with our original program, ABINIT-MP(X) [3,4].

II. Correlated calculations

Higher-order treatments up to CCSD(T) have been available with a hybrid parallelization of OpenMP/MPI. The FMO-CCSD(T)/6-31G job for a complex between HIV-1 protease (198 residues) and lopinavir could be processed in 9.8 h on the Earth Simulator (ES2) with 512 processors. The largest target was an influenza hemagglutinin trimer (HA3) with two Fab fragments (total 2351 residues) at the FMO-MP3/6-31G level, where this job was completed in 5.8 h with 1024 processes of ES2.

CIS(D) type calculations incorporating some higher-order effects have been used to evaluate the electronic transition energies of photoactive proteins as well as the hydrated molecules. The excitation energies of yellow- and blue fluorescent proteins (YFP and BFP) were estimated to be 2.53 and 3.36 eV, respectively, being in good agreement with the corresponding experimental values of 2.41 eV and 3.21/3.25 eV [5].

III. Molecular dynamics

Molecular dynamics (MD) calculations could be performed with the FMO-based energy gradients straightforwardly [6]. Several organic reactions in water were analyzed by FMO-MD, and the dynamical features such as diversity of pathway were revealed. The hydration structures of metal ions were simulated as well.

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Linear-Expansion Shooting Techniques for Accelerating Self-Consistent Field Convergence

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Based on the corrected Hohenberg-Kohn-Sham energy functional (cHKS) [1,2], we present a new method to accelerate self-consistent field (SCF) convergence by utilizing the shooting method in numerical analysis [3]. We have developed several different linear-expansion shooting techniques (LIST) by imposing different conditions [4]. Case studies show that overall our LIST methods are robust and efficient algorithms for accelerating SCF convergence. More importantly, the LIST methods outperform Pulay's DIIS [5,6] and its recent improvements, including EDIIS [7] and ADIIS [8].

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Chiral Spectroscopy: Towards a Reliable Comparison Between Theory and Experiment

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Chiral enantiomers — pairs of dissymmetric molecules that are merely mirror images of one another — often exhibit dramatically different chemical behavior when reacting in chiral environments, and the need to distinguish between such enantiomers drives much of the multibillion-dollar research efforts of the pharmaceutical industry. Enantiomeric pairs also exhibit mirror-image responses to circularly polarized electromagnetic fields in absorption (dichroism), refraction (birefringence), and scattering: if the left-hand enantiomer of a chiral compound preferentially absorbs right-circularly-polarized light, the right-hand enantiomer will preferentially absorb the left-handed light, and vice versa. However, such responses are useful for the identification of the handedness of a chiral sample only if a reliable reference is available. This lecture will focus on our recent work to establish high-level quantum chemical methods such as coupled cluster theory as just such a reference. [1, 2] In particular, we will discuss the impact of various physical factors — electron correlation, basis-set completeness, gauge invariance, molecular vibrations, and solvent — on the predictive capabilities of the coupled cluster model in comparison to both gas- and solution-phase measurements of optical rotation, electronic circular dichroism, and vibrational Raman optical activity. In addition, we will discuss approaches for reducing the computational scaling of coupled cluster methods in order to extend their range of applicability to large chiral molecules and explicit solvent configurations.^[3]

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Molecules in strong magnetic fields

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In strong magnetic fields, chemistry changes: electronic states change character, molecules change their shape, and their interactions with radiation are affected, often in a dramatic manner. Such magnetic-field induced changes are not only fascinating as a contrast to the chemistry observed on the earth, they are also relevant to astrophysics, where molecules in stellar atmospheres are subject to strong magnetic fields.

We have undertaken a quantum-mechanical study of molecules in strong magnetic fields, using a recently developed computer code for the calculation of manyelectron molecules at the Hartree–Fock, Kohn–Sham, full-configuration-interaction (FCI) and complete-active-space multiconfigurational self-consistent-field (CASSCF) levels of theory. Moreover, implementations of molecular gradients and linearresponse theory allow molecular structures and excitation energies to be studied in strong fields. Gauge-origin invariance is ensured by the use of London atomic orbitals.

Our calculations on molecular systems in strong magnetic fields have revealed and highlighted many interesting phenomena, such as the transition to diamagnetism of paramagnetic molecules in strong fields, changes in molecular structure such as the squeezing and flattening of ammonia, and large changes in excitation energies and oscillator strengths in strong fields. Typically, the most dramatic changes are observed at field strengths of about one atomic unit; in weaker fields, chemistry is dominated by electrostatics; in stronger fields, by magnetic interactions.

In the present talk, we concentrate on the role of electron correlation in magnetic fields, as described at the FCI and CASSCF level of theories, for small molecules. In particular, we shall study how the electronic states of small molecules change character with increasing magnetic field—resulting, for example, in a strongly bound He₂ molecule in the electronic ground state. In the future, our FCI and CASSCF code will be used to elucidate the role of the current dependence in the exchange–correlation functional of Kohn–Sham theory; our plans for such studies are outlined.

Near-Edge X-ray Absorption Fine Structure from Coupled Cluster Damped Response Theory using an Asymmetric Lanczos-chain driven algorithm

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Abstract

Coupled cluster methods are considered among the most accurate tools in electronic structure theory. Nonetheless relatively limited attempt seems to have been made to extend their applicability to the description of the core-excitation phenomena that are behind largely used spectroscopic techniques like x-ray absorption spectroscopy and x-ray circular dichroism.

As a first step to redeem for such situation, we present an implementation of damped response theory (aka complex polarization propagator approach) based on an asymmetric Lanczos algorithm for the CCS, CC2 and CCSD hierarchy of coupled cluster methods, and apply it to the simulation of the K-edge x-ray absorption spectra of various closed-shell systems, including Neon, CH₄, H₂O, HF and CO [1]. Triple excitation effects on the excitation energies are estimated by means of the CCSDR(3) approximation, and relativistic effects are accounted for using the Douglas-Kroll approach. Results are compared with experiment as well as results obtained with other computational methods.

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A study into the low-lying excited states of small and medium-sized molecules using the (unrestricted) ADC(2) scheme: a close comparison with experiment

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The algebraic diagrammatic construction (ADC) scheme is one of the scarce excited state methods [1] allowing for a direct comparison with experiment without *a priori* knowledge of the system under investigation. At the employed level, the ground and primary excited states are both calculated consistently up to second order of perturbation theory according to the well-known Møller-Plesset partitioning of the Hamilton operator. Strict and extended schemes [ADC(2)-s and ADC(2)-x] exist [2], in which the 2p–2h block is calculated within zeroth and first order, respectively.

In a study of the vertical excited electronic states of linearly fused polyacenes (PACs), it is shown that a combined application of both versions nicely reveals the importance of doubly excited configurations in the description of the excited state spectrum of neutral PACs. In contrast to general expectation, our calculations of the radical cations of the PACs employing unrestricted ADC(2)-s and ADC(2)-x identified one B_{1g} electronic transition whose excitation energy increases with increasing molecular size.

Since experimental gas-phase data for medium-sized radical molecules are generally only scarcely available in the literature, use has been made of photo-electron spectra (PES) of neutral molecules to further test the recently developed unrestricted ADC(2) methods. Indeed, adding the first ionization energy to the excitation spectrum of the radical compound gives rise to the PES of the neutral species. As a proof of principle, the ionization spectra of ethane, formaldehyde, formic acid and difluoromethane are simulated using the UADC(2)-s and UADC(2)-x schemes, applied to the radical cations at the singlet ground state equilibrium geometries. Since it is impossible within this theoretical approach to calculate partial overlaps between the neutral ground state and the cation, the reflection principle is used to compute intensities [3]. Comparison is made with experimental spectra as well as those obtained by the reflection principle using TDDFT/B3LYP data and by the established ionization-ADC(3) scheme.

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Quantum fluctuations can promote or inhibit glass formation

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Understanding the transformation of liquid into glass is one of the outstanding problems in the physical sciences. The major difficulty in understanding the glass transition is the fact that glass itself is an ill-defined state of matter: unlike a crystal, a glass is not a thermodynamic phase. Quantum mechanical systems ranging from electron liquids to superfluid helium appear to form glasses, but as yet no unifying framework exists connecting classical and quantum regimes.

Here we present new insights from theory and simulation into the impact of quantum fluctuations on glass formation. As intuition may suggest, we observe that

large quantum fluctuations serve to inhibit glass formation as tunneling and zero-point energy allow particles traverse barriers facilitating to movement. However, as the classical limit is approached a regime is observed in which quantum effects slow down relaxation making the quantum system glassier than the classical system. This dynamical 'reentrance' occurs in the absence of obvious structural changes and has no counterpart in the phenomenology of classical glass-forming systems.



Dynamic phase diagram calculated from a quantum mode-coupling theory for a hard-sphere fluid

T. E. Markland, J. A. Morrone, B. J. Berne, K. Miyazaki, E. Rabani and D. R. Reichman, "Quantum Fluctuations Can Promote or Inhibit Glass Formation", *Nature Physics* 7, 134-137 (2011).

3B2-3I

Extended Concept of Solvation toward Unified Analysis of Molecular Binding in Weakly Ordered Systems

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A key function of such weakly ordered systems as lipid membrane, micelle, and protein is their ability of acting as a host and binding other molecules. In the present work, a diverse class of binding is treated in unified manner as the solvation in an extended sense. The basic idea is view a solution system with host structure (membrane, micelle or protein) as a mixed solvent. The host is described not as solute species, but as part of the mixed solvent system, and the guest molecule is the only species regarded as the solute. A unified treatment is then implemented as the solvation in a mixed-solvent system, which often involves nano- or mesoscale inhomogeneity.

The key quantity governing the binding ability is the standard change of free energy. Within the (extended) notion of solvation, the quantity of interest is the solvation free energy, the reversible work to introduce the solute-solvent interaction. The free energy is notorious, however, for its heavy computational demand. A fast and accurate computation of free energy is a major challenge of theoretical/computational chemistry at present. We approach the free-energy computation by combing the molecular simulation with a statistical-mechanical theory of solutions.

Since the notion of solvation is not only extended to abovementioned nano-organized systems, but is also strongly desired to handle such emerging systems as ionic liquid, supercritical fluid, and quantum-classical coupled system, the theory of solutions needs to be (re-)formulated to treat these frontline subjects. To meet this necessity, we present a new type of solution theory called the method of energy representation. In this method, the solute-solvent distribution is expressed over the one-dimensional coordinate of solute-solvent pair interaction energy, and the energy distribution functions in the solution and reference solvent systems constitute an approximate but accurate functional for the solvation free energy. The method achieves a high computational efficiency compared to the standard free-energy perturbation method, while no deterioration is observed in terms of the agreement with experiment.

Two types of application are discussed. One is the molecular binding into lipid membrane and micelle. The distribution of hydrophobic solutes is investigated in DMPC bilayer and SDS micelle. Water is shown to delocalize the spatial distribution of hydrophobic solutes within DMPC membrane. The interaction of transmembrane protein with lipid membrane is also examined and the driving force of binding is discussed.

The other is the cosolvent effect on protein stability in aqueous system. Water and the cosolvent such as urea are viewed as mixed solvent, and all-atom analysis of protein solvation is conducted. The "direct" and "indirect" effect of cosolvent is examined by decomposing the solvation free energy into the water and cosolvent contributions.

Computation of reaction free energies by the QM/MM-ER approach - Exact treatment of the many-body interactions -

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I. Introduction

Reaction pathway in a condensed phase with thermal fluctuation is governed by the free energy change associated with the reaction. It is, therefore, a matter of great significance to develop an efficient methodology to compute free energy change. For this purpose we recently proposed a novel method, termed QM/MM-ER[1], by combining the QM/MM approach with the theory of energy representation (ER)[2]. In formulating QM/MM-ER, however, a difficulty arises from the fact that the QM-MM interaction is *not* pairwise additive. Here, we report a simple and *exact* approach to compute free energy contributions due to the many-body interactions.

II. Methodology

The point of the QM/MM-ER method is to split the total solvation free energy $\Delta \mu$ into two contributions, that is, the free energy $\Delta \bar{\mu}$ due to the two-body interaction and the others $\delta \tilde{\mu}$. We show that the free energy $\delta \tilde{\mu}$ originating from many-body interaction can be formulated by introducing an energy coordinate η which contains the solute-solvent interaction energy due to the electronic polarization of the QM solute. In terms of the distribution functions $Q(\eta)$ and $Q_0(\eta)$, respectively, for solution and reference systems, the free energy $\delta \tilde{\mu}$ corresponding to the electron density fluctuation around an arbitrary fixed electron density \tilde{n} can be evaluated exactly without any approximate functional. Thus, the total solvation free energy $\Delta \mu$ at temperature T can be simply expressed as

$$\Delta \mu = \Delta \bar{\mu} + \delta \tilde{\mu} = \Delta \bar{\mu} + \int d\eta \left[k_{\rm B} T Q(\eta) \ln \left(\frac{Q(\eta)}{Q_0(\eta)} \right) + \eta Q(\eta) \right] \tag{1}$$

In Eq.(1) $\Delta \bar{\mu}$ is the solvation free energy of a QM solute with the electron density fixed at \tilde{n} , which can be computed with the standard version of the method of energy representation.

III. Benchmark test calculation

To test the performance of Eq.(1), we computed solvation free energy of a QM water molecule into MM water solvent. The QM solute is described by DFT with BLYP functional, while the MM solvent is represented by 499 SPC/E water molecules. The thermodynamic condition of the solution was set at T = 300 K, and $\rho = 1.0$ g/cm³. Then, the solvation free energy $\Delta \mu$ was obtained by Eq.(1) as -6.5 kcal/mol, which shows excellent agreement with the experimental value of -6.3 kcal/mol. This result clearly suggests the efficiency of the new approach.

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Classical Cumulant Dynamics

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We have proposed a quantal cumulant dynamics (QCD) method for the investigation of weak quantum effects on model and molecular systems including proton transfer reactions [1-3]. The essence of this method is to treat with an extended dynamics of distribution characterized as expectation values generating from the distribution. Within this scheme, not only the position and momentum but also the cumulant variables, which are functions of mixed position and momentum moment operators plays central role in its propagation. In the present study we utilized the same procedures to treat problems appearing in classical statistical mechanics. We referred to it as classical cumulant dynamics (CCD). The same kind of methodology was proposed by Prezhdo and co-workers. In their method, the expectation value of the total energy is directly substituted into the Boltzmann factor that results in introduction of an additional prefactor for rescaling the inverse temperature in order to apply their theory to the exactly soluble models such as the free-particle and the harmonic oscillator [4]. For the harmonic oscillator, the Boltzmann factor substituting the expectation value of the total energy $\langle H \rangle$ is expressed as

$$Q_{c} = \exp\left(-\beta\left(\frac{1}{2}\left(p^{2} + \lambda_{0,2} + \omega^{2}q^{2} + \omega^{2}\lambda_{2,0}\right)\right)\right),$$

where β is the inverse temperature and $\lambda_{m,n}$ is the *m*-th and *n*-th order cumulant variables with respect to the coordinate and momentum. With our 2nd-order cumulant variables approximation to the expectation values, we demonstrate that the expectation value of the Boltzmann operator $Q = \langle \exp(-\beta H) \rangle$ has quite different structure as

$$Q = \tau^{-1/2} \exp\left(-\frac{1}{2}\beta\tau^{-1}(\tau_{0,2}q^2 - 2\tau_{1,1}pq + \tau_{2,0}p^2)\right),$$

where $\tau_{2,0} = 1/\omega + \omega\beta\lambda_{2,0}$, $\tau_{1,1} = \beta\omega\lambda_{1,1}$, $\tau_{0,2} = \omega(1 + \beta\lambda_{0,2})$, and $\tau = \tau_{2,0}\tau_{0,2} - \tau_{1,1}^2$ are effective cumulant variables. The former approximation is derived from an approximation of the expectation value of the Boltzmann operator as $\langle \exp(-\beta H) \rangle = \exp(-\beta \langle H \rangle)$. The latter has pq and $\lambda_{1,1}$ dependence, but the former does not. Integration of the latter Boltzmann factor within phase space gives exact distribution function $Z_{\rm HO} = 1/\beta\hbar\omega$. On the other hand, the later still has additional term to be cancelled. With these Boltzmann factors, the statistical average of the energy can be derived. We found that in the high temperature limit both Boltzmann factors result in giving the same energy.

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Molecular modeling of the dynamics and structure of molecular aggregates in liquid solution and their spectroscopic signature

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In this talk, I will present three examples of our ongoing attempts towards developing a theoretical and computational framework for modeling the dynamics and structure molecular aggregates in liquid solution and its spectroscopic signature

In the first example, I will discuss our attempts to model the recently observed signatures of coherence transfer in the 2DIR spectra of dimanganese decacarbonyl in liquid cyclohexane. To this end, we describe the system in terms of a vibrational excitonic Hamiltonian and the dynamics in terms of a quantum master equation that can account for population relaxation, dephasing, coherence-to-coherence transfer and coherence-to-population transfer. A unique feature of our approach is that, in principle, it does not rely on any adjustable fitting parameters. More specifically, the anharmonic vibrational Hamiltonian is derived from ab-initio electronic structure theory and the system-bath coupling is expressed explicitly in terms of liquid degrees of freedom whose dynamics can be obtained via molecular dynamics simulations.

In the second example, I will discuss our attempts to model the unique spectroscopic signature of nonequilibrium dynamics in the case of hydrogen-bonded methanol oligomers in methanol/carbon-tetrachloride liquid mixtures. To this end, we employed a mixed-quantum classical approach where the hydroxyl stretch of one of the methanol molecules is treated quantum mechanically, while the remaining degrees of freedom are treated classically. The ability of different force fields to reproduce the experimental absorption, emission and pump-probe infrared spectra of the hydroxyl stretch was examined as well as the insights it gives regarding hydrogen-bonding structure, dynamics and photochemistry. I will also show how nonlinear mapping relations between the hydroxyl transition frequency and bond length and the electric field along the hydroxyl bond axis can be used in order to reduce the computational cost of the mixed quantum-classical treatment to that of a purely classical molecular dynamics simulation. In the third example, I will discuss our attempts to understand the photochemistry of electronically photoexcited silsesquioxanes octa-functionalized by organic dyes. I will present evidence from DFT calculations that employ range-separated hybrid functionals and from continuum and mixed quantum-classical solvation models for the emergence of dark states involving charge transfer between dyes. I will argue that these charge transfer states are responsible for the unusually large Stokes shift between the electronic absorption and emission spectra of these systems in comparison to the individual dyes, and that these systems can be thought of as dye aggregates held together by the otherwise inert silsesquioxane cage.

Multi-Exciton Dynamics in Molecular Aggregates

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Excitation energy transfer in supramolecular architectures covers a broad range of dynamical regimes, depending on the electronic properties of the constituent dye building blocks, their mutual Coulomb interaction, and the coupling to vibrational degrees of freedom and to some solvent environment. In view of the size of these complexes quantitative insight can be provided only by combination of first principles simulations of parametrized models yielding spectroscopic observables.[1]

In the first part of this presentation, electronic structure theory is utilized to construct a Frenkel exciton Hamiltonian for a J-aggregate-forming perylene bisimide dye (see figure). In particular it will be shown that the optical properties are strongly dependent on the aggregate size. In accord with experimental fluorescence studies, the J-aggregate turns into an H-aggregate with decreasing number of monomers.

On the basis of this Frenkel exciton Hamiltonian quantum dynamical simulations are performed putting emphasis on the interplay between laser-driven



multi-exciton generation, exciton-vibrational coupling, and exciton-exciton annihilation.

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3B3-5C

Mixed Quantum-Classical Description of Excitation Energy Transfer in a Model Fenna-Matthews-Olsen Complex

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The Fenna-Matthews-Olsen (FMO) complex has recently become a paradigmatic model system in terms of understanding the long-lived electronic quantum coherence that has been experimentally observed in photosynthetic systems. We offer an investigation of the quantum dynamics of an FMO model within a mixed quantum-classical dynamics approach known as the Poisson bracket mapping equation (PBME), and explore the consequences of adopting this approximate description by simulating population transfer and electronic coherence. The results obtained via the Poisson bracket mapping formalism are explicitly compared with a selection of recent results on the FMO complex. The PBME is shown to be in excellent agreement with benchmark computational results at physiological temperature, and thus provides a computationally efficient and physically consistent algorithm that may be easily integrated in all-atom molecular dynamics simulations.

Reduced Hierarchy equations of motion approach to multidimensional spectroscopies of biological systems

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In complex media such as molecular liquids and biological systems, multidimensional spectroscopy has been shown to be variable tools due to the sensitivity of nonlinear response functions. In this talk, we first give an overview of reduced hierarchy equations of motion approach focusing on its theoretical background and applications to multidimensional spectroscopies. We then apply this methodology to see a possibility to explore a role of dissipation and fluctuation on quantum dynamics of biochemical systems. As the observables of linear and two-dimensional (2D) spectroscopies, the first- and third-order response functions of polarization are calculated for different physical conditions. The profiles of the 2D spectra reflect variety of heat-bath effects including dissipation, fluctuation, dephasing and inhomogeneous broadening.

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Bridge-mediated electronic coupling between two excited states, calculating based on the localized Slater determinant

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I. Introduction

The excited energy transfer (EET) is a fundamental reaction in various energy-exchange processes between photons and others. The EET rate is proportional to the square of the electronic coupling between the initial and final electronic states in weak coupling regime. The electronic coupling can be influenced by the bridge fragment connecting between the donor and acceptor. The Green's function technique with the perturbation of the donor-bridge/ acceptor-bridge interactions is often employed to calculate the bridge-mediated electronic coupling.

II. The electronic coupling

We improved a computational method to calculate the electronic coupling including effects of surrounding bridge fragments. The donor, acceptor and bridge groups are defined using the localized excited-state configurations constructed by the localized molecular orbitals (LMO) [1]. The electronic coupling calculation is generalized from the atomic orbital (AO) based to Slater determinant based. The approach has an advantage to reduce the approximation level of the Green's function technique from the perturbation of chemical-bond interaction (between AOs) to the perturbation of the configuration interaction (between Slater determinants). The method is applied to the EET reaction concerning to the pair of an electron and hole.

III. EET pathways in model systems

The LMO determinant makes convenient view for the pathway analysis of the electronic coupling on the bridge area. We categorized indirect pathways into three types of mediating bridge configurations as in Figure 1. In these pathways, the

through-exciton is long-range and charge transfer (CT) is short-range terms. The through-direct CT can be in the direct-term category driven by the Dexter mechanism. We applied the method to EET model systems with the donor, bridge and acceptor fragments and calculated the electronic coupling as well as the direct and through-bridge terms. We analyzed how each localized excited-state configuration contributes to the whole electronic coupling.



Fig.1 Types of direct and indirect pathways of EETs.

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Nonadiabatic theory in electron wavepacket dynamics

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Nonadiabatic transition is one of the most important and interesting quantum effects in chemical dynamics, in which sudden change in electronic states takes place. There have been proposed so many theoretical methods to treat such nonadiabatic transitions ranging from the very classic theories of Landau, Zener, Stueckelberg to state-of-the-art theories such as Zhu-Nakamura, the fewest switch surface hopping method and natural decay of mixing, and indeed their contributions to the progress of elementary dynamical processes of chemical reactions have been enormous. Yet, due to the rapid progress of experimental studies, we quite often face complicated and difficult experimental situations that have not been studied before. For instance, we are often interested in systems of densely degenerated electronic states, in which the concept of Born-Oppenheimer adiabatic potential energy surface (PES) can make only a weak sense due to the energy-time uncertainty relation. In those cases the nonadiabatic theories based on an assumption of transition among a few (mostly two) PESs at a time should be accordingly reformulated. Furthermore, advances in laser technology now make it possible to modify native molecular electronic states with an intense electromagnetic vector potential, which can induce novel nonadiabatic coupling in addition to the native one. Such nonadiabatic chemistry in intense laser field clearly constitutes a strong driving force to establish new theories of nonadiabatic transition.

In this talk, we report our recent theory of nonadiabatic transition from the view point of electron wavepaket dynamics [1]. In particular, we discuss the fundamental features of nonadiabaticity and quantum entanglement in electron-nucleus dynamics. We also discuss the interaction of molecular nonadiabatic states with intense laser fields [2]. It is also stressed that even without laser fields the dynamical electron theory can offer a useful tool to analyze and conceptualize chemical reactions. The present theory may be regarded as a general theory of mixed quantum-classical dynamics in which quantum and classical subsystems kinematically contact each other, letting the quantum mechanical entanglement survive in the classical subsystem.

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Stochastic Time-Dependent Current-DFT: a functional theory of open quantum systems

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"Standard" density-functional methods can only deal with Hamiltonian dynamics, and not with open quantum systems, namely systems dynamically coupled to baths/reservoirs. There is, however, a large class of physics problems where one needs to consider this interaction explicitly. These include energy relaxation and dephasing, non-radiative decay, quantum measurement theory, etc. In order to address these issues, we have introduced a new theory we have named Stochastic TD-CDFT [1,2] and extended it to the correlated motion of electrons and ions [3]. I will describe this theory in detail, its range of applicability, and show some applications with and without ionic motion.

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On the nonadiabaticity of molecular quantum dynamics

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We propose to measure nonadiabaticity of molecular quantum dynamics [1,2] rigorously by the quantum fidelity between the Born-Oppenheimer quantum dynamics and the full nonadiabatic quantum dynamics. It is shown that this measure works in situations where the standard criteria (such as the magnitude of nonadiabatic couplings, energy-gap criterion or the population transfer) fail to detect nonadiabaticity. Our nonadiabaticity criterion is estimated efficiently with a generalization of the dephasing representation (DR) [3,4] of quantum fidelity to several potential energy surfaces and its computational cost is the cost of dynamics of a classical phase space distribution. It can be implemented easily into any molecular dynamics program and also can utilize on-the-fly ab initio electronic structure information. The methodology is tested on three model problems introduced by Tully, photodissociation of NaI, and the 18-dimensional on-the-fly CASSCF nonadiabatic dynamics of the methaniminium cation. The results show that unlike the mixed quantum-classical methods such as surface hopping or Ehrenfest dynamics, the DR can capture more subtle quantum effects than the population transfer between potential energy surfaces (see Figure). Hence we propose using the DR to estimate the dynamical importance of diabatic, spin-orbit, or other couplings between potential energy surfaces. The acquired information can help reduce the complexity of a studied system without affecting the accuracy of the quantum simulation.

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Figure. An example of a nonadiabatic transition detected by fidelity but unnoticed by the population transfer criterion.



Photo-excited Non-adiabatic Dynamics in Nano Materials

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Confinement of charge carriers in quantum dots (QDs) of sizes smaller than the Bohr exciton radius of the corresponding bulk material determine the electronic properties of the QD, leading to a variety of applications.[1] High cross-sections for light absorption make QDs excellent materials for photovoltaic devices. Further advantages of QDs in photovoltaic devices are due to the possibility of generating multiple electron-hole pairs upon absorption of a single photon. This is called the inverse Auger process, and provides great potential for increasing solar energy conversion efficiencies relative to those in bulk systems. It provides new mechanisms for utilization of the excess photon energy and avoiding energy loss to heat.



We have recently developed an atomistic simulation method for studying the Auger and inverse Auger processes, where single exciton (SE) and double exciton (DE) generation and annihilation are allowed to happen simultaneously. Our atomistic simulation is performed by directly solving the time-dependent Schrödinger equation with the NA couplings and energies obtained by the time-domain *ab initio* simulation on a Ge QD. Our simulation elucidated a dephasing process and a new mechanism, the phonon-assisted Auger process, which are both important for understanding the Auger and inverse Auger processes in QDs. We also found that the DE generation dynamics starting from the SE states depend upon the initial excitation energies and that its generation rate increases as the initial excitation energy increases. The population relaxation of the initially excited DE states indicated that the lowest DE state is most strongly coupled to the SE states and can be a main gateway to the Auger process. The insights obtained from our simulations will be important for improving the efficiency of solar energy conversion using QDs.[2]

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Simple wavepacket modeling of electron and nuclear dynamics

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Introduction

The current main-stream of theoretical/computational chemistry appears to be directed toward highly-accurate first-principles large-scale computational technologies. As an alternative, we are developing a simple and semi-quantitative method based on the Gaussian wavepacket (GWP). It has some similarity to the conventional thawed GWP [1], but has an advantage that the extended Hamiltonian formalism offers a pictorial view of effective quantum potential, an aspect shared with the expectation-value approaches such as the quantized Hamilton dynamics [2] and the quantized cummulant dynamics [3].

Semiquantal time-dependent Hartree approach

We will first briefly review the approach with applications to: a system-bath model deriving a semiquantal generalized Langevin equation [4], the geometric isotope effect of hydrogen-bond structure [5], the kinetic isotope effect in the adiabatic hydrogen transfer rate [6], and a realistic molecular dynamics simulation of liquid water [7].

Valence-bond electron wavepacket approach

The theory was extended to take account of the anti-symmetry of electronic wavefunctions by exploiting the valence-bond theory. To overcome the so-called N!-problem steming from the non-orthogonality of the wavepacket orbitals, various decoupling approximations to electron-pairs are examined [8]. Encouraging results have been obtained with use of a single floating and breathing wavepacket orbital per electron.

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Dynamics of Biomembranes in nano- to micro-meter scales

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Bilayer membranes exhibit many interesting phenomena such as shape deformation induced by phase separation or chemical reaction, membrane fusion, and membrane fission. Since the length scale of these phenomena widely varies from nano- to micrometer scale, different types of membrane models are required to simulate each length scale [1]. Thus, we have developed two types of membrane models: solvent-free coarse-grained molecular model [2,3] and meshles membrane models [4]. In these models, we can widely vary membrane properties such as the fluidity, bending rigidity, and the line tension of membrane edges. We will present self-assembly into vesicles, membrane fusion, and vesicle rupture using these simulation models.



Fig. 1: Sequential snapshots of vesicle rupture to worm-like micelle.

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Roles of Water and ATP in Functioning of ATP-Driven Proteins

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Upon the biological self-assembly, the number of accessible translational configurations of water in the system increases greatly, leading to a large gain in the water entropy. Using our theoretical methods wherein this effect is treated as the key factor, we have succeeded in reproducing the thermodynamic data of apoplastocyanin folding [1], elucidating the pressure [2] and cold [3] denaturation of proteins, suggesting a measure of thermal stability of proteins [4], and developing a free-energy function which is capable of discriminating the native fold from misfolded decoys [5]. The tool is either the three-dimensional integral equation theory [6] or the angle-dependent integral equation theory [7] combined with the morphometric approach [8].

We believe that the water-entropy effect plays critical roles in the functioning of ATP-driven proteins. We have recently made significant progresses in the following subjects: (1) the unidirectional movement of a linear-motor protein along a filament [9]; (2) rotational mechanism of F_1 -ATPase [10]; and (3) insertion of an unfoled protein and release of the folded one into and from the chaperonin GroEL [11]. In this talk, I will discuss the roles of water (especially, its translational entropy) coupled with the cycle of the ATP binding, hydrolysis, and release of the products (Pi and ADP) in the functioning of these ATP-driven proteins.

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Resolving Mixed Protein Amyloid-Aggregate Distributions

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I. Introduction

Although the correlative evidence relating the presence of amyloid fibrils and certain disease states (e.g. Alzheimer's disease and Type 2 Diabetes) is overwhelming, a direct causative role for amyloid has proved harder to establish. Current thinking links a certain region of the aggregate protein size distribution, the so called 'early aggregate' domain to cellular toxicity. Further development of this hypothesis is dependent upon the availability of techniques capable of finely resolving amyloid protein aggregate distributions. Size exclusion chromatography (SEC) is a powerful technique for separating mixtures of components on the basis of their molecular dimensions. In this paper we investigate the theoretical potential of SEC for resolving mixtures of protein aggregates (of various sizes and shapes) produced in the generation of amyloid fibrils presenting our findings in the form of an equilibrium model. We first discuss the general characteristics of SEC and then review the physicochemical basis of the phenomena of preferential partition. We demonstrate a new method for estimating partition coefficients for the various components of aggregate mixtures on the basis of their molecular dimensions. Finally we detail procedure for relating SEC column characteristics to their likely resolving power for a given aggregate size range. This information should provide a basic appreciation of the competing factors at work and allow for an informed choice to be made, prior to commencement of experiment, for selection of the optimal SEC column media to achieve efficient separation of a desired range of aggregate size distribution.



Fig. 1: In this talk we examine the problems associated with physically resolving protein amyloid aggregates and quantitatively interpreting their elution profiles using the technique of size exclusion chromatography.

3D1-6C

Adding Dynamical Insight to Protein X-ray Images by Solution and Crystal Molecular Dynamics Simulation

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Decades of investigation have confirmed the importance of protein dynamics for biological functions. X-ray crystallography has been playing the major role in structural biology, providing information on protein conformations. However, interpretation of this data is not always trivial. While proteins are flexible and adopt different conformations, X-ray structures represent only a single snapshot of the conformational ensemble. Some structures may represent conformations that are indeed most stable in solution environment, while some may be unrepresentative of the physiologically relevant forms since they may be subject to artificial forces such as crystal packing. At present, there is no general guideline for interpretations of X-ray structures.

Here we compare solution and crystal lattice molecular dynamics (MD) simulations¹ to add dynamical insight to the interpretation of X-ray images. As a model system we consider the dimeric λ Cro transcription factor² whose crystal structures range from a closed DNA-free conformation to an open DNA-bound form. Here we attempt to unveil the true solution structures of the dimer and the extent of energetically accessible conformations using Replica Exchange Molecular Dynamics³ in explicit solvent. The simulated conformational ensemble shows remarkable correlation with available X-ray structures. Clustering and network analysis¹ together with free energy profiles constructed along the open/closed transitions of the dimer reveal an ensemble dominated by open and closed dimer forms, with a modest barrier separating these two states. Intersubunit salt bridging between Arg4 and Glu53 during simulation stabilizes closed conformations, but open states are clearly accessible and relatively stable. Thus, Cro-DNA binding may not entail large conformational change relative to the dominant dimer forms in solution, supporting an extension of the "conformational selection" model. Our results provide a robust description of Cro conformational space in solution and reveal the functional context of available X-ray structures.⁴ Our methods of performing crystal MD simulations may also improve the interpretation of other protein X-ray images to aid in establishing structure-function relationships.

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Giant enhancement of the second hyperpolarizabilities of open-shell singlet molecular systems by an external electric field and donor-acceptor substitution

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We have theoretically found an external field (*F*) induced giant enhancement of the second hyperpolarizability γ of open-shell singlet systems with intermediate diradical characters [1]. As realistic examples, we examine the field effects on the γ of polyaromatic diradicaloid having intermediate diradical character, *s*-indaceno[1,2,3-*cd*;5,6,7-*c*'*d*']diphenalene (IDPL), in comparison to a closed-shell analogue of similar size composed of two pyrene moieties (PY2) by carrying out spin-unrestricted density functional theory, LC-UBLYP, calculations (see Figure 1) [2].

For IDPL, the field-induced enhancement ratio is estimated to reach 4 orders of magnitude for an electric field of 0.0077 a.u., whereas it is less than a factor of 2 for PY2. Moreover, an enhancement is also observed by substituting both-end phenalenyl rings of IDPL by donor (NH₂)/acceptor (NO₂) groups but this enhancement is limited to about two orders of magnitude. These enhancements are associated with a reduction of the diradical character - and therefore an improved thermal stability as well as with the appearance of substantial Type-I contributions to γ .



Figure 1. Static electric field (F) effect on γ [a.u.] of IDPL and PY2 calculated by the LC-UBLYP/6-31G* method.

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Nonlinear chiroptical properties and spectroscopies

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In this talk the speaker will review the latest developments in the theoretical and computational studies of nonlinear optical properties and spectroscopies involving the concept of chirality.

The results of a combined experimental-computational analysis of the two-photon circular dichroism of some bi-aryls (BINOL, VANOL, VAPOL) exhibiting structural chirality will presented. The challenges faced in the *ab initio* calculation of nonlinear optical properties in molecules of the size and complexity of those mentioned just above will be discussed. They involve the careful choice of appropriate basis sets, electronic structure and condensed phase models, besides the need to account properly for the

effect of molecular vibrations, conformational variety and magnetic gauge origin invariance [1].

The focus will then shift to other nonlinear spectroscopic properties, proven to be amenable to ab initio simulation resorting to the tools of modern analytical response theory: excited state electronic circular





dichroism, circular intensity difference arising in second harmonic generation and a general family of birefringences and dichroisms arising in the interaction of radiation with chiral samples [2]. Special emphasis will be on the phenomenon of



asis will be on the phenomenon of magnetochirality, the axial birefringence and the related dichroism observed when an unpolarized light beam interacts with chiral sample in the presence of a magnetic field with a component parallel to the direction of propagation [3].

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Theoretical Study of Gas-Adsorption to Metal-Organic-Framework (MOF)

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Metal-organic framework (MOF) attracts a lot of recent interests as separate absorption material, functional material, and catalyst. For instance, the Hoffmann type MOF induces the high spin (HS) to low spin transition (LS) by CS_2 adsorption.¹ Theoretical evaluation of interaction between gas molecule and MOF is necessary for well understanding of such functions of MOF and further development of the MOF chemistry. However, the evaluation of the interaction is not easy because of its very large size. Here, we wish to report highly reliable approximate method to evaluate binding energy of molecular cluster and its application to the interaction between gas molecule and MOF. Also, we wish to report the high-spin to low-spin transition of the Hoffmann type MOF by CS_2 adsorption.

In our new method, the binding energy of molecular cluster/complex is provided by eq 1,²

 $BE = BE(HF) + \Sigma [BE(Mi-Mj)^{MP2.5} - BE(Mi-Mj)^{HF}]$ (1) where HF represents the Hartree-Fock method, and Mi etc. represents a molecule involved in the molecular complex. This equation can be derived based on the MP2 and MP3 energies.

We applied this method to evaluate the binding energy of CS_2 and CO_2 molecules with the Hoffmann type MOF $\{Fe(Pz)Pt(CN)_4\}_n$ (Pz = pyrazine); see Scheme 1.¹ In this MOF, CS_2 is sandwiched by two Pz molecules. The binding energy is not different very much between CS_2 and CO_2 when two Pz molecules are considered, but very different between them when total MOF framework is considered. Detailed discussion of the binding energy and the mechanism of the high-spin to low-spin transition will be presented in the talk.



Scheme 1

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Dehydrogenation Mechanism of Chemical Hydrogen Storage Materials: Catalytic Role of Metal

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Hydrogen is a promising choice of clean energy carrier for both transportation and stationary applications. Hydrogen storage materials via chemical approach have attracted intense interest nowadays. Varieties of promising materials, for instance metal-hydride and metal-N-H systems, have been developed in recent years with high hydrogen %wt and promising reversible hydrogen storage capacity. Molecular-level, mechanistic understanding of the hydrogenation and dehrogenation mechanisms of these hydrogen storage materials is critical for optimizing existing materials and rational development of novel hydrogen storage materials. In general, limited mechanistic information is available in experimental studies. Theory provides a powerful and insightful complementary approach to map out the detailed mechanism and understand the governing factors of the thermodynamics and kinetics of requirements of a particular hydrogenation/dehydrogenation reaction. In this presentation, we report our computational studies of the dehydrogenation mechanisms of several boron-based metal-N-H systems. We found that the various stages of H₂ release of these hydrogen storage materials are characterized by a common two-step mechanism: hydride transfer followed by H₂ release. The metal atom plays an important and crucial catalytic role in bringing two hydrogen atoms (H^{δ^+} and H^{δ^-}) in close proximity and lowering the activation barrier of hydrogen release. A similar catalytic role is found for metal-doped hydrogen storage materials.



Computational Molecular Electrocatalysis: The Role of Proton Relays in H₂ Oxidation and Evolution Catalysts

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The rational design of improved molecular electrocatalysts for small molecule activation (for example H₂, O₂, N₂, H₂O, CO₂) requires a detailed molecular level understanding of the energetic and mechanistic factors controlling the movement of protons and electrons during the catalytic cycle. Ni(P₂N₂)₂²⁺ complexes are a family of mononuclear nickel complexes with cyclic diphosphine ligands that incorporate amine bases, in a mimic of enzyme functionalities. The presence and positioning of the amine bases near the metal center is the critical, enzyme-mimicking structural feature for the activity¹ and the efficiency of these catalysts, as these bases facilitate the heterolytic cleavage or formation of the H-H bond while acting as proton relays in the management of the proton and electron movement during the catalytic cycle.

We will highlights computational studies (electronic structure and *ab initio* meta-dynamics calculations) of the catalytic cycles in $Ni(P_2N_2)_2^{2+}$ catalysts.

Proton-hydride species are key intermediates. H_2 oxidation and evolution proceed via heterolytic bond cleavage or formation of the H-H bond. We will discuss what we have learned about these catalysts, the importance of the proton relays, their number, their active and inactive states, and the role of solvent and water molecules in giving rise to fast turnover rates. The concept of proton relays is being extended to O_2 and N_2 reductions reactions as well as H_2O oxidation.



Typical Potential Energy Maps for Ni(P₂N₂)₂²⁺ Complexes Depicting the Role of Pendant Amine Relays in H₂ Oxidation or Evolution (shown here based on ΔG)

Acknowledgements:

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3D3-7C

Theoretical study of counter anion displacement in phenoxyimine-based catalysts of ethylene polymerization activated with perfluorophenylborate

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I. Introduction

The search for new catalysts of olefin polymerization focuses on the modification of both ligands [1] and counter anions [2]. At the same time, theoretical calculations accompanying experimental works help reveal intricate details of the polymerization mechanism. Knowledge acquired in this way will make it possible to design new catalytic systems *in silico*.

II. Results and Discussion

Certain phenoxyimine-based catalysts turned out to be exceptionally active in ethylene polymerization [3]. The energetic profiles of the polymerization process calculated by DFT for selected titanium bis(phenoxyimine) complexes activated with perfluorophenylborate indicate that the counter anion is very weakly bound to the cationic active site [4], unlike in metallocenes and numerous postmetallocene catalytic systems [5,6]. We believe that this fact might rationalize unprecedented activities of certain bis(phenoxyimine) catalysts.

We have also noticed significant structural flexibility of the cationic active sites formed after the activation and counter anion separation.

Table 1. Energetic barriers, kcal/mol.				
Catalytic system	Separation	Insertion		
Salan	14.9			
$Phenoyimine^{a}$	8.4	6.9		
$Phenoxyimine^{b}$	0.7			
Substituents at the imine N atom:				

^a methyl; ^b phenyl.

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Why the silica surface is negatively charged at pH=7?

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Silica surface is known to be negatively charged when the pH value is higher than 2-3. An average surface density of Si-OH of amorphous is suggested to be 4.6 Si-OH/nm², which is much lower than those of the "ideal surface" ~ 9.57 Si-OH/nm², assuming the geminal Si-(OH)₂, on quartz (0001) surface. Here, by using first-principles molecular dynamics simulations, we have found that water molecules dissociate into H⁺ and OH⁻, when new-cleaved quartz (0001) surface is immersed in the water. And the OH⁻ immediately bind chemically with Si and H⁺ bind chemically with Si-O^{*} radicals at the surface, the resulting Si-OH density is 5.72 Si-OH/nm² in average for different starting configurations and thermal conditions. The rest of Si-O^{*} radicals, presumably negatively charged, is at sub-surface regime and protected by new-formed Si-OH. This may be the fundamental reason that the silica surface is negatively charged.

3D4-1I

Toward Coherent Control in the Nanoscale

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Inelastic electron tunneling via molecular-scale junctions can induce a variety of fascinating dynamical processes in the molecular moiety. These include vibration, rotation, inter-mode energy flow and reaction. Potential applications of current-driven dynamics in heterojunctions range from new forms of molecular machines and new modes of conduction, to new directions in surface nanochemistry and nanolithography.

In the first part of the talk, I will discuss the qualitative physics underlying currentdriven dynamics in molecular-scale devices, briefly outline the theory we developed to explore these dynamics, describe the results of ongoing research on surface nanochemistry and molecular machines, and sketch several of our dreams and plans in these areas.

The application of light to control molecular motions and electronic transport in junctions is intriguing, since photonic (by contrast to electronic) sources offer (sub)femtosecond time resolution and tunable phase and polarization properties. One of several challenges, however, is the requirement of coherent light sources that are tightly localized in space. It is here that plasmonics offer an opportunity.

In the second part of the talk, we will combine plasmonics physics with concepts and tools borrowed from coherent control of molecular dynamics with two goals in mind. One is to introduce new function into nanoplasmonics, including ultrafast elements and broken symmetry elements. The second is to develop coherent nanoscale sources and apply them to coherent control of both molecular dynamics and electric transport in the nanoscale.



Several simple elements in what we envision developing into coherently controlled nanoplasmonics are schematically illustrated in Fig. 1. The T-junction of Fig. 1A guides electromagnetic energy traveling down the leg into one or the other of the two symmetry-equivalent arms of the junction. Figure 1B depicts a hybrid construct, which combines elements that provide local enhancement with elements that provide long distance propagation in order to minimize losses. The structural parameters of the construct are optimized using a genetic algorithm. Fig. 1C depicts a plasmonic nanocrystal, developed to separate an

incident plane wave into two frequency components and funnel each component in a different direction normal to the direction of incidence. To conclude the talk, we will return to nanoelectronics, and illustrate the application of plasmonics to control of transport in the nanoscale, with a view to ultrafast electric switches.

Hierarchical equations of motion for quantum dissipation and quantum transport

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In the mesoscopic world the nano-structured environment is not just of quantum in nature but also often nonperturbative and non-Markovian for its influence on the system of primary interest. In this talk, I will discuss the hierarchical equations of motion (HEOM) approach [1–4] that can be considered as a fundamental formalism in quantum mechanics of dissipative and open systems.

HEOM is formally equivalent to such as the Feynman-Vernon influence functional and nonequilibrium many-body Green's function formalisms [5], but numerically more implementable. It provides a unified treatment of various decoherence and quantum transport processes. It renders also a unified view on various existing approximated theories, such as the quantum master equation and stochastic Liouville equation [6], and consequently, often further results in some simple but important modifications to those conventional approximations [7].

I will also discuss about two recent developments, the best/minimum stochastic environment basis set for optimal HEOM construction [8] and the efficient on-the-fly numerical filtering algorithm [9], that significantly enhance the numerical tractability of the exact HEOM dynamics. Numerical results on the 2D spectrum of a model light harvesting antenna system and the quantum transport through Anderson model quantum dots system will be presented.

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Theoretical Study for Pseudo Degenerated Multi-electron Systems and Applications for Real Systems

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I. Introduction

Lately, organic and inorganic pseudo degenerated multi-electron systems have received much attention as nano-scale magnets, conductors and catalysts. The BS hybrid density functional theory (DFT) method has been applied to a various pseudo degenerated multi-electron systems with considerable success. Our group proposed an Approximately spin projection (AP) method and geometry optimization procedure based on the AP method, namely the AP-opt method. Then, we apply the AP and AP-opt method to the organic radical and metal containing systems.

II. Calculation results

As organic and inorganic pseudo degenerated multi-electron model systems, *p*-NPNN and Cu(II) ion containing artificial DNA systems are investigated.

The β -phase *p*-NPNN was found to be the first organic bulk ferromagnet below 0.6 K. First-principle calculations of its sign and magnitude are crucial for theoretical elucidation and understanding of the mechanism of its organic ferromagnetism. Here, in order to determine the effective exchange integrals for all four phase of *p*-NPNN crystals, hybrid density functional theory (HDFT) calculations are carried out for *p*-NPNN clusters, whose geometries are taken from the X-ray structures of the four different phase crystal. Moreover, Monte Carlo simulations are used to estimate its transition temperatures (*T*_c). the ferromagnetic transition temperatures (Tc) calculated using the J values calculate by UB2LYP (0.35) are 0.7 K. The obtained ferromagnetic transition temperature is in good agreement with the experimental result. Therefore, it could be concluded that the obtained results are in qualitatively agreement with the experimental results.

The magnetic and other physical properties between Cu^{2+} ions coordinated by salen –base pairs (Cu^{2+} –DNA) are examined by using DFT calculations. The total energies of the HS and the BS LS states are degenerated but J_{ab} values show weak anti-ferromagnetic couplings within the examined model structures. These results agree with Metal–DNA based on natural B-DNA. So, we can conclude that this artificial Metal–DNA system shows anti-ferromagnetic interaction, which is consistent with the experimental result. The Jab values strongly depend on the ligand structure caused by en but not backbones.

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Zero-field splitting tensors of arylnitrenes: A theoretical study

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Zero-field splitting (ZFS) is a separation of the electron spin multiplet sublevels of atomic/molecular systems in the absence of an external magnetic field. Its origins are spin-spin dipolar (SS) and spin-orbit (SO) couplings. Reliable first principle calculations of ZFS tensors (D tensors) are a long-standing issue in the field of electron spin science from the theoretical side. Recently, we have proposed a hybrid CASSCF/MRMP2 approach to quantitative calculations of the spin-orbit term of the **D** tensor (\mathbf{D}^{SO} tensor) [1–3]. This approach uses spin–orbit coupling matrices computed at the CASSCF level and MRMP2 energy difference in the sum-over-states formula, to efficiently eliminate errors in the \mathbf{D}^{SO} tensor arising from inaccurate CASSCF energies in the conventional SOS-CASSCF approach. In this work the hybrid approach is applied to spin-triplet arylnitrenes (Figure 1), focusing on the aryl ring size and topological effects on the **D** tensor.



The equilibrium geometry is optimized at the UB3LYP/6-31G* level. The \mathbf{D}^{SO} tensor calculations are carried out by the hybrid CASSCF/MRMP2 method with the cc-pVDZ basis set. The spin-spin part of the D tensor (D^{SS} tensor) is calculated by using McWeeny–Mizuno's equation with RO-HCTH/407/EPR-II spin densities [2,3].

The theoretical and experimental ZFS parameters $D (D = D_{ZZ} - (D_{XX} + D_{YY})/2)$ are summarized in Table 1. In all nitrenes under study, the spin-orbit contribution to Damounts to about 10%. Except for 6, the D^{SS+SO} value reproduces the experimental D

one within 10% of error. Errors in the calculations are possibly from the \mathbf{D}^{SS} term. Origins of the errors in the putative DFT-based **D**^{SS} tensor calculation will also be discussed.

<i>Table 1.</i> Theoretical and experimental <i>D</i> values.					
Molecule	$D^{\rm SS}/{\rm cm}^{-1}$	D^{SO}/cm^{-1}	$D^{\rm SS+SO}/{\rm cm}^{-1}$	$ D(\text{Exptl.}) /\text{cm}^{-1}$	
1	+0.8820	+0.1118	+0.9938	0.9978	
2	+0.6642	+0.0809	+0.7451	0.793	
3	+0.7925	+0.0965	+0.8890	0.925	
4	+0.5254	+0.0682	+0.5936	0.6625	
5	+0.6451	+0.0838	+0.7289	0.7779	
6	+0.3476	+0.0487	+0.3963	0.47	

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Interactions with electromagnetic fields: frequency-dependent magnetizability and electric permittivity

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Materials with a negative index of refraction are substances in which either one or both of the permittivity and the permeability of the medium is nega- tive. Whereas the permittivity of the medium is well defined and related to the frequencydependent polarizability, the dispersion behaviour of the permeabil- ity is not as well defined. The relation between the macroscopic permeability and the microscopic quantity describing the interaction with the magnetic com- ponent of the electromagnetic field, the frequency-dependent magnetizability, is in contrast poorly understood. Indeed, even the definition of the frequency- dependent magnetizability appear unsatisfactory.

A theory for the frequency-dependent magnetizability has been presented by Raab and de Lange [1], and these authors have also considered the frequency- dependent permeability [2]. However, the expression derived for the frequency- dependent magnetizability is based on a number of assumptions, making the theory somewhat unsatisfactory.

A macroscopic analysis of the interaction between matter and electromagnetic fields using multipole theory leads to origin-dependent expression of the material constants. Since material constants are observable quantities, we expect that multipole theory, which correctly describes several optical phenomena, would provide originindependent expression of them. Thus origin-independent definitions of the material constants, which describes the response of the matter to an external electromagnetic perturbation, should be derived.

In this talk, we will discuss our recent analysis of the frequency-dependent magnetizability, and propose a new way of deriving the frequency-dependent permittivity, inverse permeability and magnetizability starting from an analysis of the currentcurrent response function and of the scattering amplitude.

References

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Novel Polarization-Phase Selective (PPS) Models: Probing and Imaging Unusual Electronic Behavior

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We are developing novel PPS models with broad applications from ultrafast tunneling electron (wavefunction) probing and imaging in atoms and molecules (New J. Phys.) to the electron-proton transfer studies associated with metal clusters and substrates in proteins, enzymes and bio-hybrids (JBIC, JACS). We show that the models provide a very good insight into the drivers of the key redox electrons. Indeed, models of spin-coupling mechanisms and energy levels clearly indicate some unusual electronic behavior driven by the specific clusters and bio-ligands. They also provide theoretical framework for related electron properties and image morphing. The results of PPS modeling are now also confirmed by PPS structural characterization at NHMF Laboratory using very high magnetic fields. We expect that the new Split-Florida helix will facilitate these efforts.