

**Abstracts of Invited
and Contributed Talks, Sep. 7**

Interfacial dipole and geminate pair energetics at pentacene/C₆₀ heterojunctions

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Among the successive steps describing the light-to-electricity conversion process in organic photovoltaic cells, the splitting of the Coulomb bound electron-hole pairs at the donor/acceptor interface into free charge carriers remains an open question. The so-called electric-field assisted mechanism assumes that interfacial electric fields, arising from local interfacial dipoles, can favor the charge separation [1].

To characterize the dipole moments at pentacene/C₆₀ heterojunctions, we have coupled quantum-chemical and microelectrostatic (ME) calculations on molecular aggregates of various sizes and shapes. The results show that the interfacial dipoles mostly originate in polarization effects due to the asymmetry in the multipolar expansion of the electronic density distribution between the interacting molecules. The local dipoles are found to fluctuate in sign and magnitude over the interface and appear as sensitive probes of the relative arrangements of the pentacene and C₆₀ molecules [2].

Then, the geminate pair energetics at the pentacene/C₆₀ interface has been addressed by increasing the electron-hole separation across the interface. The results indicate that geminate pair dissociation critically depends on the orientation of the pentacene π -system relative to the adjacent C₆₀. Indeed, these calculations predict that recombination of the electron-hole pairs is favored over separation at the pentacene(011)/C₆₀ interface, while the geminate pair splitting can easily occur at the pentacene(01-1)/C₆₀ interface [3].

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Modeling Dynamic Electronic Processes in Organic Electronic Devices

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Some of the important electronic processes which occur in organic materials under device condition are electron-hole recombination, triplet-triplet annihilation, excited state quenching and fluorescent resonant energy transfer, to name a few. The electrons in molecules for organic devices experience strong correlations and need to be modeled by long range interacting electron models such as the Pariser - Parr - Pople model. Besides, to understand the cross sections for various processes, one needs to follow the real time dynamics of many of these processes. We discuss the results of our time dependent quantum many body studies of the various processes that occur in these materials under device conditions.

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Theories and applications for electronic coupling in electronic transfer and excitation energy transferChao-Ping Hsu

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The transport of charges and excitation energy are two processes of fundamental importance in diverse areas of research. Characterizations of electron transfer (ET) and excitation energy transfer rates are essential for a full understanding of many biological systems and opto-electronic devices. The electronic coupling factor is an off-diagonal Hamiltonian matrix element between the initial and final diabatic states in the transport processes. ET coupling is essentially the interaction of the two molecular orbitals (MOs) where the electron occupancy is changed. Singlet energy transfer (SET) contains a Förster dipole–dipole coupling term as its most important constituent. Triplet energy transfer (TET) involves an exchange of two electrons of different spin and energy; thus, it is like an overlap interaction of two pairs of MOs.

In the past, we have developed or improved the strategies for calculating ET, SET, and TET couplings. In the presentation, I plan to report (1) the theory and development in the characterization of SET coupling with application examples. The fragment excitation difference (FED) is developed to calculate SET coupling, which yields the overall coupling under the Hamiltonian employed, including the through-bond, exchange and orbital overlap effects. With FED and a precise account of the Coulomb coupling, the exchange and overlap effects on SET can be studied. And, (2) our recent progresses in the charge transport properties in tris(8-hydroxyquinolato)aluminum(III) (AlQ3). With intermolecular configurations derived from crystal structures, we found that most of the commonly seen configurations with π - π interaction are further stabilized with CH- π interactions involving other ligands on AlQ3. The CH- π interaction drives the structure of the AlQ3 pair towards a large lowest unoccupied molecular orbital (LUMO) overlap, and a small overlap in the highest occupied molecular orbital (HOMO), accounting for the preference in electron transport. This result provides an insight for the charge transport properties for AlQ3 from the structural perspectives, which is important for designing new materials with desirable charge transfer property.

Quantum Dots – Artificial Atoms, Large Molecules or Small Pieces of Bulk?
Insights from Time-Domain Ab Initio Studies.

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Quantum dots (QD) are quasi-zero dimensional structures with a unique combination of solid-state and atom-like properties. Unlike either bulk or atomic materials, QD properties can be modified continuously by changing QD shape and size. Often, the bulk and atomic viewpoints contradict each other, leading to differing predictions about the behavior of QDs. For example, the atomic view suggests strong electron-hole and charge-phonon interactions, as well as slow energy relaxation due to mismatch between electronic energy gaps and phonon frequencies. In contrast, the bulk view advocates that the kinetic energy of quantum confinement is greater than electron-hole interactions, that charge-phonon coupling is weak, and that the relaxation through quasi-continuous bands is rapid.

QDs exhibit new physical phenomena. In particular, the so-called phonon bottleneck to the electron and hole energy relaxation and generation of multiple excitons upon absorption of a single photon can be used to improve efficiencies of photovoltaic devices. Slowing down of the energy relaxation can result in extraction of hot electrons and holes, thereby increasing the solar cell voltage. Generation of multiple electron-hole pairs can increase the current.

Our state-of-the-art non-adiabatic molecular dynamics techniques, implemented within time-dependent density functional theory, allow us to model the response of QDs at the atomistic level and in real time. The studies provide a unifying description of quantum dynamics in nanoscale materials, resolve the debated issues, and generate theoretical guidelines for development of novel systems for solar energy harvesting and other applications.

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Electron Tunneling in Respiratory Complex I

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I. Introduction

NADH:ubiquinone oxidoreductase (complex I) plays a central role in the respiratory electron transport chain by coupling the transfer of electrons from NADH to ubiquinone to the creation of the proton gradient across the membrane necessary for ATP synthesis. The crystal structure of hydrophilic domain of complex I from *Thermus thermophilus* was reported in 2006 [1]. However, until now, the atomistic details of electron transfer along the chain of Fe/S metal clusters have remained unknown. In this study, the atomistic details of electron tunneling along seven Fe/S clusters in complex I are examined by using the tunneling current theory and computer simulations [2].

II. Electron Tunneling Pathways

Distinct electron tunneling pathways between neighboring Fe/S clusters are identified; the pathways primarily consist of two cysteine ligands and one additional key residue. The identified key residues are further characterized by sensitivity of electron transfer rates to their mutations, examined in simulations, and their conservation among complex I homologues.

III. Enhancement of Electron Transfer Rates due to the Internal Water

Internal water between protein subunits is identified as an essential mediator enhancing the overall electron transfer rate by almost three orders of magnitude to achieve a physiologically significant value. With the water included, the negative slope of the distance dependence of the electron transfer rates becomes close to a typical 1.4 in natural logarithm [3]. The unusual electronic structure properties of Fe/S clusters in complex I explain their remarkable efficiency of electron transfer.

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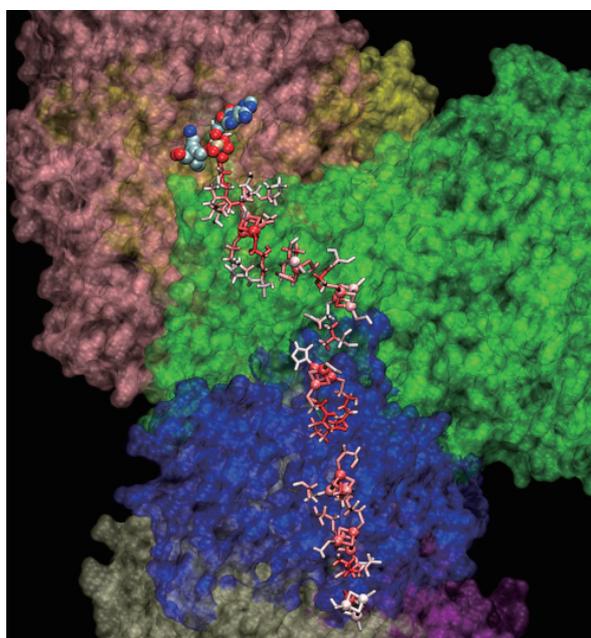


Figure 1. Calculated complete electron tunneling pathways from FMN to N₂ of complex I. The atoms with significant electron tunneling probability are highlighted with red color intensity corresponding to their total atomic currents.

Theoretical Study of the Structure Order in Supercritical Water

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In the recent years, supercritical water (SCW) has attracted intensive research interests because of its important potential as an environmentally benign green alternative to toxic organic solvents. Most of precious theoretical investigations about SCW were devoted to the the hydrogen bonding network and its influence on physicochemical properties as well as local density inhomogeneities in SCW.[1-3] It was revealed that hydrogen bonds still exist in SCW but their number will decrease with the increase of temperature or the decrease of the density. The decrease of hydrogen bonds induces the local density inhomogeneities, which is the microscopic origin of the enhanced solubility of SCW. However, the structure order of SCW have received relatively little attention. Actually, the anomalous kinetic and thermodynamic properties of water have long been been found to be able to be interpreted qualitatively in terms of underlying structural causes.[4]

In this work, we present studies on the structure order of SCW along a supercritical isotherms, $T = 1.03 T_c$ ($T_c = 666$ K), and over a wide density range, from 0.01 to 2.0 ρ_c ($\rho_c=0.322$ g/cm³), by isochoric-isothermal molecular dynamics simulations of the simple point charge extended (SPC/E) model. It is found that the translational structure order is nearly invariant under supercritical conditions regardless of their different bulk densities and it is significantly lower than that of the ambient water. Meanwhile, the enhanced energy fluctuation under supercritical conditions make some energetically unfavorable water-dimer structures emerge. Therefore, the pure r_{OH} -based geometric criterion which is widely used in the hydrogen bonding (HB) statistics under normal liquid water conditions is not applicable for SCW. The further inclusion of a energy-based criterion or a more general geometrical criterion is needed in the HB statistics under supercritical conditions. At the same time, the orientational tetrahedral order parameter decreases from positive to negative with the decreasing SCW bulk density due to the emergence of energetically unfavorable water-dimer structures by the enhanced fluctuations. When the SCW tends to be gas-like with very small bulk density, the orientational tetrahedral order parameter increases and approaches to zero because of the significant disorder and strong fluctuation.

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Spanning QTAIM Topology Phase Diagrams of Isomer Sets.

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Structural and chemical properties of a variety of isomer sets including the small clusters of water W_4 , W_5 and W_6 , $(\text{SiO}_2)_6$ [1, 2] and lithium respectively are investigated with the quantum theory of atoms and molecules (QTAIM). We then proceed to extend the isomer sets topology space using QTAIM; the Poincaré-Hopf topological sum rules are applied to create rules to identify the spanning set of conformer topologies. The topological stability of degenerate solutions to the Poincaré-Hopf relation are compared by evaluating the proximity to rupturing of critical points of the gradient vector field of the charge density. We introduce a QTAIM topology space to replace the inconsistent use of Euclidean geometry to determine whether a cluster is -1, -2 or 3-D. In particular, we show from the topology of the charge density that the conformers of the W_4 , W_5 clusters are more energetically stable in less compact, planar forms, in contrast, the conformers of W_6 are more energetically stable with compact 3-D topologies. Quantifying the degree of covalent character in the hydrogen bonding [3] for the W_4 , W_5 and W_6 clusters independently verifies this finding. Conversely our new quantum topological definition of geometry shows that the four most energetically stable $(\text{SiO}_2)_6$ conformers are quantified as two-dimensional (2-D_{QT}) within the new quantum topology.

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Water Catalyzed Overtone Induced Reaction for Hydrate Fluoromethanol: Fact of Fiction?

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I. Introduction

For Diels-Alder, dehalogenation, dehydration and decarboxylation reactions, reactivity in the aqueous phase is much greater than in the gas phase. Using the hydrate cluster model, previous quantum chemistry studies have provided answers to this by showing that the existence of water can lower the potential energy barrier of several hydrogen transfer reactions [1]. For thermal reactions this analysis based on the potential barrier height is appropriate to provide explanations to the aforementioned trend. On the other hand, one is not certain if this analysis stays valid for situations that start with a “non-equilibrium state” such as initiation of reaction by a photon using overtone excitation, spontaneous internal conversion, or stimulated emission. In the present study we performed “on the fly” dynamics simulations using B3LYP/6-31+G(d,p) to quantify the plausibility of water catalyzed overtone induced reaction using the HF elimination of fluoromethanol hydrate clusters as example, $\text{CH}_2\text{FOH}\dots(\text{H}_2\text{O})_n + h\nu \rightarrow \text{CH}_2\text{O} + \text{HF} + (\text{H}_2\text{O})_n$, $n=1,2,3$. [2]

II. Results and Discussion

As can be seen in Figure 1, the addition of water causes the barrier height of the HF elimination reaction to decrease from 40 (green arrow) to 20 (blue arrow) and 15 kcal/mol (red arrow) for the mono and dihydrate, respectively. On the other hand, when one looks at the quantum yield of the dynamics simulation results (circles and squares) one can clearly see that the reaction turns on at a much larger energy, 55 and 38 kcal/mol for mono and dehydrate, respectively. Thereby showing that the non-equilibrium distribution of the overtone excitation causes a delay in the threshold energy and water does not catalyze the overtone induced reaction in the present case.

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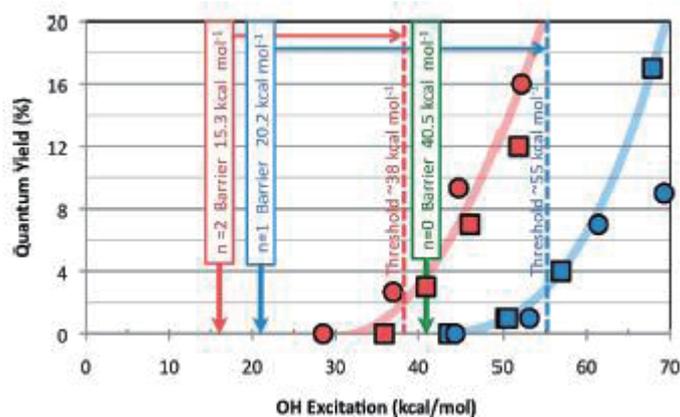


Figure 1. Quantum Yield of reactive trajectories versus photon energy for mono- (blue) and di- (red) hydrate fluoromethanol clusters. Barrier height positions are also given with arrows

Low energy structures of (H₂O)₂₅ studied with Basin Paving Monte Carlo simulation and with perturbation theory based on locally projected molecular orbitals

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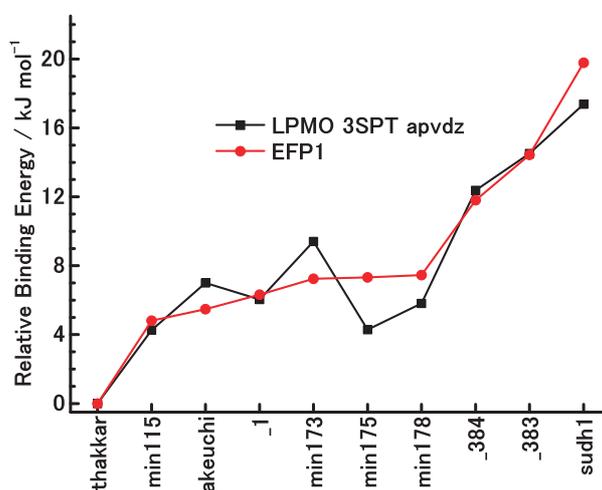
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Finding low energy structures of water clusters and estimation of their relative energies is one of the most challenging problems in physical chemistry. Although there is a large body of works for smaller water clusters, for clusters of size more than 20, the number of works is limited. The difficulty in investigating large water clusters comes from two reasons. First is the large number of low energy distinct structures, which grows rapidly with the system size. The second is the difficulty in accurate estimation of the relative energies among the different isomers of the cluster. In this work, we have investigated water cluster of size 25 by performing (a) Basin Paving Monte Carlo simulation [1] using the effective fragment potential (EFP) [2] and (b) the third order single excitation perturbation theory based on the locally projected molecular orbitals (LP MO 3SPT), which is an efficient ab initio MO method approximating the counterpoise corrected SCF binding energy.[3] Figure demonstrates the very good correlation of the binding energies among the isomers of (H₂O)₂₅. The isomers are found by the Basin Paving Monte Carlo simulation, which is a non-Boltzmann sampling by changing the probability of finding structures dynamically based on the history of the simulation.

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Comparison of the relative energies evaluated by EFP1 and the LP MO 3rd SPT



Structure and chemical activity of transition metal oxides and new carbon K4 structures: A Theoretical DFT Study

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Transition metal oxides are particularly interesting systems because of their well defined framework structures, the wealth of experimental studies, and their technological and industrial importance as catalysts, adsorbents, supports, etc. Recently, a remarkable mathematical basis is given for the new allotropic structure of carbon (denoted as K4 crystal) because of its high symmetry and similar decagonal rings with the three-coordinated and three-dimensional crystal structure. However, there are no systematic cluster calculations to shed light on tiny properties of these compounds and for a number of fundamental reactions that take place on their surface.

We present here the recent our results of DFT cluster quantum chemical calculations on structures and chemical activity of representative transition metal oxides and new metallic carbon K4 crystal having high surface areas. First, we underline the ultimate importance of proper modeling the structure and chemical activity of transition metal oxides as well as support structures to understand the mechanism of formation of precursor defect structures on $\text{TiO}_2(110)$ and other surface catalytic reactions. Next we will demonstrate that the use of the finite cluster approach has well defined advantages in shedding light on tiny properties of these materials and could be complimentary for other band structure or periodic slab calculations. Based on the results obtained, some discrepancies with the results of other theoretical studies in literature will be critically pointed out.

Interface Water on TiO₂ Anatase (101) and (001) Surfaces: First-Principles Study with TiO₂ Slabs Dipped in Bulk Water

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We investigated the TiO₂ anatase (101) and (001) interfaces dipped in bulk water on the atomic scale by first-principles density-functional molecular dynamics (MD) simulations. We verified that the water adsorption models proposed in the previous studies with less than a couple of water layers on the vacuum surfaces still hold. On the contrary, novel adsorption structures of interfacial water molecules are also found. Our results indicate that water molecules around the interface between the TiO₂ and bulk water can be described by the following two-layer model: The first water layer can be defined as the water molecules adsorbed at Ti_{5C} sites molecularly on the anatase (101) surfaces and dissociatively on the (001). Second layer on the anatase (101) surface can be defined as the water molecules adsorbed to O_{2C} or adsorbed water to Ti_{5C} via strong HB. Second layer on the (001) consists of water molecules bound to the first-layer water molecules via the strong and weak HBs. Contour maps of the atomic densities show that water molecules in the second layers are relatively mobile. This two-layer model well accounts for the experimental results of solid-state ¹H-NMR. The presence of strong HBs regardless of the water adsorption manners suggests that OH termination does not strongly affect the interfacial water structure, and the surfaces of TiO₂ anatase nanocrystals are hydrophilic intrinsically, leading to novel scenarios for the photocatalytic reaction mechanism.

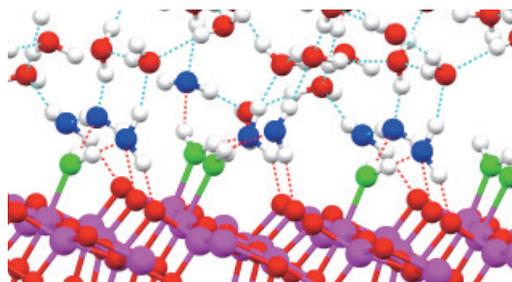


Fig. 1. A snapshot in the equilibrium trajectory of first-principles molecular dynamics of TiO₂ anatase (101) surface dipped in bulk water.

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Real-time electron dynamics with correlated wavefunction methods

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In recent years, due to progress made in generating and controlling intense laser fields, the timescale of dynamical processes in atomic and molecular systems has been pushed into the attosecond domain (1 as=10⁻¹⁸ s). In parallel with experiments, theoretical methods are being developed to treat explicitly time-dependent electronic motion after photoexcitation. This talk describes correlated, explicitly time-dependent, wavefunction based N-electron methods as alternatives to real-time density functional theory, and their application to selected molecular problems.

The focus of the talk is on many-electron methods in which the time-dependent N-electron wavefunction is expanded as a sum of Slater determinants. The first approach of this type to be described is time-dependent configuration interaction (TD-CI), where only the coefficients of the determinants are time-dependent. The second approach is the time-dependent complete active space SCF method (TD-CASSCF), for which both the coefficients and Slater determinants are time-dependent. Extensions of the methods to include ionization, dissipation, and optimal control strategies for excited electron dynamics, are also presented.

The methods will be applied (i) for laser-pulse excitation and switching of real molecules without [1] and with [2] dissipation and / or ionization, (ii) for the calculation of response properties of small molecules [3], (iii) for long-range intermolecular charge transfer [4], and (iv) for controlled electron dynamics in molecules [5].

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Mössbauer spectroscopy for heavy elements: a 4-component relativistic study

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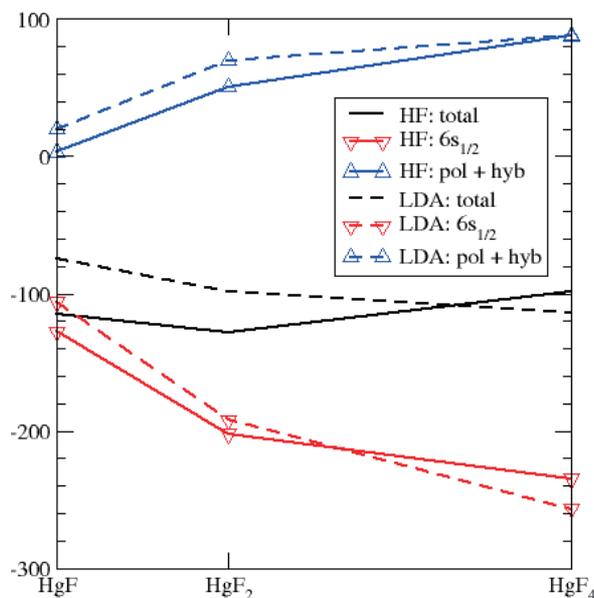


Figure 1: Dominant contributions (in atomic units a_0^{-3}) to projection analysis of relative contact densities of mercury fluorides at the 4-component relativistic HF and LDA level. pol=polarization, hyb=hybridization.

Mössbauer spectroscopy is an example of a spectroscopic technique showing extreme sensitivity to the electronic density in nuclear regions such that its modelling requires consideration of relativistic effects even for quite light species. In the present talk we report 4-component relativistic studies of the contact density (the density at the nucleus) of molecular species containing the Mössbauer active elements mercury[1] and xenon. We investigate the performance of relativistic density functional theory, using coupled-cluster calculations for calibration. We present a detailed analysis of the observed relative contact densities between molecular species, bringing into light the effect of polarization as well as overlap between ligands and the central atom. All calculations have been carried out with the DIRAC code for relativistic molecular calculations [2].

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Electronic excited states of large conjugated molecules

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Electronic structure and electronic excitations of large π -conjugated molecules such as porphyrins and phthalocyanines are being widely studied because of their importance in many fields. However, accurate calculations of electronic excited states of large π -conjugated systems are still challenging subjects because of their computational costs and delocalized characters. Recently, we have developed the direct SAC-CI method [1] that can be applied to excited states of large systems within moderate computational costs and reasonable accuracy. The method combined an efficient MO direct scheme and perturbation-selection technique that does not assume local nature of systems.

The electronic absorption spectra of free-base tetraazaporphyrins (H_2TAP : $C_{16}H_{10}N_8$), phthalocyanines (H_2Pc : $C_{32}H_{18}N_8$), naphthalocyanines (H_2Nc : $C_{48}H_{26}N_8$), and anthracocyanines (H_2Ac : $C_{64}H_{34}N_8$) were calculated by the direct SAC-CI method.[2] As shown in Fig. 1, the direct SAC-CI well reproduced the experimental spectra[3]. The TDDFT calculations with common functionals have some problems for these extended systems. Electron correlation in the excited states is very important to reproduce the experimental findings of these molecules.

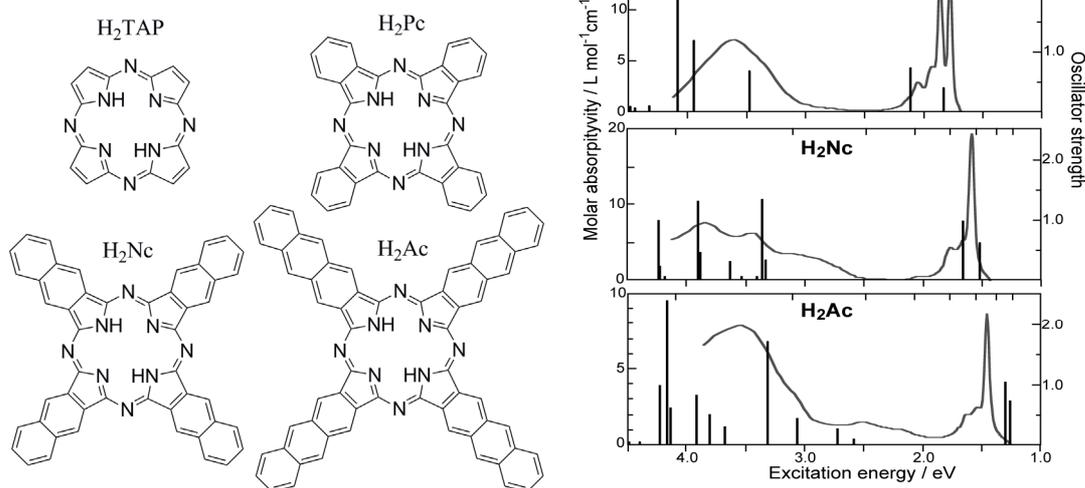


Fig. 1 Experimental and theoretical spectra.

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Absorption and Emission properties of the F, OH and NO₂ Substituted Cinnamates: A TD-DFT Investigation

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The absorption and emission properties of F, OH and NO₂ substituted at *ortho*-, *meta*-, and *para*-positions of cinnamate derivatives were investigated by using the density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. The ground (S_0) and excited (S_1) state geometries were obtained at the B3LYP/6-31G(d) and TD-B3LYP/6-31G(d) methods, respectively. Based upon the optimized structures of the S_0 and S_1 states, the TD-B3LYP/6-311G(d,p) calculations were performed to compute the absorption and emission energies of the various substituted cinnamates. The results shown that all compounds had the local minimum at the planar structure conformation except for the NO₂ substituted at *ortho*-position. In the S_1 geometry, the bond length alternation (BLA) values of F and OH compounds decreases correspond to a fully delocalized electronic system, whereas, those of NO₂ increases indicate high delocalization degree of π -bond along the molecules. The calculated absorption and emission spectra in gas phase and methanol were agreed well with the experimental spectrum. The main electronic transition of cinnamates at *ortho*- and *meta*-positions of F and OH substitution correspond to the electronic excitation from HOMO-1 to LUMO. Whereas, those of NO₂ substitution correspond to the electronic excitation form HOMO to LUMO+1. In addition, the main electronic transition of cinnamates at *para*-positions of F, OH and NO₂ substitution correspond to the electronic excitation from HOMO to LUMO. Moreover, the predicted radiative lifetimes of cinnamate derivatives which discuss the origin of the stoke shift were also investigated. Our TD-DFT investigation can provide a useful insight into the optical and electronic properties of these molecules and a useful tool for designing and developing the novel UV absorbers.

Keywords: Cinnamate, Density functional theory (DFT), Time-dependent DFT (TD-DFT)

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Properties of hollow molecules containing a double core hole, probed by single-photon double ionization

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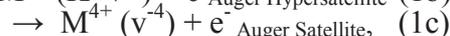
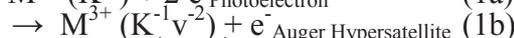
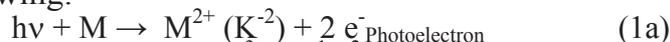
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Although hollow atoms were known and observed for a long time, it is only very recently that experimental observation of hollow molecules (N₂) was possible thanks to sequential inner-shell ionization using x-ray free electron laser [1]. We have demonstrated [2] that such double core hole states can also be studied in detail by single photon double core ionization using synchrotron radiation, even if the associated double photoionization cross section is extremely weak.

The experiments were performed on BL-16A beamline at Photon Factory (Japan) and on TEMPO beamline at SOLEIL (France) using a magnetic bottle time-of-flight spectrometer.

We studied N₂, O₂, CO and CO₂ molecules. The formation and decay process is the following:



where v designates a valence shell, and the emitted Auger electrons are called ‘hypersatellite’ or simply satellite, depending on whether the K-shell is filled in the presence of a second K hole or of valence holes. The hypersatellite Auger electron line has higher energy than the main Auger line associated with single K-shell ionization, and is characteristic of double K-shell ionization. By detecting in coincidence all four electrons released in the process (1), we have been able to characterized double core-hole states with two K-shell vacancies on the same atom and their satellites. We deduced in this way the binding energy of N₂²⁺ (K⁻²) states (and their satellites), their respective Auger decay paths and their relative intensity with respect to N₂⁺ (K⁻¹) states. Single photon double ionization in the K-shell (K⁻²) represents a small fraction (10⁻⁴ to 10⁻³) of single K-shell ionization for N₂, O₂, CO and CO₂ molecules. In N₂, we could set an upper limit of 1.2% for the 2-site double K-shell ionization (K⁻¹K⁻¹) on neighbor atoms compared to 1-site (K⁻²).

These results raise important questions for the theoretical description of the formation, spectroscopy and decay mechanism of the highly excited species involved. We will also present at the conference our most recent results on 1-photon double K-shell ionization.

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Ionization of Helium in Strong XUV Laser Pulses – a Theoretical Simulation

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I. Introduction

The work presented is part of study of mechanisms of gas ionization in laser sparks. In our model, isolated gas molecules interact with laser field with a wavelength of 50 nm and the intensity of the tens of TW cm⁻². This process is studied for different lengths of pulses, from short femtosecond pulses to picosecond pulses. We calculate the populations of excited states of the emerging helium cation.

II. Details of the theoretical methods

The theoretical description, being at ab initio level, is based on the classical dipole approximation. The ionization effect is numerically secured by using the complex scaling transformation. Time-dependent wavefunction of helium atom interacting with the laser pulse is calculated beyond the adiabatic Floquet approximation, using an expansion in the basis set of time-dependent Floquet states. The Floquet energies and coupling elements between the Floquet states are calculated for several field intensities spanning from zero to the peak intensity of the laser pulse, prior to the non-adiabatic propagation. The Floquet states are defined in the basis set of primitive dressed states (defined as the direct product of the complex scaled field-free states of helium and photon states), where the field-free states of helium are obtained using the full CI method. An extensive basis set of even tempered Gaussians, which is carefully converged with respect to the complex Floquet energies, is used.

Automated Exploration of Global Reaction Route Maps on the Potential Energy Surface

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I. Introduction

It has been believed that systematic exploration of the entire reaction channels on the potential energy surface (PES) is not possible except for very small systems, because uphill tracing along reaction pathways up to transition structures (TS) from an equilibrium structure (EQ) is difficult to be made without intuition [1].

An attempt to explore global reaction route maps in an automatic way has been made by an uphill tracing algorithm noting anharmonic downward distortion (ADD) of the PES [2-4]. The present talk shows how to make a global reaction route mapping on PES automatically and what could be explored by the ADD following, “a compass of the chemical world”.

II. Global reaction route mapping based on ADD following

As shown in Fig.1, use of *Scaled Normal Coordinate*, $q_i = \lambda_i^{1/2} Q_i$, leads to minima on hyperspheres around an EQ, since ADD along reaction pathways give the lower energies with respect to the reference harmonic energies which define isoenergy hypersphere surfaces. Uphill tracing along reaction

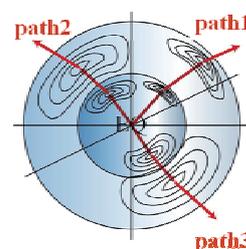


Fig.1 Uphill tracing by ADD following

pathways up to TS can thus become possible. After arriving at TS conventional IRC tracing reaches either another EQ or dissociation channel (DC). Subsequent hypersphere search yields further reaction pathways. Such procedures can be continued to search many EQ and TS one after another and finally to obtain the global reaction route map, as can be seen in Fig.2.

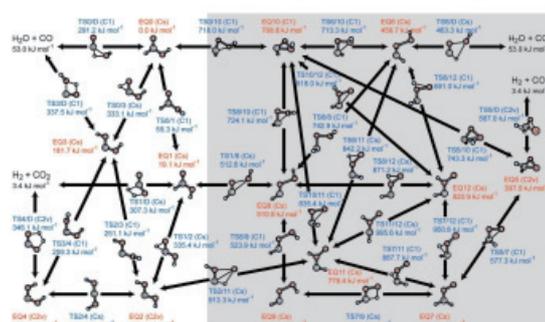


Fig.2 Global reaction route map for H₂CO₂.

III. Automated exploration of unknown chemistry

The ADD following procedures can be performed with no intuition. It follows that unknown chemistry can be discovered by the one-after-another search of the global reaction route map. Lower energy parts of reaction routes can be explored efficiently by a limited search, Automated data processing system further facilitates to analyze new chemistry discovered in the global reaction route map.

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Nonadiabatic Reactions Studied by Automated Reaction Path Search Methods

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Introduction. Nonadiabatic transition plays a key role in many chemical reactions.¹ It takes place efficiently within a seam of crossing hypersurface in which two adiabatic potential energy surfaces (PESs) cross. In many kinetic studies, minimum structures on the seam of crossing (MSX) have been searched as critical points of nonadiabatic transition. However, some key MSX structures with highly unexpected geometries are very difficult to guess, which makes their geometry optimizations very difficult. Hence, we have developed automated methods for finding unknown/unexpected MSX structures systematically.^{2,3} In this talk, these methods are introduced and applied to searches for photodissociation pathways of NO₃ and for ignition pathways of unsaturated hydrocarbons.^{4,3}

Methods. We have developed two methods to explore reaction pathways on single PESs automatically: the global reaction route mapping⁵ (GRRM) method and the artificial force induced reaction⁶ (AFIR) method. These two are independent but complementally to each other. Reaction pathways of type A → X (+ Y) can be explored by the GRRM method, while the AFIR method can search for those of type A + B → X (+ Y). In MSX searches, these methods are applied to a model function on which approximate MSX structures are obtained as local minima; many (true) MSX structures can finally be obtained by geometry optimizations starting from such approximate MSX structures.^{2,3}

Results. Figure 1 shows an excited state roaming O atom path, in which one of O atoms in NO₃ partially dissociates on the first excited doublet (D₁) PES and then roams around the NO₂ fragment before producing O₂ and NO on either the D₁ or the ground (D₀) state PESs.⁴ This mechanism, which was revealed by the GRRM method, explains a recent experimental result.⁷ New nonadiabatic ignition pathways of unsaturated hydrocarbons discovered by the AFIR method are also presented.³

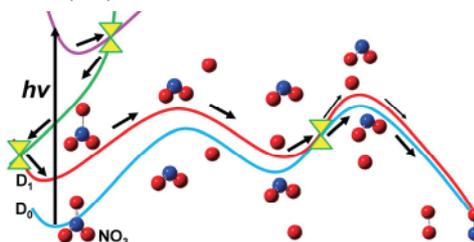


Figure 1. The excited state roaming path discovered for photodissociation of NO₃.

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Strong and Weak Coordinates within the Context of the Multi-Coordinate Driven Algorithm

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The multi-coordinate driven (MCD) algorithm [1] is the application of a simple gradient search algorithm to a reaction path problem. A central part of the MCD algorithm is the differentiation between driving and driven geometry coordinates. Driving coordinates are used to expand the energy of the system in a Taylor series at any given point of the reaction path. The MCD algorithm picks the next step into the direction of the slowest ascent or steepest decent based on the conditions. The driven coordinates, which are the majority, are optimized as usual within the molecular framework as defined by the driving ones. The MCD algorithm follows a minimum work path on the potential energy surface of the system. The choice of the reaction pathway to be explored is determined by the selection of the driving coordinates. Therefore, the MCD algorithm can be used to search for unknown products and transition states starting from a minimum energy structure while keeping the computationally expensive Hessian matrix at a minimum size.

Problems arise when weak and strong coordinates are mixed in the set of driving coordinates. Weak coordinates have small gradients and small force constants. The energy penalties for changes in weak coordinates are low during the energetic climb phase of the search. As the MCD search algorithm follows the path of the smallest energy increase, weak coordinates tend to dominate the energetic uphill search. For example, one of the driving coordinates can lead to a change of the molecular conformation away from the investigated reaction path and ultimately to unphysical jumps in the energetic profile of the system. Several methods, such as dynamic step size control, harmonic and anharmonic corrections to the energy prediction, external optimization steps, and on the fly path analysis are applied to resolve this problem. The application of the aforementioned methods to chemical reactions are investigated, too. It is discovered that the handling of three groups of coordinates instead of the driving and driven two originally defined in the MCD algorithm greatly simplifies the application of the MCD algorithm to chemical reactions.

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Dominant reaction pathways of macromolecules: from classical to quantum mechanical calculations

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The investigation of the kinetics of thermally activated reactions by means of Molecular Dynamics (MD) simulations is very inefficient, because most of the computational time is wasted to simulate the exploration of the (meta-) stable states and because the internal dynamics of macromolecules is characterized by widely decoupled time scales. In this seminar, I will discuss how such problems are rigorously bypassed in the recently developed Dominant Reaction Pathways (DRP) approach [1, 2, 3]. As an illustrative example of application, I will report on the first calculation of the dominant folding pathways of a peptide, based on *ab-initio* electronic structure calculations, rather than on an empirical force field [4]. Very recently, the DRP method has been upgraded to systematically include also the quantum corrections to the diffusive motion of the atomic nuclei [5]. We have found that such corrections are quite large and give raise to some counter-intuitive phenomenology.

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A first-principles density functional approach for charge transfer & transport

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Abstract:

We present a first-principles density functional theory (DFT) which is successful in classes of problems traditionally considered "too tough for DFT". The basic elements of this method are briefly reviewed (first principles tuning of the Baer-Neuhauser-Livshits range-separated hybrid), but the focus is on recent applications. Unlike most DFT approximations, our approach yields orbital energies that closely approximate the ionization potentials and electron affinity of atoms, molecules, clusters and solids. We demonstrate the success of the method in treating the breaking of 3 electron bonds and reaction barriers. The time-dependent version of the method falls within the Runge-Gross TDDFT framework, using generalized time-dependent Kohn-Sham equations. The method is capable of describing Rydberg and electron-transfer excitations. We give examples with comparison to experiment on coumarin dyes, aromatic molecular complexes and bipeptides. Finally, we discuss an application to molecular electronics, where a gate potential tunes the conductance level of a molecular junction. Concepts such as Coulomb blockade and exciton binding energy are clearly illustrated using the orbital energies of our first principles DFT method.

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Better Ways to Get Excited States and Reaction Barriers From DFT

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Density functional theory (DFT) is the *de facto* standard for simulating the electronic ground state near equilibrium. At the same time, standard functionals have some well-advertised problems in dealing with electronic excited states and molecules that are near the transition state region. In this talk we show that, in many cases, the problem isn't as much that DFT gives the wrong answer as that electronic structure theorists insist on asking the wrong questions. Using chemical intuition, one can often choose initial and final states lead to accurate predictions (via cancellation of errors) even in cases where DFT nominally fails. For example, applying constraints to the charge density leads to reliable electron transfer energies; Δ SCF calculations give accurate results for valence and Rydberg excitations; localized charge states provide a basis for improving reaction barrier heights; configuration interaction based on a DFT active space gives a qualitatively correct description of conical intersections between ground and excited states. Time permitting, we will discuss how these developments could be leveraged to improve existing functionals.

Recent progress in long-range corrected density functional theory

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Recent studies on long-range corrected (LC) density functional theory (DFT) [1] and its applications are presented.

So far, it has been reported that LC-DFT solves or clearly improves various properties that conventional DFTs have seriously failed to reproduce: e.g. van der Waals and other weak bond energies and structures [2], optical properties of long-chain molecules [3] and diradicals [4], and charge transfer energies and oscillator strengths in time-dependent DFT (TDDFT) [5]. In particular, it was recently found that LC-DFT quantitatively reproduces valence orbital energies for the first time [6]. We have recently suggested that several properties are unexpectedly poorly reproduced are clearly improved by using LC-DFT. In this talk, I will introduce these properties and will explain why these are significantly improved by LC-DFT.

However, there remains several serious problems that cannot be solved even by LC-DFT. We have worked on finding out these problems and have suggested new approaches to solve them. For example, we found that long-range correction hardly affects core excitation energies in TDDFT that have been significantly underestimated in TDDFT even using up-to-date functionals. To improve these core excitation energies, we have therefore suggested a regional self-interaction correction method, in which short-range exchange functionals in the regions of self-interacted electrons are only replaced with Hartree-Fock exchange integral based on the pseudo-spectral method. We have also made it possible to calculate spin-orbit splittings of excitation energies in TDDFT by implementing spin-orbit couplings into TDDFT program. I will briefly review these correction methods for LC-DFT in this talk.

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Improved DFT from Electrons on a Sphere

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Density functional theory (DFT) is now popular within the chemical physics community, but it still suffers from some serious deficiencies and most of these are now well understood [1]. One of the key goals of modern research, therefore, is to develop new methods that preserve the low cost of DFT calculations while offering significantly enhanced accuracy.

Many of the weaknesses of DFT stem from the fact that most functionals are based on the uniform electron gas, a model consisting of an infinite number of electrons in an infinite volume. Unfortunately, this system does not resemble the electron density in most molecules and one route to the improvement of DFT is to replace this foundation with a new one.

In recent years, there has been growing interest in the quantum mechanics of pairs of confined electrons. The helium atom, of course, has been studied from the early days and the Hooke's Law atom was introduced in the 1960s. But, more recently, accurate solutions have also been found for pairs of electrons trapped inside a ball [2] and on its surface [3–8] and these are now being used for the development of new functionals in density functional theory (DFT).

The electrons-on-a-sphere model is particularly attractive because it is defined by a single parameter (the radius R of the sphere) and varying this takes us from a weakly correlated system (small R) dominated by dynamical correlation, to a strongly correlated system (large R) dominated by static correlation.

I will review this model and show how it can be used as the starting point for a new way of understanding and improving DFT.

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Following the exact results [1] on the confined one electron systems which highlight the novel spectral-features arising due to the spherical confinement we proceed to present the state of art calculations for the confined N -electron atoms. Radial, angular and total correlation energies are calculated [2] for four different two-electron systems with atomic numbers $Z = 0 - 3$ confined within an impenetrable sphere of radius R . We report accurate results for the non-relativistic, Hartree-Fock and radial limit energies over a range of confinement radii from $0.05 - 10 a_0$. At small R , the correlation energies approach limiting values that are independent of Z while at intermediate R , systems with $Z > 1$ exhibit a characteristic maximum in the correlation energy resulting from an increase in the angular correlation energy which is offset by a decrease in the radial correlation energy. The correlation calculations are reported with the 70 term Hylleraas expansion in s , t and u . We also report [3] a new expression for the expectation value integral of Hermitian operators for spherically-symmetric states in Hylleraas coordinates for the Helium atom confined in a cavity with infinite potential barrier walls. The expression is comprised of two components spanning different domains of space which is shown to be a third faster than the conventionally employed expression for confined systems derived by ten Seldam – de Groot [4]. It is further shown that in the limit of the free Helium atom, our expression for well-behaved wave functions is equivalent to that originally derived by Hylleraas. Finally, we shall present accurate Hartree-Fock estimates of the critical radius [5] for the spherically confined atoms in the periodic table. The critical radius is defined as the radius of the impenetrable spherical cavity at which the highest occupied orbital of the confined atom corresponds to a zero eigenvalue and its estimates provide a new set of *characteristic* data relating to the electronic structure of atoms. Finally, we present accurate computations [6] of static and dynamic dipole polarizabilities for the ground and excited states of hydrogen atom confined at the center of multiwalled fullerene cage, using the Galerkin variational method developed on a B-spline basis set. It is shown that the addition of new walls does not modify the polarizability of the ground state, but significantly modifies those of the excited states. A condition on the ratio of the scaled second derivative of density to the scaled density evaluated at the nuclear position is tested in case of the cage confined atoms for the first time and the significance of such numerical results are discussed. Similar results of scaled density at the nucleus in case of hydrogen atom in presence of ultra-high magnetic fields as those present in the neutron stars have been performed using the Lagrange mesh [7] to provide a measure of the non-sphericity of electron in the vicinity of the nucleus.

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Towards an order N scaling force field with an accurate treatment of many-body dispersion and polarization

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There are many physical systems where the non-pairwise additive nature of polarization and dispersion interactions becomes very important, in particular, the complex heterogeneous systems of interest in chemistry, biology and physics. For example, the dipole moment of water changes from 1.85 Debye in the gas phase to approximately 2.6 Debye in the bulk liquid and attains intermediate values at hydrophobic interfaces due to many-body polarization. Similarly, although the bulk properties of hydrophobic fluids can be modeled using a pair potential, this underestimates the surface tension by 30% due to many-body dispersion interactions. In order to model both the full many-body polarization and dispersion interactions in atomic and molecule systems, a system of quantized Drude oscillators is introduced and a $O(N)$ simulation method based on quantum path integrals is described using diagrammatic expansions of the propagator. Applications to simple, xenon, and more complex systems, water, are given.

Development of the Explicit Solvation Shell Model

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I. Introduction

Accurately calculating the free energy of solvation is a long-standing challenge in computational chemistry. Predictions of the free energy of solvation for ions are particularly challenging. The most widely used models for such calculations are continuum solvation models. A key limitation is that they can not capture specific chemical features of solute-solvent interactions. One approach to get around this limitation is to add solvent molecules in the continuum calculations. The explicit solvation shell (ESS) model [1] is based on this approach. The present paper reports a refinement of the model and application to calculation of base strength.

II. Methods

In the ESS model solute-solvent clusters are extracted from liquid simulations. Calculations are carried out on an ensemble of a 100 clusters, the calculations being based on linear averaging of energies from the clusters. In the present version of the model 5 solvent water molecules are included for all solutes. Cluster calculations are carried out at the HF/6-31+G(d) level and the continuum model utilized is the Poisson-Boltzmann model implemented in the DIVCON code.

The refinement in the model consists in adding a correction term proportional to the surface area of the cluster.

In calculations of amine base strength the ESS model were utilized to calculate the solvation energy of the protonated species. Gas-phase base strengths were carried out with the CBS-QB3 method, while solvation energies for the neutral species were calculated with the SM8 solvation model.

III. Results

Ion solvation energies were calculated for 33 cations and 33 anions. The average unsigned error was 2 kcal/mol for both anions and cations. Base strengths were calculated for 23 species, the unsigned average error was in this case 1.4 pK_a units. We believe these are very encouraging results, particularly for a model that has no tunable parameters.

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***Ab Initio* Composite Methods: Beyond Ground State Main Group Species**

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Ab initio composite methods provide a powerful means to address thermochemical properties of main group species. Despite their tremendous popularity, there has been limited application of these methods beyond ground state main group species. Several years ago, we introduced the correlation consistent Composite Approach (ccCA) as an approach that was not only able to address main group chemistry, but also could address transition metal chemistry. A similar algorithm of multireference methods, the multireference correlation consistent Composite Approach (MR-ccCA), was developed to address problems for which a single reference wavefunction may not be suitable, such as for excited states and bond formation and dissociation. As well, because of the synergy of the steps within MR-ccCA, the method has been effective in the prediction of potential energy surfaces.

Recent developments for ccCA and MR-ccCA are discussed, including developments and successes for transition metal chemistry, where ccCA provides a powerful gauge of the performance of density functional approaches, particularly in the absence of experimental data.

Over 200 transition metals species have been investigated, and over a thousand main group species have been investigated, ranging from weakly to tightly bound systems. Overall, ccCA is one of the most effective *ab initio* composite methods available.

Solvent Effects on Electronic Excited States

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The effective fragment potential (EFP) is a general model potential that is based in quantum mechanics. Recently, the EFP method has been interfaced with several quantum mechanics (QM) methods for excited electronic states, including CI singles (CIS), CIS with perturbative double excitations (CIS(D)), time-dependent density functional theory (TDDFT), equations of motion (EOM) coupled cluster (CCSD(T) theory, multi-reference perturbation theory (MRPT), and multi-reference CI (MRCI). In studying solvent effects on excited states, an interesting question is how important it is to include the response of the solvent method to the excited state electron density. A detailed analysis of the contributors to excited state solvent effects has been developed to address this question. Theoretical considerations, as well as applications of the EFP method to a variety of applications in excited state chemistry will be discussed.