Electronic and Optical Properties of Borophene, a Two-dimensional Transparent Metal

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Abstract:

Borophene is a recently synthesized metallic sheet that displays many similarities to graphene and has been predicted to be complimentary to graphene as a high density of states, optically transparent 2D conductor. The atomic arrangement of boron in the monolayer, which can strongly depend on the growth substrate, can significantly alter the optoelectronic properties. Here, we report a first-principles density functional theory and many-body perturbation theory study aimed at understanding the optoelectronic properties of two likely allotropes of monolayer boron that are consistent with experimental scanning tunneling microscopy images. We predict that both structures possess a free-electron-like metallic system with absorbance of 1-3%. However, the two allotropes have substantially different bandstructure and optical properties, with one structure being fully reflective up to 3 eV and the second partially transmitting in the UV/visible region. We demonstrate that this strong structure-dependence of optoelectronic properties is present with the application of strain. Lastly, we will discuss the strength of electron-phonon and electron-hole interactions within these materials. Overall, we determine precise control of the growth conditions in necessary for controlled optical properties.

Recent Progress in the Electron-Attached, Ionized, and Active-Space Equation-of-Motion Coupled-Cluster Methodologies

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Abstract:

The full and active-space doubly electron-attached (DEA) and doubly ionized (DIP) equation-of-motion (EOM) coupled-cluster (CC) methods with up to 4-particle–2-hole (4p-2h) and 4-hole–2-particle (4h-2p) excitations, which utilize the idea of applying a linear electron-attaching or ionizing operator to the correlated, ground-state CC wave function of an N-electron closed-shell system in order to generate the ground and excited states of the related (N±2)-electron species of interest, such as biradicals, have been developed [1,2]. In the case of the DEA approach, we have further simplified the active-space DEA-EOMCC(4p-2h) method to a more cost-effective model at the 3p-1h level, where both 3p-1h and 4p-2h terms are selected using active orbitals [3].

By examining the low-lying singlet and triplet states of the methylene, (HFH)−, and trimethylenemethane biradicals, and bond breaking in F2, we demonstrate that the DEA- and DIP-EOMCC methods with the active-space treatment of 4p-2h and 4h-2p excitations reproduce the results of the analogous full calculations at the small fraction of the computer effort, while improving the DEA/DIP-EOMCC theories truncated at 3p-1h/3h-1p excitations and making the DEA/DIP-EOMCC results less sensitive to the type of orbitals used in the calculations [1-3]. Using the above and several additional examples, including singlet-triplet gaps in a series of antiaromatic molecules, such as cyclopropenyl anion, cyclobutadiene and its derivatives, and cyclopentadienyl cation, we show that our newest DEA-EOMCC method with the active-space treatment of 3p-1h and 4p-2h excitations and its lower-level counterpart neglecting 4p-2h contributions are capable of accurately reproducing the results obtained using their relatively expensive parent counterparts with a full treatment of 3p-1h and full or active-space treatment of 4p-2h excitations at the small fraction of the computer effort [3,4]. This work brings us one step closer to a situation, where we may be able to perform high-accuracy, relatively inexpensive, and spin- and symmetry-adapted CC computations for multi-reference (MR) problems, such as those encountered when balancing quasi-degenerate high-spin and low-spin electronic states, without resorting to genuine MRCC theories.

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An examination of thermally activated delayed fluorescence using the particle-particle random phase approximation

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Abstract:

Thermally-activated delayed florescence (TADF) mechanism increases the efficiency of light emission in organic light emitting diodes by enabling triplet exciton harvesting. TADF is made possible due to the small energy difference between the first singlet and triplet excited states, which is minimized by spatial separation of the donor and acceptor moieties. The resultant charge-transfer excited states are difficult to model using standard excited-state methods such as time-dependent density functional theory because of the delocalization error of approximate exchange-correlation (xc) functionals. The error associated with this approach can be reduced by varying the amount of Hartee-Fock exchange contribution to the xc functional. However, the amount of exchange necessary to reproduce electronic spectra is system dependent, and can differ for singlet and triplet excitation energies. In this work, we apply the particle-particle random phase approximation to a set of known TADF molecules and show that this method can accurately predict the small singlet-triplet energy gaps, which is attributed to the reduced delocalization error and a consistent treatment of excited states. Therefore this approach is recommended for designing new TADF emitters.

Mechanical unfolding of single- and multi- motif proteins

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Abstract:

The energetics and structural characteristics of several model peptides or proteins stretched at opposing ends can be obtained through the integration of nonequilibrium molecular dynamics trajectories leading to a potential of mean force (PMF). Our adaptive steered molecular dynamics (ASMD) method, and several variations, provides efficient convergence for a large range of stretching distances. We will present details of the algorithms necessary for implementation, timing data illustrating computing performance in comparison with steered molecular dynamics, and the comparisons of the free energies with respect to several underlying force fields. The ASMD scheme allows for the determination of additional observables such as hydrogen-bonding contacts and the persistence of secondary structure motifs as a function of end-to-end extension. These observables have been computed for the several proteins selected so as to represent varying degrees of α-helical and β-sheet character. The computed values provide quantitative insight into the structural characteristics of the protein in the reduced-dimensional landscape corresponding to its mechanical unfolding.

This work has been partially funded by the National Science Foundation through grant number CHE 1700749. The computing resources necessary for this research were provided in part by the National Science Foundation through XSEDE resources provided by Comet under grant number TG-CTS090079.

Proton Transfer Rates from Quantum-Classical Path Integral Simulations

Thomas C. Allen and Nancy Makri

Abstract:

Proton transfer reactions play a major role in the chemistry of the condensed phase and have applications throughout biological and materials science. The most accurate theoretical description of these processes is via quantum dynamics, but these quantum calculations become prohibitively expensive for more than a handful of degrees of freedom. Fortunately, the recent development of the quantum-classical path integral method provides a rigorous approach which unites a classical molecular dynamics description of the environment with a highly accurate quantum treatment of the reactive proton coordinate, allowing for computationally tractable simulations of quantum dynamics in large, complex environments. We apply this method to the Azzouz-Borgis problem, an atomistically detailed model of phenol-amine proton transfer in liquid methyl chloride, to extract proton transfer rates and consider some future extensions and applications of the method.

Dynamic Polymer Networks

Eric Alt and Adam P. Willard

Abstract:

Statistical mechanical theories of polymer networks can be useful in relating a material's properties to characteristics of its underlying molecular components. This understanding can be applied to infer molecular-level information from macroscopic measurements, or to guide the rational design of the precursors needed to produce a material with some desired properties. While existing theories are premised on fixed network topologies, there is increasing interest in developing new materials with dynamic networks. This class of materials includes gels formed by polymer chains that crosslink via end groups capable of forming reversible bonds at network nodes. Because their initial network realization is capable of rearranging, these networks relax towards an equilibrium arrangement in a process that is not available to permanent networks. Consideration of the competing entropic forces that drive network relaxation allow for the understanding of the resulting structures of these dynamic networks.

Characterization of electrostatic relaxation dynamics in water

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Abstract:

The non-equilibrium response of water to an applied electric field through the introduction of a solvated charge has been studied with molecular dynamics (MD) simulations. The relaxation and reorientation of the solvating waters is characterized at short timescales, with an interest in elucidating the mechanism of charge screening at short times and developing a methodology to characterize the electrostatic response of water to an applied field. Fluctuations in the local electrostatic environment are described through the analysis of isoconfigurationally averaged MD trajectories, and the magnitude of the response is found to depend on the details of the solvation structure.

Recovering the flat plane condition in semi-local density functional theory

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Abstract:

Energies from any exact electronic structure method should exhibit piecewise linearity with respect to fractional electron removal or addition, necessitating a derivative discontinuity at integer electron number. Semi-local density functional theory (DFT) approximations are known to deviate from this behavior with a convex energy profile for electron removal or addition and no derivative discontinuity. The additional requirement that the energy is invariant with respect to the spin of an electron in isoenergetic orbitals produces a tighter constraint known as the flat plane condition, wherein two linear planes meet at a fractional spin line seam. All approaches that have aimed to correct deviations from piecewise linearity in semi-local DFT are known to worsen already concave behavior on the fractional spin line, increasing static correlation error. We return to the original functional form of semi-local DFT errors along the flat plane and quantify the convexity along the fractional charge line and concavity along the fractional spin line. Analysis of the functional form of this error enables identification of the first no-computational-overhead corrections that can recover the flat plane condition within semi-local DFT. We compare these functional forms to more established approaches, including range-separated hybrid functionals and our earlier observations on how Hubbard model functionals recover the derivative discontinuity.

Second order molecular properties from the random phase approximation (RPA)

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Abstract:
Semi-local density functional theory (DFT) is surprisingly inaccurate for second-order molecular properties such as polarizabilities of large conjugated systems. Here we investigate to what extent the RPA for the ground state correlation energy overcomes these limitations. To this end, an efficient implementation of RPA second analytical derivatives is presented. We derive expressions for the RPA orbital rotation Hessian and discuss their physical meaning. This leads to an iterative algorithm with the same $O(N^4 \log N)$ operation count and at most $O(N^3)$ storage scaling with the system size N as the RPA energy. Applications to static polarizabilities of conjugated hydrocarbon chains show dramatic improvements over semi-local functionals if optimized RPA orbitals are employed. This suggests that there is considerable error in the semi-local density of large conjugated systems.

This material is based upon work supported by the National Science Foundation under CHE-1464828.

Protein Co-localization in Membrane Domain Interface and Mediation of Interface Line Tension

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Abstract

Because of the lateral heterogeneity in membrane environments, membrane proteins can partition in to different condensed phases or at the interface between phases. This co-localization leads to an increase in effective protein concentrations and consequently, protein function. Proteins are also hypothesized to promote and stabilize the domain formation in membranes. While fluorescence spectroscopy studies, detergent resistance membranes studies and some theoretical works support these claims, there is no consensus among their reported values. The difficulty of characterizing membrane domain interfaces, its free energy contributions (like line tension), and the effect of proteins on the domain interface, introduces further complications.

Here, we utilized coarse-grained molecular dynamics simulations to investigate protein co-localization in domain-separated membranes, and the effects of proteins on the line tension of the domain interface.

Employing an array of protein types, we demonstrated that proteins preferentially partition in to the interface between ordered and disordered stripe domains. To explore the effect of this co-localization further, we developed a molecular composition based algorithm that calculates the line tension based on the instantaneous fluctuations of the domain interface. Using this method, we demonstrated that proteins tend to decrease the line tension by 40%-50%. We also compared this approach with the existing methods such as the line tensions estimated based on anisotropy in the pressure tensors, and provide some discussion of comparability between these methods, and potential sources of errors in each method.

Efficient Hydroxyquinoline based C3-Symetric Tripodal Chemosensor: Density Functional Studies

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Abstract:
A novel polyfunctional C_3-symmetric tripodal chelator, N,N,N-Tris(8-hydroxyquinoline-2-yl)cyclohexane-1,3,5-tricarboxamide, (HQCC), containing three pendant oxine units linked to the cyclohexane central unit by amide spacers has been developed. The chelator exhibits interesting photophysical properties and shows high selectivity towards trivalent iron amongst other transition and biologically relevant metal ions by displaying a significant quenching in emission spectra in the environmental pH that establishes its potential use as a fluorescent sensor for the detection of Fe(III) ions.

The molecular structures of protonated, neutral and deprotonated species involved in the equilibria of the tripodal chelator HQCC, have been studied by using DFT at B3LYP level with 6-31G** basis sets whereas for coordination compounds of the metal ion, the B3LYP/LANL2DZ was used. The B3LYP and cam-B3LYP hybrid functional parameters have been successfully applied to determine the proton transfer reactions, specially for the PET and the ESIPT mechanisms. The calculations of the vibrational frequencies showed no imaginary frequency confirming the structures as minima. This calculation also provided information about the thermodynamic parameters. Electronic transition energies in ground state as well as in the excited state were calculated at CIS level by Time Dependent Density Functional Theory (TD-DFT) using B3LYP/Cam-B3LYP density functional with all electron Pople double-ζ basis set including two polarisation functions on heavier atoms 6-31G**. Emission wavelengths were elucidated on the TD-DFT (Cam-B3LYP) optimized structures of the excited state.

The electronic spectra of the ligand at neutral pH, showed hyperchromic effect on both the peaks corresponding to π-π^* transitions of the quinoline moiety in presence of Fe(III) ions. The chemical hardness of the ligand in different pH and its metal complexes indicated that the stability of its acidic form is higher than the neutral and basic forms. However, protonation of the pyridoxal nitrogen atom has favoured towards the acidic form. The theoretical results showed the good agreement with the experimental ones.

Effect of Electrode Surface Structure on Electron Transport in Molecular Junctions

Andrea N. Becker and Sharani Roy

Abstract:

Molecular junctions are the smallest form of nanoelectronic circuits, consisting of one molecule bound between two metallic tips that function as electrodes. The properties of these junctions have been of great interest to the scientific community for decades; however, there is still much unknown about the transport of electrons through the junction, and how it is affected by various electronic and geometric properties of the bridging molecule and the electrodes. Our research uses density functional theory (DFT) to computationally examine the effects of chemistry at the molecule-electrode interface on the transport properties of the junction. Since the structures of molecular junctions cannot be directly ascertained in a laboratory and their measured conductance show large fluctuations, our goal is to develop fundamental structure-property relationships that can guide the design of effective molecular junctions. We are particularly interested in understanding how variations in the structure of the electrode affect junction conductance. The electrode tips are modeled using the (111) face of a gold crystal, and the conducting molecules of interest consist of a benzene ring with either thiol or amine terminal groups (i.e., benzenedithiol (BDT) or benzenediamine (BDA)), as well as various other aromatic molecules. Transport calculations have been performed on static model BDT-gold and BDA-gold junctions using non-equilibrium Green's functions in combination with DFT (NEGF-DFT). *Ab initio* molecular dynamics calculations have been performed in conjunction with NEGF-DFT to calculate conductance histograms. Results show that models that include motion of electrode atoms are important to accurately capture the dynamical uncertainty of conductance in molecular junctions.

Recent Developments in Ab Initio Tools for Spin Nonadiabatic Systems

Nicole Bellonzi and Joseph E. Subotnik

Abstract:
When molecules interact with light, their electrons can be excited to higher energy states. As the molecule relaxes, it can undergo inter-system crossings (transitions between different spin states) through the spin-orbit coupling (SOC). The SOC can play an important role in the dynamics of the system (as can be seen for instance in the relaxation of benzaldehyde [Q. Ou and J. E. Subotnik]), but, while much progress has been made to include the SOC in dynamics by, e.g., the Gonzalez group, it is not typically included in standard ab initio molecular dynamics software. Here, we present our recent work in developing methods for investigating spin nonadiabatic systems.

Interfacial Properties of Two-dimensional CdS/Graphene Nanocomposites

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Abstract:

Cadmium sulfide is an attractive photocatalytic material that is challenged by low photocatalytic efficiency. The photocatalytic performance of CdS can be improved by pairing it with graphene in a nanocomposite with strong interfacial coupling. Interfacial contact would be maximized in a two-dimensional nanosheet bilayer architecture. This study explored the photocatalytic potential of a graphene/CdS bilayer by using density functional theory (DFT) to analyze the atomic-level interactions and electronic properties of the interface. We first determined an appropriate DFT method for bulk CdS and graphene, validating the accuracy of the Perdew-Burke-Ernzerhof (PBE) and Heyd-Scuseria-Ernzerhof (HSE) functionals. PBE and HSE were then used to examine the interfacial interactions in various models of the graphene/CdS nanocomposite. The optimized structures exhibited high interplanar distances and low adhesion energies, which are indicative of weak interfacial coupling. Bader charge analysis and interfacial electronic structures also suggest a weak chemical interaction between the layers. The weak coupling and minimal interfacial adhesion signify the low photocatalytic potential of the pure graphene/CdS nanocomposite. Current work investigates improving the interfacial coupling in these nanocomposites via boron and nitrogen doping and codoping of graphene.

Multiscale principles of photosynthetic light harvesting

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Abstract:

Photosynthetic light harvesting, the conversion of photons into chemical energy, is responsible for all food and atmospheric oxygen on earth. Understanding the design principles underpinning light harvesting from the atomic to cellular length scales offers the potential of rationally engineering increased photosynthetic yield. The challenge, however, is bridging the large range of length and timescales involved. I will present two stories aimed at developing a multiscale model of light harvesting. In the first, I will address how the vibrational environment of a pigment bound in a protein scaffold can control pathways of excitation energy transfer (EET) in the antenna protein PC645. In the second, I will model EET on the 100 nm length scale of photosystem II (PSII) to describe light harvesting in high efficiency (dim light) and photoprotective (bright light) states. Taken together, these two projects suggest a path towards understanding the emergent properties of pigment-protein complexes in their biological context, providing a first step towards rational re-design of the photosynthetic apparatus.

Multiconfiguration Quantum Embedding Methods

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Abstract:

Embedding schemes are a promising way to exploit highly accurate electronic structure methods with a lower computational cost. Unfortunately, exact methods that are currently used as impurity solvers such as Full Configuration Interaction (FCI) are still prohibitively demanding in terms of computational resources. To surpass current limitations related to the size of the CI problem, we have combined multiconfiguration self-consistent field (MCSCF) methods with density matrix and density embedding theories to treat extended systems with mutireference methods. This methodology allows us to understand the electronic structure of systems that present inherently multiconfigurational character, due to transition metals or actinides. We will present results on 1, 2, and 3 dimensions' systems, using complete active space (CAS)SCF theory as the impurity solver. Our results comprise Hubbard model examples, multiple bonds dissociation, and transition metal containing systems, where it is demonstrated that a full system problem can be reduced to an impurity one.

Quantum Mechanical Rate Calculations in Condensed Phase Reactions

Amartya Bose and Nancy Makri

Quantum mechanical simulations of condensed phase reactions are very challenging because of the high dimensionality involved and the long time typically required for completion of the reaction. Our group has recently developed a rigorous quantum-classical path integral methodology, which treats the interaction between the quantum system and the classical trajectories of the environment in full detail and without any ad hoc assumptions. We present two reactive flux-inspired methods suitable for quantum-classical rate calculations. In addition to allowing determination of the reaction rate constant, one of these methods captures the initial nonexponential transient dynamics which can significantly affect the time for completion of fast reactions. Calculations of the ferrocene-ferrocenium electron-transfer reaction in several solvents will be presented.

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Cyanine Dye Aggregation Behavior on Scaffolded DNA Origami

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In natural photosynthetic systems, quantum coherent effects contribute to a more efficient energy transfer pathway when light-harvesting chromophores are closely packed or aggregated. These effects may be imitated by exploiting the J-aggregation behavior of certain dyes, such as cyanines. A proof-of-concept study has established that J-aggregated pseudoisocyanine (PIC) dyes can be rationally attached to DNA scaffolding (Boulais, E. et al. In Revision), where they self-assemble in the minor groove of poly-A/T DNA sequences. In this work, we first use density functional theory (DFT) to analyze the interaction energy landscape between PIC dimers in order to determine a physical model for PIC aggregation behavior in solution and in the minor groove of DNA. Next, excitonic transport properties of the modeled PIC aggregates are calculated to learn how the physical aggregation behavior of PIC influences its efficiency of energy transfer. This physical aggregation information will be further utilized when designing or optimizing a DNA-dye excitonic circuit using PIC dyes on DNA origami nanostructures.

Monitoring water clusters “melt” through vibrational spectroscopy

Sandra E. Brown, Andreas W. Götz, Xiaolu Cheng, Ryan P. Steele, Vladimir A. Mandelshtam, Francesco Paesani

Abstract:

The ability of small water clusters to serve as model systems for elucidating the complicated structure and dynamics of bulk, condensed-phase water has made them the subject of intense and on-going interest. Playing a special role as the prototypical system for studying hydrogen-bonding in water is the water hexamer, as it is the smallest water cluster whose minimum energy configurations exhibit three-dimensional structures similar to those found in bulk water. In this work, we monitor the “melting” of the water hexamer from well-defined “solid-like” structures to disordered “liquid-like” structures by tracking the evolution of both the vibrational spectrum and the distribution of orientational bond order parameter as a function of temperature. To achieve this, we combine the unrivaled accuracy of the MB-pol potential energy surface with quantum dynamics methods which are able to capture both the anharmonicity and quantum effects that are critical for an accurate description of hydrogen-bonded systems. A range of temperatures over which “melting” occurs is identified for both $(H2O)_6$ and $(D2O)_6$, with the greater quantum-character of the $(H2O)_6$ cluster resulting in a lower melting-temperature range. Experimentally, the temperature-controlled determination of vibrational spectra for neutral water clusters remains out of reach. Thus, while we find that our results agree with the limited, low-temperature experimental data which is presently available, this work can be seen as a testament to the predictive capabilities of theory.

Low-Resolution Methods For Simulation Of Amyloid Formation

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Abstract:

Amyloidogenic proteins and peptides have been linked to a number of disease pathologies, provoking distinct interest within the biochemical community as to the mechanisms by which these species give rise to fibrillar aggregates within the cell. Recent experimental evidence suggests that natural cellular processes make use of colloidal droplets of protein material, and links between species involved in these droplets and amyloidogenesis have been identified. Despite these observations, insight into the mechanism of fibrillization from colloids remain scarce. Use of simplified models allow for the computational simulation and study of droplet systems with sizes significant enough to provide insight into how droplet-to-fibril phase transitions can occur. Coarse-grained and stochastic simulation methods can investigate systems with relatively few computational resources, while still providing useful insight into the general pathways by which amyloid fibrils can arise from colloidal droplets.

Quantum – Classical Path Integral with Langevin friction

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Abstract

Dynamical processes in condensed phase involving a low dimensional system coupled to a large molecular environment can be studied using the quantum classical path integral1-4 methodology developed in our group, where the system is treated with full quantum mechanics while its environment is treated via classical trajectories and system - environment interaction is included with full atomistic detail without any approximations. We extend QCPI with the addition of Langevin friction, allowing proper thermalization even when only a few classical degrees of freedom are included explicitly. The Langevin-QCPI methodology is equivalent to an additional harmonic bath coupled to the degrees of freedom of the system's immediate environment at a fraction of the computational cost associated with QCPI dynamics in full space. A Markovian friction kernel leads to a δ-correlated stochastic force according to the fluctuation-dissipation theorem5, which mimics a white-noise environment at the statistical limit of an infinite reservoir.

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Electron Transfer Assisted by Vibronic Coupling from Multiple Modes

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Abstract

Understanding the effect of vibronic coupling on electron transfer (ET) rates is a challenge relevant to a broad range of systems within the biological and physical sciences. The Marcus–Jortner–Levich (MJL) theory offers a model for calculation of ET rates based on a simple analytic expression with a few adjustable parameters. Here we accurately calculate ET rates spanning over four orders of magnitude in the 106 –1010 s−1 range, thereby demonstrating that the MJL equation in conjunction with density functional theory can be used as a predictive first-principles methodology. This is achieved by evaluating the full MJL equation with a Monte-Carlo sampling of the complete active space of thermally accessible vibrational modes. The contribution to the rate of individual modes is illustrated, providing insight into the interplay between vibrational degrees of freedom and changes in electronic state. The findings are valuable for understanding ET rates modulated by multiple vibrational modes.

Inchworm Monte Carlo for exact non-adiabatic dynamics

Hsing-Ta Chen, Guy Cohen, David R. Reichman

Abstract:

Real-time diagrammatic Quantum Monte Carlo (dQMC) formalism using the inchworm algorithm is presented for the exact study of spin–boson dynamics. We formulate the method in terms of two distinct expansions: the first with respect to an expansion in the system–bath coupling and the second as an expansion in the diabatic coupling. The latter approach motivates the development of a cumulant version of the inchworm dQMC method, with the benefit of improved scaling. We present extensive benchmark results for two different inchworm dQMC expansions for the spin–boson model, which are presented in the companion paper. We discuss convergence properties and error propagation, and compare the newly presented methods with previously developed numerically exact approaches for this problem at a wide range of parameters. Our results and analysis allow for an understanding of the benefits and drawbacks of inchworm dQMC methods, as compared to other numerically exact approaches to non-adiabatic quantum dynamics.

Title: Electron-transfer-induced heat transport in molecular environments

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Abstract:

In contrast to metals and semiconductors, charge and energy transport in molecular environments are generally assumed to be independent. Charge transport takes place through electron transfer while heat transport occurs through phononic interactions. Consequently, the examination of heat transport in molecular systems has traditionally focused on the contributions from phonons. However, it has been recently shown that the electrons transfer between molecular sites of different local temperatures is accompanied by heat transfer solely generated by the electron transport, which combines additively with the standard phononic heat transport. To obtain the unified picture of these two energy transport channels, we have developed a theory of heat transport in environments that sustain intersite phononic coupling and electron hopping by merging multithermal Marcus formalism with stochastic Langevin dynamics. The heat currents generated through both phononic transport and electron transfer between sites characterized by different local temperatures have been calculated and compared. We find the electron-transfer-induced heat current is comparable to that of the standard phononic transport for donor-acceptor pairs with efficient bidirectional electron transfer rates (relatively small intersite distance and favorable free-energy difference). In most other situations phononic transport is the dominant heat transfer mechanism.

Understanding of solvent effects on surface-enhanced Raman scattering: insight from atomistic description of electrodynamics combined with classical molecular dynamics

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Abstract:
A pyridine molecule in the dilute aqueous solution binding to a tip of nanoparticle dimer, where the electromagnetic field is enhanced and extremely confined in angstrom dimensions, shows the prominent signals in surface-enhanced Raman scattering (SERS) compared to the contributions from the solvent water molecules. Many efforts have been mainly put into the understanding of the chemical effects arising from solvent in terms of solvent-solute, solute-solute, and solvent-solvent interactions. However, compared to the enhancement from electromagnetic mechanism the chemical contribution is extremely tiny. Our previous studies have shown the molecules in vicinity of the metallic nanoparticle significantly modify the electric field distribution, which could reflect in the near-field spectroscopy as expected. In this work, we combine the atomistic electrodynamics with classical molecular dynamics in the dressed-tensor formalism to explore the SERS fluctuation with time evolution under the solvent screening effects. The simulations indicate pyridine and water molecules moving together with the field and field gradient varying lead to the enhancement distribution and spectral signatures. Compared to the results in the homogeneous field, where the solvent is represented by the water dielectric constant, the SERS intensity of pyridine is 6 times larger in the solvent of explicit water. Moreover, the water SERS intensity in the inhomogeneous field is smaller than that in the homogeneous field indicating the screening effects from the local environment of individual water molecule contribute to the SERS enhancement differently. The homogenous field can not properly describe the location-dependent electric field leading to the prominent signal of water. Our research provides the fundamental information for understanding the solvent effects from the viewpoint of the electromagnetic mechanism.

Multireference density functional theory with generalized auxiliary systems

Zehua Chen, Du Zhang, Ye Jin, Yang Yang, Neil Qiang Su and Weitao Yang

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Abstract:

A new scheme of density functional theory (DFT) calculations is presented in this work. Unlike traditional Kohn-Sham (KS) DFT, this new scheme starts from a generalized auxiliary system, whose density is different from that of the real system. The utilization of generalized auxiliary systems enables the combination of a KS-DFT calculation with linear response theories to include static correlation, leading to a multireference implicit DFT. Self-consistency can be reached. There are multiple candidates for the excitation energy term in the total energy expression. In this work, the particle-particle random phase approximation (pp-RPA) is selected as an example. Systems with significant multireference characters, such as diradicals and dissociated diatomic molecules, are tested with this method. Performance on excitation energies is also presented. Results show that this multireference DFT successfully describes molecule dissociation and double bond rotation barrier.

Adsorption dynamics and structure of ligands on gold nanoparticles

*Gene Chong,[1] Xi Zhang,[2] Yongqian Zhang,[3] Leili Zhang,[3]
Qiang Cui,[3] Robert J. Hamers,[3] Catherine J. Murphy,[2] and
Rigoberto Hernandez[1]*

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Abstract:
The shape, size, and surface chemistry of gold nanoparticles can be tuned to make targeted sensors and drug delivery agents. In addition to satisfying the requisite function, such particles and their transformations must have zero, minimal, or reduced impact on environmental processes. Using atomistic molecular dynamics, we determine the layer-by-layer adsorption dynamics, ligand densities, and structure of engineered gold nanoparticles. We compare and validate the model to experiment. We have also implemented bottom-up coarse-grained models—benchmarked relative to the all-atom models—to characterize nanoparticle transformations—such as biomolecular corona formation—at longer time and length scales.

This work has been partially funded by the National Science Foundation through a grant to Center for Sustainable Nanotechnology under grant number CHE-1503408. The computing resources necessary for this research were provided in part by the National Science Foundation through XSEDE resources provided by Stampede and Bridges under grant number TG-CTS090079.

Classical Molecular Dynamics Simulation of Electronically Non-Adiabatic Processes via a Symmetrical Quasi-Classical Windowing Model

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Abstract:

A symmetrical quasiclassical (SQC) windowing model for "quantizing" the electronic harmonic oscillator degrees of freedom (DOF) in the Meyer-Miller (MM) classical vibronic (nuclear + electronic) Hamiltonian has previously been shown to be a simple approach for extending classical molecular dynamics (MD) simulation to the treatment of electronically non-adiabatic processes. The SQC/MM approach treats the electronic DOF in non-adiabatic dynamics fully classically, thereby maintaining dynamic consistency with the standard classical MD treatment of the nuclear DOF and potentially scaling well to the treatment of complex chemical systems. The accuracy of the approach has been demonstrated (via benchmarking against exact quantum results) for a number of applications (particularly in the context of popular spin-boson-type models of condensed-phase electronic dynamics) where the methodology is seen capable of treating quantum coherence effects in extreme regimes of strong to weak coupling between the electronic states, and of accurately simulating the decoherence of such effects as caused by coupling to the nuclear DOF. Here we present further recent developments in the SQC/MM approach including: (i) the development of a new SQC windowing model which elegantly handles the weak-electronic coupling limit (and is universally superior to the original model), (ii) an extension of the SQC model for extraction of the full electronic density matrix from a standard SQC calculation (arising through viewing the SQC window functions as pre-limit Wigner functions in action-angle variables), and (iii) a "kinematic" adiabatic representation of MM vibronic dynamics which totally eliminates the need to calculate second-derivative couplings (as appear in the adiabatic multi-state/channel Schrödinger Eq.) when it is desirable to use standard Born-Oppenheimer electronic states and energy surfaces (e.g., calculated via *ab initio* quantum chemistry) in realistic simulations.

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Multicomponent and Electronic Density Functional Theory Embedding

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Abstract:

Density functional theory (DFT) embedding approaches are of interest in the field of computational chemistry because they enable calculations on larger systems by treating subsystems at different levels of theory. To avoid the calculation of the non-additive kinetic potential, the orthogonality constrained basis set expansion (OCBSE) procedure, which enforces subsystem orbital orthogonality without requiring a level shifting parameter, was implemented. The main advantage of the OCBSE procedure is that excellent convergence behavior and accuracy are attained for DFT-in-DFT embedding without freezing any of the subsystem densities for the three chemical systems studied. The OCBSE procedure was also implemented in an embedding formulation for multicomponent DFT, which treats electrons and nuclei quantum mechanically on the same level within the nuclear-electronic orbital (NEO) framework. Electron-proton correlation is included through electron-proton correlation functionals based on explicitly correlated wavefunctions. Multicomponent DFT-in-DFT embedding theory was applied to the HCN and FHF^- molecules. The results illustrate that this approach provides qualitatively accurate nuclear densities in a computationally tractable manner.

Temperature Studies of the Solvation Environment of CO2 in Ionic Liquids

Clyde A. Daly, Jr., Steven A. Corcelli (University of Notre Dame)

Abstract:
Ionic liquids have attracted enormous attention for their various "green" properties, including a remarkable ability to solvate carbon dioxide. However, much is still unknown about the structure and dynamics of the solvation environment of the CO2 molecule in an ionic liquid. Using 2D-IR spectroscopy combined with molecular dynamics simulations it is possible to use the carbon dioxide molecule itself to probe these dynamics. Using a previously developed spectroscopic map, extensive molecular dynamic simulations at a variety of temperatures are performed for the model system of CO2 in 1-butyl-3-methylimidazolium hexafluorophosphate ([C4C1im][PF6]). Timescales for spectral diffusion and orientational relaxation are obtained, and 1D-IR spectra are calculated. The timescales are compared with experiment, and are correlated with the changes in temperature.

Reactive Coarse-grained Molecular Dynamics

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Abstract:
Coarse-grained (CG) models can be used to study long time and length scale properties of a variety of systems; however, when a system undergoes chemical reactions, current CG models are not able to capture this behavior. In order to develop CG models that can take into account chemical changes, a method is needed that can change its bonding topology and CG site-site interaction to switch between multiple bonding structures (or topologies). This challenge is especially great for “bottom up” CG models that are developed from the fundamental underlying atomistic-scale interactions. I will present the reactive multiscale coarse-grained (rMS-CG) method that uses all-atom (AA) data to create a CG model that is able to represent chemical reactions that undergo changes in bonding topology. As an example, the rMS-CG method was applied to a model SN2 reaction of 1-chlorobutane with a chloride ion in methanol solvent. The calculated CG PMF is found to be in excellent agreement with the fully AA reaction potential of mean force (PMF).

Extending Pressure Matching to Interfacial Systems

Michael DeLyser and Dr. William Noid

Abstract:

Structure based coarse-grained models often dramatically overestimate the system's pressure. We have previously resolved this issue by introducing an additional term in the potential that only depends on the global density. The resulting models accurately reproduce structural properties and the local pressure equation of state of all-atom models of bulk liquids. We demonstrate that this potential can be easily adapted as a many-body potential dependent upon particles' local densities. Using the potential in this form retains the structural accuracy from before. However, we find that, if we optimize the local-density potential to accurately reproduce fluctuations in the local density, then a global-density potential is still required to accurately describe the pressure equation of state. Finally, we show that the latter models provide a reasonable description of the liquid-vapor interface.

Localized Intrinsic Valence Virtual Orbitals for Automated Classification of Core Excited States

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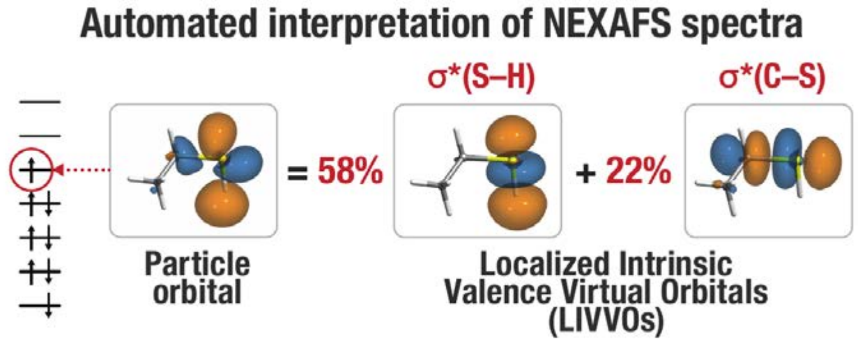
Abstract:
Accurate assignments of the unoccupied molecular orbitals involved in electronic excited states are crucial to the interpretation of experimental spectra. Here we present an automated approach to the assignment of excited states by introducing a unique orbital basis known as localized intrinsic valence virtual orbitals (LIVVOs), which are a special case of the previously reported valence virtual orbitals.1-3 The LIVVOs are used to quantify the local contributions to the virtual molecular orbitals, providing an assignment of atomic-level specificity. This localized set also allows us to define the total valence character of an excited state, giving immediate insight into how compact or diffuse an orbital is. We highlight the utility of our approach by studying the local orbital changes in core-excited states at the sulfur K-edge of ethanethiol and benzenethiol as well as hydrogen bonding in water.



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Embedded Mean-Field Theory for High-Efficiency Electronic Structure

Feizhi Ding and Thomas F. Miller

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Abstract:
A central challenge in theoretical chemistry is the development of efficient electronic structure methods to enable the accurate description of properties and dynamics for complex systems. Quantum embedding has emerged as a powerful strategy in which the total system is divided into a small, chemically active region described by a high level of theory, while the surrounding region is treated at a lower level of theory. Here, we present embedded mean-field theory (EMFT), which provides a general framework for quantum embedding at the mean-field level. EMFT employs a partitioning of the one-particle density matrix in the representation of an atomic-orbital (AO) basis set or a block-orthogonalized AO basis, and allows for self-consistent solution of the density through minimization of the EMFT energy functional. EMFT avoids the need to specify or fix the number of electrons and spin state in each subsystem, allowing for the description of charge flow and fluctuation between subsystems. Being a mean-field theory, EMFT enables straightforward formulation of analytical gradients and response theories. We then present the time-dependent (TD) linear response formulation of EMFT for describing excited electronic states in complex systems. Over a diverse set of chemical systems and applications, we find EMFT and TD-EMFT to perform accurately and stably, smoothly converging to the high-level of theory as the embedded subsystem becomes larger. These results indicate that EMFT and TD-EMFT are promising methods for the efficient, multi-level description of electronic structure and dynamics in complex systems.

Plasmon-Coupled Resonance Energy Transfer

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Abstract:

A recently developed real-time electrodynamics approach will be presented for determining the rate of resonance energy transfer (RET) between two molecules in the presence of any space-dependent, frequency-dependent, or complex dielectric function materials. In this approach, a classical electrodynamics expression is found for the energy transfer matrix element. We demonstrate that this approach yields RET rates in homogeneous media that are in precise agreement with analytical theory based on quantum electrodynamics. Furthermore, the theory allows us to develop the concept of a generalized spectral overlap (GSO), which is the integral of the molecular absorption coefficient, normalized emission spectrum, and the coupling factor (CF). Numerical simulation of the coupling factor enables us to extract important orientation and distance dependence of resonance energy transfer in the presence of metallic nanoparticles.

Toward Energy-Conserving, Linear-Scaling, Real Space Ab Initio Molecular Dynamics

Ian S. Dunn, Daniel Osei-Kuffuor, Jean-Luc Fattebert

Abstract:

Born-Oppenheimer molecular dynamics (BOMD) calculates forces on nuclei via an iterative quantum-mechanical electronic optimization at each time step. A tight convergence of this optimization is typically required in order to prevent a systematic drift in the total energy over time. Using extended Lagrangian BOMD (XL-BOMD), where the initial guess to this optimization procedure is propagated alongside the nuclei, energy conservation can be achieved without requiring an expensive tightly converged electronic solution. We have adapted XL-BOMD for use with the scalable real-space BOMD algorithms developed by Fattebert and Osei-Kuffuor. The fusion of these two methods requires the propagation of both the initial guess for the Kohn-Sham subspace as well as the centers of localized electronic orbitals. XL-BOMD has shown remarkable energy conservation when the localized orbitals are not truncated. We are currently exploring the magnitude and nature of the energy drift caused by truncating the localized orbitals.

Ultra-Coarse-Graining: Detecting and Optimizing Coarse-Grained Representations

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Abstract:

Biological systems couple phenomena at multiple scales in time and space, e.g. small molecule reactions control actin filament formation which in turn facilitates parts of mechanotransduction, connecting events on disparate magnitudes. This complexity creates challenges when using traditional atomistic simulation methods. Systematic coarse-graining techniques provide a statistical mechanical framework to produce models which allow us to rigorously probe these systems by creating principled data driven representations of the phenomena under study.

We describe advances in a new methodology in systematic coarse-graining aimed at studying biological systems: Ultra Coarse-Graining (UCG). UCG provides a framework to create CG models which combine multiple simpler CG models in a probabilistic framework. Critical to the quality of these UCG models is the mixture representation of the system under study: this is formulated as a probabilistic map from the high resolution system to the CG representation.

We focus on techniques aimed at improving the probabilistic aspect of specific coarse-grained representation used in models of systems such as lipid bilayers and proteins with non-conserved tertiary structure, leveraging established techniques such as dimensional reduction, hidden markov models, and mixture models.

An electrochemically active, coarse-grained model of transport through an ion conducting polymer electrolyte

Kaitlyn Dwelle and Adam Willard
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Abstract:
The production of smaller, safer, and more reliable lithium ion batteries depends on the development of new electrolyte materials. While solvent-free ion conducting polymers offer a promising alternative to traditional liquid electrolytes, they are generally less conductive and the microscopic origin of ion transport through polymers is poorly understood. In order to better characterize ion transport through disordered solids, we have developed a coarse-grained model of an electrochemically driven system. The model combines a coarse-grained representation of ion motion through a polymer network coupled to electrochemically active, polarizable electrodes. We demonstrate that the steady-state ion concentration profiles and average ion flux through the system are dependent on heterogeneous constraints and treatment of the electrode boundary conditions.

Rational Design of Triblock peptide-linker-lipid Targeting Family B GPCRs

Amendra Fernando, Yingying Cai, Heidi P. Hendrickson, Jeremiah Sims, Lucky Ahmed, Kelly J. Culhane, Yang Yang, Victor S. Batista, Elsa C.Y. Yan

Department of Chemistry, Yale University

Abstract:

Parathyroid hormone 1 receptor (PTH1R) is a family B G protein-coupled receptor (GPCR) which modulates calcium and phosphate homeostasis and is activated by parathyroid hormone (PTH) and parathyroid related proteins (PTHrP). GPCRs have been extensively studied as drug targets, especially with most focus on the largest subgroup of family A GPCRs. Family B GPCRs gained a wide popularity recently for the treatment of metabolic diseases. All the 15 members of the family B GPCRs bind to peptide hormones making it more difficult to study. As such, the structural and functional information between the peptide-receptor bridge of family B GPCRs is lacking. In this study, we used a combined experimental and computational approach to investigate a triblock peptide-linker-lipid molecular construct to target PTH1R, with PTH(1-14) as the signaling peptide, glycine-serine repeats as linker group, and DPPE as the lipid. These triblock molecular constructs have improved biostability and bioactivity than currently available drugs for osteoporosis. We have employed homology modeling, molecular docking calculations, and molecular dynamics simulations to investigate the binding mechanism of the triblock molecular construct with a full model of PTH1R. We showed that the molecular interactions between the peptide and the receptor are sensitive to the glycine-serine linker length. Molecular construct with the eight glycine-serine repeats serves as the optimum linker length with more favorable interactions. Our results can guide future design of triblock constructs targeting PTH1R for osteoporosis treatment, as well as other family B GPCRs.

Multiple time step integrators for accelerating ab initio molecular dynamics

Jason E. Ford, Stefan Seritan, Todd J. Martínez

Abstract:

By understanding the mechanism of a chemical reaction, we can predict when reactions occur and manipulate features of the pathway to adjust reaction rates. The Martínez group has recently used *ab initio* nanoreactors to simulate and discover chemical reactions. The computational cost of the underlying *ab initio* molecular dynamics is high, but cheaper methods currently cannot accurately describe bond-breaking and bond-forming events. In this work, we explore the use of multiple time step (MTS) integrators to accelerate reactive molecular dynamics simulations. Traditional MTS methods such as r-RESPA split forces based on which degrees of freedom they act on; this isn't possible in *ab initio* molecular dynamics simulations. Instead the forces are split into a low frequency *ab initio* force and high frequency model force. We show that by combining *ab initio* methods with less accurate models such as density functional tight binding (DFTB) or reactive force fields (ReaxFF) we can reduce the number of *ab initio* potential energy/gradient evaluations necessary for a given amount of simulation time, while maintaining accuracy of the underlying dynamics.

New Computational Tools for High-Throughput Discovery in Transition Metal Catalysis

Terry Z. H. Gani[1], Jon Paul Janet[1] and **Heather J. Kulik**[1], (1)Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA

Virtual high throughput screening has emerged as a powerful tool for the discovery of new materials. Nevertheless, screening of inorganic complexes is presently limited by the high cost of accurate property evaluation and the large, complex search space. To address these challenges, we have recently developed molSimplify, an open-source toolkit that automatically generates highly accurate inorganic molecular structures through a unique divide-and-conquer approach and automatically performs property analysis to accelerate high throughput screening of inorganic complexes. In conjunction with our structure generation toolkit, we have also developed and implemented a robust and automated workflow involving: (1) selection of a test set of ligands maximizing relative molecular diversity, (2) prediction of electronic structure outputs with a neural network prior to simulation for pre-screening and (3) screening of multi-million molecule organic libraries according to the discovered design rules to discover experimentally accessible ligand candidates. We demonstrate the broad utility of our integrated approach to inorganic complex discovery across the following applications: design of redox active functionalized ferrocenium complexes for selective ion separation and discovery of octahedral Fe(II/III) redox couples with nitrogen ligands.

Adding to the perovskite universe - inverse hybrid perovskites

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Abstract:

Perovskites are a rich family of functional materials with many interesting physical properties. Usually, the ABX_3 lattice contains two cationic species on the *A*- and *B*-sites surrounded by anionic species on the *X*-site. However, compounds are known that invert the ion types on the respective lattice sites, forming so-called inverse perovskites, further adding to the unique variety of perovskite compounds. Lately, conventional perovskites with one inorganic cation substituted by an organic molecule are intensively studied, due to the promising performance of $CH_3NH_3PbI_3$ based solar-cells. Here, for the first time, we combine both concepts, investigating the properties of inverse-hybrid perovskites by first-principles calculations, adding yet another structural variant to the variable perovskite universe.

Atomistic Simulation of Energy Transfer Between Nanocrystalline Semiconductors and Organic Semiconductors

Nadav Geva; James Shepherd; Lea Nienhaus; Moungi Bawendi; Troy Van Voorhis

Abstract:
Recently, the novel properties of nanocrystalline(NC) semiconductors have been used to create optical up- and down-conversion devices that can allow capturing more of the solar spectrum, through energy transfer to and from organic semiconductors(OSC)[1][2].

In this work, we produce design principles for the transfer rate between NCs and OSC from two perspectives: geometry and electronic structure. We here simulate nanocrystals using atomistic molecular dynamics, allowing for the resolution of novel structural details about ligand shell. We find that the ligands undergo a transition from being upright to laying flat. Therefore, NC-to-NC and NC-to-OSC distances differ from the expected length based on the length of the NC ligands. The end result is quantitative elucidation of the morphology of the ligand shell, and the impact of the morphology on the distances across which the energy transfer occurs, which we have corroborated using TEM. The geometries we gained from the MD allows us to calculate the electronic structure of a realistic dot. Starting from the MD geometries, we use configuration interaction with constrained density functional theory (CDFT-CI) to predict the transfer rate enchantment from the ligands.

Title: **Modeling Electronic Dynamics in Large Systems Using Semiempirical Effective Hamiltonians**

Authors: Soumen Ghosh, Niranjan Govind, Laura Gagliardi, Christopher J. Cramer

Performing large-scale static and dynamic calculations of electronic structure has become increasingly essential to understand the properties of complex chemical systems. With current computational resources, it is possible to perform *ab initio* calculations on systems with $O(10^3)$ atoms, typically to obtain time-independent solutions for static structures. To consider environmental effects with atomic detail, system sizes of $O(10^4)$ atoms become necessary, as does accounting for ensemble averaging. Semiempirical methods, with their dramatically enhanced computational speed, can be useful for the study of such systems provided their accuracy is sufficient. We have implemented a real-time (RT) dynamics approach for semiempirical electronic structure methods in *NWChem* using the Chebyshev propagator to follow density matrix evolution in large systems. We have studied the UV-visible spectra of various organic molecules using the INDO/S Hamiltonian by Fourier transforming the time-dependent dipole moment obtained from the time-dependent density, which is in turn obtained by subjecting the system to a delta-function electric field kick in order to calculate the excitation energies. The INDO/S model has previously been demonstrated in combination with configuration interaction approaches or the random phase approximation, to accurately predict small numbers of low-lying excitations in small to medium size systems. In very large systems, though, even a relatively small energy range may encompass thousands of individual excitations, and real-time methods are an efficient way to study such systems. We have applied the RT-INDO/S method to study the UV-vis spectra of the chromophores P3B2 and *f*-coronene, as well as those of much larger systems like ubiquitin in the gas phase and betanin dye solvated by explicit water and methanol molecules. RT-INDO/S provides qualitatively and very often *quantitatively* accurate results when compared with RT-TDDFT or experimental spectra for these systems.

Semiempirical Modeling of Plasmonic Ag Nanoclusters and the Chemical Mechanism in Surface-Enhanced Raman Scattering

Rebecca L. Gieseking, Mark A. Ratner, George C. Schatz
Department of Chemistry, Northwestern University, Evanston, Illinois

Quantum mechanical studies of Ag nanoclusters have shown that plasmonic behavior can be modeled in terms of excited states where collectivity among single excitations leads to strong absorption. However, new computational approaches are needed to provide understanding of plasmonic excitations beyond the single- excitation level. We show that semiempirical INDO/CI approaches with appropriately selected parameters reproduce the TD-DFT optical spectra of various closed-shell Ag clusters. The consideration of double excitations in all cases improves the agreement of the INDO/CI absorption spectra with TD-DFT, suggesting that the SDCI calculation effectively captures some of the ground-state correlation implicit in DFT. Using this approach, we model the surface-enhanced Raman scattering (SERS) spectra of two geometries of the prototypical Ag_{20}-pyridine cluster and decompose the enhancement factors at each wavelength into electromagnetic and chemical terms, with proper treatment of resonant charge-transfer contributions to the enhancement. We show that the electromagnetic enhancements for the Ag20 cluster are < 10 far from resonance but can increase to 10^2-10^3 on resonance with plasmon excitation in the cluster. The decomposition also shows that for the systems studied here, the chemical enhancements are primarily due to resonance with excited states with significant charge-transfer character. This term is typically < 10 but can be $> 10^2$ at electrochemical potentials where the charge-transfer excited states are resonant with the incoming light, leading to total enhancements $> 10^4$.

Nonadiabatic Proton-Coupled Electron Transfer at Electrochemical Interfaces: Hydrogen Evolution on Gold in Non-Aqueous Media

Zachary K. Goldsmith, Yan Choi Lam, Alexander V. Soudackov, Sharon Hammes-Schiffer

Abstract:

The first step of the hydrogen evolution reaction, a reaction crucial to carbon-neutral energy storage applications, is the Volmer reaction, or the discharge of a proton to form a surface-adsorbed species. A nonadiabatic theory for electrochemical proton-coupled electron transfer (PCET) that incorporates the electrostatic environment near an electrode via the Gouy-Chapman-Stern model is applied to proton transfer from triethylammonium (TEAH) and diisopropylethylammonium (DIPEAH) in acetonitrile solvent to a gold electrode. Experiments demonstrate that these two proton donors exhibit qualitatively different electrochemical kinetics for the Volmer reaction. Our theoretical model is utilized to generate the Tafel plots and subsequently the electrochemical transfer coefficients and kinetic isotope effects for TEA(H/D) and DIPEA(H/D). Differences in electrochemical kinetics between the protium/deuterium donors are attributed to both distance from and orientation with respect to the electrode, as well as contributions from different vibrationally excited states. This model unravels the complex kinetics of a fundamental electrochemical process and may be extended to other interfacial PCET reactions.

Role of Active Site Conformational Changes in Photocycle Activation of the AppA BLUF Photoreceptor

Puja Goyal and Sharon Hammes-Schiffer

Department of Chemistry, University of Illinois at Urbana-Champaign

Abstract:

Blue light using flavin adenine dinucleotide (BLUF) proteins are essential for the light regulation of a variety of physiologically important processes such as photosynthetic gene expression, phototaxis and photophobia in bacteria. They also serve as a prototype for protein-modulated photoinduced proton-coupled electron transfer (PCET). An understanding of the fundamental signaling mechanism of these proteins can guide the design of novel systems for optogenetics applications. Free energy simulations elucidate the active site conformations in the AppA BLUF domain before and following photoexcitation. For the dominant Trpin/Metout conformation, the hydrogen-bonding pattern conducive to the proton relay from Tyr21 to the flavin chromophore is not thermodynamically favorable on the ground electronic state but becomes more favorable, corresponding to approximately half of the configurations sampled, on the locally excited state of the flavin. The calculated energy gaps between the locally excited state and the charge-transfer state associated with electron transfer from Tyr21 to the flavin suggest that electron transfer from Tyr21 to the flavin is more facile for configurations conducive to proton transfer. When the active site conformation is not conducive to PCET from Tyr21, Trp104 can compete directly with Tyr21 for electron transfer to the flavin through a nonproductive pathway, impeding the signaling efficiency. These insights pave the way for nonadiabatic dynamics studies of the system following photoexcitation using quantum mechanical/molecular mechanical (QM/MM) surface hopping methodology that has been applied recently to photoinduced PCET in a phenol-amine complex in 1,2-dichloroethane solution, leading to important insights into the roles of solvent dynamics and vibrational relaxation.

The TT-SOFT Method: An Efficient Approach to High-Dimensional Quantum Dynamics Simulations Based on the Tensor-Train Decomposition

Samuel M. Greene and Victor S. Batista

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Abstract:

We introduce the implementation of the split-operator Fourier transform (SOFT) method based on adaptive Tensor-Train (TT) representations generated by mode unfolding and singular value decomposition. The resulting *tensor-train split-operator Fourier transform* (TT-SOFT) method is a rigorous approach to quantum dynamics simulations of systems with many degrees of freedom. The time-evolving wave function is represented as a tensor with reduced rank in TT format and is propagated by recursively applying the time-evolution operator as defined by the Trotter expansion to second order accuracy. In effect, the TT-SOFT method bypasses the need for full-rank representations and provides a systematic approach to propagating the time-evolving wave function with a reduced number of basis functions, subject to the constraint of a desired accuracy. The TT format significantly reduces the memory requirements and improves the efficiency of multi-dimensional Fourier transforms necessary for propagation based the Trotter expansion of the time-evolution operator. This poster provides a detailed description of the implementation of the TT-SOFT method and demonstrates its accuracy and capabilities as applied to model systems, including the numerically exact propagation of the 24-dimensional wave-packet describing the S_1/S_2 interconversion dynamics of pyrazine following UV photoexcitation.

Stark control of electrons

Bing Gu, Liping Chen and Ignacio Franco
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In this poster, we present theoretical and computational advances in the Franco group toward understanding and controlling the electronic properties of matter that is dressed by non-resonant laser fields. Through the dynamic Stark effect, nonresonant lasers of intermediate intensity (non-perturbative, but non-ionizing) have the potential to dramatically modify, in a reversible fashion, the electronic structure of materials, inducing transient electronic properties that can be very different to those observed near equilibrium. We focus the presentation on two basic aspects: 1) The theory of light absorption for materials driven far from equilibrium by laser fields, and; 2) The simulation of recent experiments that use nonresonant light to induce currents along nanojunctions.

A novel approach to the implementation of the J-engine on GPGPUs

R. D. Guerrero, R. M. Parrish and T. J Martinez

Pulse Institute, Stanford University

Abstract:

Achieving high performance of the GPGPU may be hampered by the amount of memory that is needed per each thread. Current implementations of the *J*-engine method uses mainly two techniques to compute the repulsion integrals: McMurechie-Davidson and Rys quadratures.[1-3] Given a shell of primitives of total angular momentum L, the scaling of the leading formal computational cost in FLOPS/MOPS is (L^9/L^6) for McMurchie-Davidson while it is (L^9/L^8) for Rys quadratures. Therefore, the GPGPU implementation of the J-engine starts losing performance for high angular moment shells because the memory requirements constraints the number of threads that can be launched simultaneously by the SM and also because the fast memory for register space is exhausted making unavoidable the usage of local memory that is about hundred times slower per memory transaction.

In this work we explore new techniques for the efficient construction of *J* matrix and its contributions to the gradient on GPGPU hardware for high angular moment shells leveraged by the usage of accurate Chebyshev interpolation for the efficient computation of the Boys function or Rys quadratures at the lowest possible costs combined with the usage of dynamic precision guided by integral thresholds. High throughput can be achieved and maintained by minimizing the amount of data transfer that is needed in order to compute a given shell of integrals and maximizing the reuse of common data. In order to achieve the best performance, we are taking an eclectic approach to the task of computing the repulsion integrals by using the McMurchie-Davidson method for low angular momentum shells and the Rys quadrature approach for high angular moment shells. The crossover in the speed of the two methods is determined experimentally.

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Gibbs Ensemble Monte Carlo with Solvent Repacking: Phase Coexistence of Size-asymmetrical Binary Lennard-Jones Mixtures

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Abstract:

We describe a Monte Carlo method for simulation of vapor-liquid phase coexistence in size-asymmetrical Lennard-Jones (LJ) binary mixtures. The method incorporates the Solvent Repacking Monte Carlo (SRMC) approach, which offers efficient trial moves for the exchange of a large particle for several small particles, into the Gibbs Ensemble Monte Carlo (GEMC) method. SRMC yields a significant efficiency improvement in simulation of dilute large species mixtures at low temperature compared to the original Gibbs ensemble Monte Carlo method with identity exchange (IE) moves. Vapor-liquid phase diagrams are reported for LJ mixtures with a diameter ratio σSS : σLL of 1:2 with well depth ratios εSS : εLL = 1.2, 1.5 and 2, producing spindle-type, azeotrope, and closed loop types of phase diagram, respectively. Further refinements of the SRMC method may enable its application to thermodynamic and phase behavior of more complex fluid systems, including aqueous solutions.

Electronic Structure Calculations of NiFe Oxyhydroxide Electrocatalysts: Characterization and Spectroelectrochemical Analysis

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Abstract:

NiFe oxyhydroxide materials are highly active electrocatalysts for the oxygen evolution reaction (OER), an important process for carbon-neutral energy storage. Recent spectroscopic and computational studies probing the structure and mechanism of these materials support iron as the site of catalytic activity but differ with respect to the relevant iron redox state. In the work presented here, hybrid periodic density functional theory calculations are performed to elucidate the redox thermodynamics and electronic structure of Ni-only and mixed NiFe oxyhydroxide thin-film electrocatalysts. First-principles calculations of proton-coupled redox potentials and magnetizations reveal that the Ni-only system features oxidation of Ni^{2+} to Ni^{3+}, followed by oxidation to a mixed $Ni^{3+/4+}$ state at a potential coincident with the onset of OER activity, whereas in Fe-doped system, the catalyst is shown to be redox inert before the onset of catalysis, which coincides with the formation of Fe^{4+} and mixed Ni oxidation states. The electronic structures of the Ni-only and Fe-doped materials as observed from the projected density of states analysis indicate that introduction of Fe dopants changes the character of the conduction band minimum from Ni-oxide in the Ni-only to predominantly Fe-oxide in the NiFe electrocatalyst. These computational results and corresponding interpretations are also consistent with the experimental data from cyclic voltammetry, operando Mössbauer, UV-vis, and X-ray spectroscopic studies. These findings provide a unified experimental and theoretical description of the electrochemical and optical properties of Ni and NiFe oxyhydroxide electrocatalysts and serve as an important benchmark for computational characterization of mixed-metal oxidation states in heterogeneous catalysts.

Designing artificial neural networks for high-throughput calculations on exciton energy transport properties

Florian Häse, Christoph Kreisbeck and Alán Aspuru-Guzik

Abstract:
Understanding the relation between structure and dynamics in excitonic energy transport processes is of great interest to many fields and could facilitate the development of more efficient solar cells. With only a small number of different excitonic systems realized in nature and considerable experimental efforts necessary to analyze them we need cheap computational methods to efficiently calculate exciton transport properties of a large range of artificial excitonic systems.

Energy transport properties of light-harvesting complexes have been computed from excitonic models in nonlocal propagation schemes such as the hierarchical equations of motion (HEOM). Solving these equations, however, is computationally costly due to the adverse scaling with the number of excitonic sites in the considered system. We therefore propose the use of artificial neural networks to bypass the computational demand of established techniques for exploring the structure-dynamics relation in excitonic systems at an acceptable prediction accuracy. We demonstrate how to efficiently employ Bayesian Optimization for designing transferable neural networks for predicting transfer times and transfer efficiencies of excitonic systems from the Hamiltonian.

Trained neural networks were found to achieve prediction accuracies comparable to approximate exciton transport models such as secular Redfield while keeping the computational cost to a minimum. Finally, we outline approaches for designing neural networks which can be applied to excitonic systems with varying number of excitonic sites.

Testing and Proposing Organic Catalysts with in silico Chemistry

Thomas Heavey, Juan Manuel Ortiz Sanchez, Wenyu Wang, John Porco, David Coker

Abstract:

α,α,α',α'-tetraaryl-1,3-dioxolan-4,5-dimethanols (TADDOLs) have been used to catalyze the enantioselective photo-cycloaddition between methyl cinnamate and 3-hydroxy-4',5,7-trimethoxy-flavone (3-HTMF) on the way to producing flavone natural products. In order to understand catalytic nature of various TADDOLs, we have completed molecular dynamics simulations using metadynamics and replica exchange molecular dynamics (REMD). Initial metadynamics results were not clearly converged, but using REMD sampling unbiased by the definition of collective variables gives qualitatively similar results. The major contributing structures of the catalysts for their catalytic activity are in a configuration largely unseen in previous literature on TADDOLs.

Characterizing Chromophore-Chromophore and Chromophore-Environment Interactions Through Computational Methods

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Abstract:

Light harvesting pigment-protein complexes (PPC) have gained much interest due to their ability to efficiently transfer energy from antenna complexes which capture the light, to reaction centers.1 Recently, quantum-coherence effects have been experimentally observed in the excited energy transfer (EET) process for PPCs such as the Fenna-Matthews-Olson (FMO) protein and phycobiliproteins PC645 and PE 545.2-4 As these processes are dependent on the interaction between pigments and the protein environment.5 We aim to characterize these interactions and their effects. We investigated these effects for the bacterial chlorophyll (BChl) pigments in FMO and the residues in PC645 and PE545 involved in EET.

Spectral densities for BChl were calculated using a combined quantum mechanics (QM)/ molecular mechanics (MM) approach. The results of the small QM region with just BChl were compared to an expanded QM region including the local protein environment. Several differences between these representations were observed and their origins are explored. The pigment-pigment interactions can be characterized using transition dipole moments when they are widely separated. However, in PPCs where the pigments are close together such as PC645 and PE545, this assumption breaks down. This break down will be explored using transition density calculations.

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Large-scale Monte-Carlo/ Molecular-Dynamics Calculations of Clusters in Intense X-Ray Pulses

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Abstract:

We present the methodology of our recently developed Monte-Carlo/ Molecular-Dynamics method for studying the fundamental ultrafast dynamics induced by high-fluence, high-intensity x-ray free electron laser (XFEL) pulses in clusters. The quantum nature of the initiating ionization process is accounted for by a Monte Carlo method to calculate probabilities of electronic transitions, including photo absorption, inner-shell relaxation, photon scattering, electron collision and recombination dynamics, and thus track the transient electronic configurations explicitly. The freed electrons, atoms and ions are followed by classical particle trajectories using a molecular dynamics algorithm. Our calculations reveal the role of electron-ion recombination processes that lead to the development of nonuniform spatial charge density profiles in x-ray excited clusters over femtosecond timescales at XFEL intensities exceeding 10^{20} W/cm^2. The Ar cluster fluorescence spectrum is found to be very different from the Ar atom spectrum, in which recombination processes enable additional pathways to reach the required electronic configurations for fluorescence transitions. In the high-intensity limit, recombination dynamics can play an important role in the calculated scattering response even for a 2-fs pulse. We demonstrate that our numerical codes and algorithms can make efficient use of the computational power of massively parallel supercomputers to investigate the intense-field dynamics in systems with increasing complexity and size at the ultrafast timescale and in non-linear x-ray interaction regimes. In particular, picosecond trajectories of XFEL clusters with attosecond time resolution containing millions of particles can be efficiently computed on upwards of 262,144 processes.

Coarse-grained directed simulations via adaptive linear biases

Glen M. Hocky, Thomas Dannenhoffer-Lafage, Gregory A. Voth

Abstract:

In the area of molecular simulation, there are many situations where we might like to do extensive and expensive sampling procedures on a subsystem within a larger macromolecular context. For example, we might want to study the free-energetics of a small molecule bound to a protein that is contained in a large complex or embedded within a membrane. This is typically modeled by putting the sub-system into solution and fixing its conformation or constraining it via harmonic potentials. A downside of this approach is that it loses the native fluctuations due to changing the environment and the imposition of the extra potential, and these fluctuations may be crucial to achieving correct estimates. In this study, we adopt the ideas developed to incorporate experimental information into a molecular simulation, and show that by using linear biases on coarse-grained observables (such as distances or angles between large subdomains within the protein), we can keep the protein in a particular conformation while also preserving correct equilibrium fluctuations. As an example, we demonstrate this algorithm by training a bias that causes an actin monomer (and trimer) in solution to sample the same average structure and fluctuations as if it is embedded within an actin filament. Additionally, we have developed a number of algorithmic improvements that greatly accelerate convergence of the on-the-fly relative entropy minimization algorithms for this type of application. Finally, we have contributed these methods to the PLUMED open source sampling library.

Design of multi-functional nanogate in response to multiple external stimuli using amphiphilic diblock copolymer

Kai Huang and Igal Szleifer

Abstract:

We use a molecular theory to study the interplay between hydrophobic and electrostatic interactions of amphiphilic polymers grafted on the inner surface of synthetic nanopores. Our theory demonstrates that sequence-designed copolymers can serve as multi-functional gate in response to multiple external stimuli, with potential applications in nanofluidics and biosensors. Our theory predicts a sharp morphological transition and a discontinuous charge regulation of the confined copolymer that reflect a spontaneous global reconfiguration of the system to balance hydrophobic interaction, electrostatic interaction and protonation reaction. Our results highlight the importance of polymer sequence in nanogating and these theoretical insights can be used to guide the rational design of polymer-coated smart nanopores.

Tuning Electron-Proton Transfer Mediators for Molecular Electrocatalysis

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Abstract:

Nature often serves as a seminal source of inspiration for the development of alternative renewable energy technologies, such as artificial photosynthesis. Central to many of these energy conversion processes is proton-coupled electron transfer (PCET) reactions. Moreover, biological systems frequently rely on mediators to couple electrons and protons between cycles/sites during catalysis, with two prime examples being the plastoquinone and the Tyr-His pair found in Photosystem II. The plastoquinone cycles between the oxidized quinone and the doubly-reduced, doubly-protonated hydroquinone states to mediate the transfer of two electrons and two protons across the membrane. In collaboration with the Stahl group, our analysis of the redox behaviors of over one hundred quinones revealed linear correlations between the 1 e^- reduction potentials, pK_a values, and 2 e^-/2 H^+ reduction potentials with an effective Hammett constant. More importantly, key deviations resulting from hydrogen-bonding, halogenated, charged, and sterically-bulky substituents were identified and analyzed. In principle, these types of deviations can be leveraged to tune the redox properties of quinone-based catalysts, mediators, or devices beyond those predicted by standard linear scaling relationships. Based on the Tyr-His redox mediator, the groups of Gust, Moore, and Moore have designed a series of benzimidazole-phenol (BIP) dyad constructs. A nonadiabatic PCET rate theory was used to calculate the kinetic isotope effects (KIEs), which are in good agreement with the electrochemically measured KIEs. Notably, theory predicted that amino-substituted BIPs would undergo a concerted two-proton transfer upon oxidation, manifesting in a ~300 mV decrease in the redox potential relative to dyads undergoing only a single proton transfer. These predictions were later validated with (spectro)electrochemical experiments. Broadly, these results help to establish design principles for managing proton activity at water oxidation sites in artificial photosynthesis.

Vibrational energy relaxation – application of quantum-classical methods

Amber Jain and Joseph E. Subotnik

Abstract:

We here investigate the applicability of quantum-classical methods to capture vibrational energy relaxation. Several methods are benchmarked for a model problem comprising a harmonic oscillator bilinearly coupled to a bath of harmonic oscillators, for which a numerically exact computation is feasible. The results show that, very often, one can recover the correct vibrational relaxation rates and detailed balance.

Training neural networks for transition metal complex screening and design

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Accurate prediction of properties is the bottleneck for virtual screening and computational material discovery, normally involving first-principles methods such as density functional theory (DFT). Machine learning methods have the potential to accelerate screening of novel materials, with artificial neural networks (ANNs) in particular being able to reproduce DFT-level accuracy for a wide range of organic molecular and crystalline inorganic chemistries at fractional cost relative to *ab initio* methods. However, fewer results are available for inorganic complexes, despite their being ubiquitous in molecular catalysis and having great potential for construction of molecular devices. These complexes pose specific design challenges owing to 1) complicated and poorly delineated metal-ligand bonding, multiple accessible spin states and uncertainty regarding DFT functional/electronic structure method choice; and 2) practical difficulties relating to generation of appropriate starting geometries, which is normally handled by SMILES and force fields for organic materials. We work to address both issues by training ANNs that are able to predict various energetic and geometric properties of octahedral single-site transition metal complexes (Cr-Ni) as well as their dependence on the fraction of exact exchange, providing estimated properties and functional sensitivity simultaneously. We base our predictions on physical atomic properties and '2D' connectivity information, which allows us to make predictions in the absence of detailed geometric information. We use a novel metal-centric approach to describe transition metal complexes and compare discrete and continuous representations from a predictive modeling perspective. Despite using relatively coarse-grained descriptors, our approach allows us to predict properties that depend on multiple geometries, for example redox potentials and adiabatic spin splitting energies, at near DFT-uncertainty levels. We address difficulties in initial structure generation by incorporating ANN-informed, oxidation- and spin-state sensitive initial metal-ligand bond lengths in our open-source inorganic complex design software package, molSimplify, outperforming force fields and our existing database lookup functionality.

"Watching" the Dark State in Ultrafast Nonadiabatic Photoisomerization Process of a Light-Driven Molecular Rotary Motor

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Abstract:

Photoisomerization dynamics of a light-driven molecular rotary motor, 9-(2-methyl-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-ylidene)-9*H*-fluorene, is investigated with trajectory surface-hopping dynamics at the semiempirical OM2/MRCI level. The rapid population decay of the S_1 excited state for the M isomer is observed, with two different decay time scales (500 fs and 1.0 ps). By weighting the contributions of fast and slow decay trajectories, the averaged lifetime of the S_1 excited state is about 710 fs. The calculated quantum yield of the M-to-P photoisomerization of this molecular rotary motor is about 59.9%. After the $S_0 \rightarrow S_1$ excitation, the dynamical process of electronic decay is followed by twisting about the central C═C double bond and the motion of pyramidalization at the carbon atom of the stator–axle linkage. Although two S_0/S_1 minimum-energy conical intersections are obtained at the OM2/MRCI level, only one conical intersection is found to be responsible for the nonadiabatic dynamics. The existence of "dark state" in the molecular rotary motor is confirmed through the simulated time-resolved fluorescence emission spectrum. Both quenching and red shift of fluorescence emission spectrum observed by Conyard et al. [Conyard, J.; Addison, K.; Heisler, I. A.; Cnossen, A.; Browne, W. R.; Feringa, B. L.; Meech, S. R. *Nat. Chem.* 2012, *4*, 547−551; Conyard, J.; Conssen, A.; Browne, W. R.; Feringa, B. L.; Meech, S. R. *J. Am. Chem. Soc.* 2014, *136*, 9692–9700] are well understood. We find that this "dark state" in the molecular rotary motor is not a new electronic state, but the "dark region" with low oscillator strength on the initial S_1 state.

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Extending the Range and Physical Accuracy of Coarse-Grained Models with Ultra-Coarse-Graining

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Abstract:
Coarse-grained (CG) models provide an efficient way to extend the time and length scales of computer simulations by averaging the details beneath the CG resolution. Despite the efficiency and speed-up of the CG model, important information lower than the CG resolution might be lost from the coarse-graining process. In order to surmount this limitation, ultra-coarse-graining methodologies have been developed by incorporating discrete state variables into configurational variables. In this work, we present the general UCG theory designed for frequent changes of internal CG states. In such quasi-equilibrium limits, the UCG force field is expressed as a mixture of the standard CG force fields according to local parameters. We have efficiently implemented the force matching technique to obtain the variationally minimized per-particle-substate force field. By utilizing UCG with the rapid local equilibrium approach, we chose different local order parameters in various model systems to modulate the interactions between the CG particles. Finally, we extended the full bottom-up UCG approaches to cooperatively associating systems and interfacial systems. Compared to the standard MS-CG theory, the UCG model of hydrophobic association can more accurately describe the solute-solute correlation functions and the cluster size distribution of solute moieties. Furthermore, UCG models for liquid/vapor and liquid/liquid interfacial systems are superior in capturing the phase coexistence by providing transferable interactions to the bulk system. These results suggest practical applications for constructing a high fidelity CG model from the UCG framework.

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Excitation energies from particle-particle random phase approximation with accurate optimized effective potentials

Ye Jin, Yang Yang, Du Zhang, Degao Peng, Weitao Yang

Abstract:

The optimized effective potential (OEP) which gives the Kohn-Sham (KS) orbitals and orbital energies accurately can be obtained from a given reference electron density. These OEP-KS orbitals and orbital energies are used here for calculating electronic excited states with the particle-particle random phase approximation (pp-RPA). Our calculations allow the examination of pp-RPA excitation energies with the exact KS density functional theory. Various input densities are investigated. Specifically, the excitation energies using the OEP with the electron densities from the coupled-cluster singles and doubles (CCSD) method displays the lowest mean absolute error from the reference data for the low-lying excited states. This study probes into the theoretical limit of the calculated with KS-DFT orbitals and orbital energies. We believe that higher-order correlation contributions beyond the pp-RPA bare Coulomb kernel are needed in order to achieve even higher accuracy in excitation energy calculations.

Ionization Potential Optimized Consistent Global Hybrid Exchange-correlation Functional

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Abstract:
This presentation focuses on the ionization potential optimized global hybrid exchange-correlation functional – QTP17. This functional and the previously published CAM-QTP00, QTP00, and CAM-QTP01 have the common feature that the negative of the Kohn-Sham eigenvalues of all the occupied orbitals are good approximations of the exact vertical ionization potentials [1,2]. This feature, as has been proved by the correlated orbital theory, is required to make the one-particle theory to converge to the exact answer. And it has been shown that these methods could improve the accuracy of many physical and chemical properties that are challenging for the traditional density functional methods and could reduce the self-interaction error [3].

The CAM-QTP00 and CAM-QTP01 – the range-separated hybrid functionals – are somewhat complicated to implement and may slightly reduce the computational efficiency, and the global hybrid functional QTP00 is designed as inconsistent since the potential is not the derivative of the functional. The QTP17, on the other hand, is the first ionization potential optimized consistent global hybrid functional. It has only two parameters and uses the LDA for the local exchange contribution. These features make it easier to implement and more computationally efficient. And the benchmark calculations indicate that QTP17 could reach almost the same accuracy of the excited states properties compared to CAM-QTP00 but with improved performance on the ground states properties.

This presentation will introduce the basic principles of QTP17, the procedure of parameterization, and its performance in different test sets.

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Extending Imaginary Time Path Integral Techniques to Evaluate Multi-time Correlation Functions

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Abstract:

Ring Polymer Molecular Dynamics (RPMD) has proven to be a practical approach for including some quantum effects in condensed phase applications. However, the standard formulation of RPMD is limited to evaluating just single time thermal correlation functions. Here, we present an extension of the RPMD method for evaluating multi-time correlation functions that we call multi-time RPMD (MT-RPMD). The symmetries of this approximation are explored as well as its relation to higher order Kubo transforms. Numerical tests demonstrate this method is accurate for short times and is only slightly more expensive than an RPMD simulation.

Theoretical Prediction of Formation Constants of Some Bio-relevant Mixed Chelates of Divalent Copper Containing Bipyridyl and N-N, N-O and O-O Donor Ligands

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Abstract:
Prediction of formation constants (log K) for some bio-relevant mixed chelates of divalent copper containing 2,2'-bipyridine (bpy) as primary ligand and number of N-N, N-O and O-O donors as secondary ligands are reported in aqueous solution using quantum mechanical calculations. Ethylenediamine (en), methylethylenediamine (men), 1,3-propylenediamine (pn), and *o*- phenylenediamine (op), were used as N-N donor ligands whereas, glycinatate(gly), L-alanine (lala), β-alaninate (bala) and o-aminophenolate (ap), and hydroxyacetate (hac), oxalate (ox), malonate (mal), and catacholate (cat) were chosen as N-O and O-O donor ligands respectively. Imagining the theoretical complex formation equilibrium reaction at 298.15 K and 1atm. pressure in the aqueous state as $[CuA(H_2O)_4]^{2+}{}_{(aq)} + B_{(aq)} \leftrightharpoons [CuAB(H_2O)_2]^{2+}{}_{(aq)} + 2(H_2O)_{(liq)}$, the free energy value G_{aq}, for all the species in the reaction were calculated with the help of density functional theory (DFT) utilizing the optimized electronic structure of minimum energy. From the free energy values of the reactants and the products, the difference in the free energy ΔG_{aq}, was calculated using $[(\sum G_{products})_{aq} - (\sum G_{reactants})_{aq}]$ and subsequently the stability (formation) constant, log K, was determined using $[\Delta G_{aq} = -RT \ln K]$. It was found that the theoretical calculations qualitatively determine the order of stability constant but significantly overestimate the absolute value of log K. The accurate determination of the energy of solvation (ΔG_{solv}) poses a formidable challenge to the quantitative prediction of log K in aqueous medium. Computational protocol that can achieve a good degree of accuracy by employing linear least square fittings of the calculated log K values to the available experimental log K values is presented. The correlations between various other experimental and theoretically calculated constants for the mixed chelates such as log β, Δlog K, and log X can also be computed. The results verify that the correlations obtained, can be employed to similar metal complexes with proper manipulation. This explores the utility of the approach in the determination of the various types of stability constants of mixed ligand complexes theoretically.

Electronic structure and redox chemistry of heme centers in protein environments: a case study of bacterial cytochrome c peroxidases

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Abstract:

Bacterial cytochrome c peroxidases catalyze the reduction of hydrogen peroxide to water in the periplasm through the use of multiple heme iron cofactors1. This family of diheme enzymes contains subclasses that are similar in structure yet differ in functionality1. Within each subclass of enzymes, the two heme sites serve different functions; the penta-coordinated, low potential heme serves as the active site for the reduction of hydrogen peroxide to water, while it is proposed that the hexa-coordinated, high potential heme serves as the electron storage and transfer site2. The redox potentials of Fe(II)/Fe(III) transitions in each heme are tuned by interaction of the heme center with the protein environment, and the difference between high and low potential hemes can reach up to 550-700 mV1. Whereas experiment provides the values of redox potentials for the two heme sites, the understanding of the specifics of the protein-heme interaction responsible for major alternation of the redox potentials of chemically identical heme units is still elusive. Here we report the results of density functional theory and multireference perturbation theory calculations describing electronic structure of various spin-states and relevant energetic parameters for further evaluation of the redox potentials for isolated heme sites and protein models.

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Advancing Path Integral Techniques for Simulations of Quantum Dissipation and Transport

Michael Kilgour, Bijay Kumar Agarwalla, Dvira Segal

Abstract:

We present developments and generalizations to the quasi-adiabatic path integral (QUAPI) approach to dynamics in open quantum systems. Open system dynamics incorporating strong environmental interactions are in general not easy to simulate. Among the many available approaches, the path integral method stands out for its relative simplicity and numerical exactness. We have been developing a path integral code for nonequilibrium simulations of dissipative quantum systems, with an eye towards simulations of heat engines strongly interacting with the environment. To this end we have generalized our approach for multilevel systems with multiple types of bath interactions, and incorporated a two-time measurement protocol to enable computation of the cumulant generating function. We will show results incorporating these and other developments for simulations of model systems.

Designing quantum dot precursors with new first-Principles inorganic discovery tools

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To address a critical outstanding challenge in materials science, first-principles computational screening has emerged as a powerful tool for the discovery of new materials. Using our recently developed inorganic discovery toolkit, molSimplify code, we leverage multimillion molecule organic libraries for inorganic complex discovery, demonstrated here on the design of precursor molecules in quantum dot (QD) synthesis. These large databases of bioactive organic molecules are typically employed for discovery of therapeutic drug-like molecules; we instead demonstrate their power as a tool to discover design rules for inorganic complexes while maintaining realism (i.e., stable, synthetically accessible substituents) and providing diversity in functional groups. We demonstrate these tools on precursor design for III-V indium phosphide (InP) QDs. InP QDs represent promising alternatives to more toxic CdSe-based QDs, but InP QD production lags behind other QD materials due to limited understanding of how to tune InP QD growth. We carry out a first-principles computational screening approach to identify design strategies for the chemistry of In carboxylate precursors to tune the kinetics of key elementary steps in InP QD growth. We identify diverse indium precursor candidates (>200), and discover chemical functionalizations that can tune In-O bond cleavage energetics, which can be a useful proxy for In-P bond formation energetics in InP QD synthesis. Our simulations suggest that weak carboxylate oxygen nucleophiles lower activation energies, tuning the reaction barrier over a 10 kcal/mol range by altering ligand nucleophilicity. Thus, our computational study provides the conjugate acid's pK_a as an experimental handle that could lead to more controlled growth conditions to improve synthesized InP QD quality.

Quantum Yields Made Easy: Towards an Evaluation of Non-Radiative Rates

Alexander W. Kohn, Zhou Lin, and Troy Van Voorhis

Abstract:

For optical and excitonic devices, understanding the competition between radiative emission rates and various nonradiative decay pathways is key for rational design of device efficiencies. In particular, organic molecules in nonpolar media of the sort that are often used in luminescent solar concentrators or organic light-emitting diodes undergo internal conversion (S1 to S0) and intersystem crossing (S1 to T1). For these devices it is desired to minimize these loss mechanisms. Herein we will examine the experimental non-radiative decay rates for various families of molecules and discuss how their intra-family variation correlates with other spectroscopic observables. Estimating the rates of these processes has proven to be very difficult, as heuristics such as the energy gap law can be unreliable. We will discuss these shortcomings, reviewing experimental data in view of new time-dependent density functional theory (TDDFT) electronic structure calculations. Additionally, we will inspect evidence suggesting that higher-lying excited states (e.g., S2, Tn) are needed to explain non-radiative decay rates, a feature that is difficult to observe without using TDDFT or sophisticated wavefunction based methods.

Calculating spectral densities for perylene-3,4,9,10-tetracarboxylic diimides (PTCDI)

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Abstract:

Perylene diimide derivatives are a promising class of electron accepting materials because of their chemical tunability and physical properties. At the center of most perylene diimide derivatives is an aromatic core that favors π-π intermolecular interactions, which allow for high electron mobility and high molar absorption coefficients which are useful for optoelectronics. Understanding the dynamical process of excitation energy transfer (EET) in perylene diimide derivatives is crucial for designing and developing efficient photovoltaic devices.[2] Intramolecular spectral densities, calculated using the normal mode frequencies and normal mode coordinates of the ground and excited state potential energy surfaces, gives insight into the nuclear coordinate dependence of the electronic excitation energy.[1]

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Modeling the Volmer Reaction on Metal Electrodes with Nonadiabatic Proton-Coupled Electron Transfer Theory and Gouy-Chapman-Stern Model of the Electrochemical Double Layer

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Abstract:

The first step of the hydrogen evolution reaction (HER), an important reaction for the storage of renewable energy, is the formation of a surface-adsorbed hydrogen atom through electrochemical proton discharge or transfer, commonly known as the Volmer reaction. We have extended the theoretical treatment of nonadiabatic electrochemical proton-coupled electron transfer (PCET) to the Volmer reaction by incorporating a Gouy-Chapman-Stern model of the electrochemical double layer to calculate the electrochemical potential of H_3O^+, H_2O, and OH^- in the vicinity of the electrode. Tafel plots and kinetic isotope effects computed by the theoretical model are in excellent agreement with HER experiments conducted on Hg electrodes and Au(111) electrodes, providing validation for our model and lending support to Volmer reaction-limited HER mechanisms on Au electrodes. The model presented here may also be extended to other electrochemical PCET reactions involving interfacial proton transfer from solution to electrode.

The state point dependence of coarse-grained potentials for liquids

Kathryn M. Lebold, Dr. William G. Noid

Abstract:

Coarse-grained (CG) models are useful for describing time- and length- scales that are typically inaccessible in atomically-detailed molecular dynamics (MD) simulations. Coarse-graining consists of formally integrating out unimportant degrees of freedom from the finer-grained model; the reduced number of degrees of freedom results in a more efficient model for MD simulations.[1] The resulting CG potential is known as the potential of mean force, or PMF. In theory, the PMF contains all structural and thermodynamic information present in the underlying model, but in practice, the PMF is too difficult to determine analytically and must be approximated by various methods.[1] Additionally, the PMF depends on the thermodynamic state point at which it is constructed, and consequently, the extension of these potentials to other thermodynamic state points is called into question. This is known as the transferability problem in coarse graining.[2] We are attempting to investigate this transferability problem in a number of ways: (1) by employing an extended ensemble (XN) approximation,[3] (2) by qualitatively comparing interatomic potentials generated at different thermodynamic state points, and (3) by calculating the entropic contribution to the PMF, which encodes its temperature dependence.[4] In the extended ensemble approach, a CG force field is optimized with respect to several independent "ensembles," which are not in thermal equilibrium with each other and are not necessarily at the same thermodynamic state point, such that the XN force field is transferable between each of the independent ensembles.[3] In this work, an alkane XN is developed with respect to independent atomistic simulations of butane, heptane, and decane. The results of our investigations with this extended ensemble show that this approach is capable of describing both the structure and thermodynamic pressure correction of this range of alkanes with excellent fidelity to the underlying all-atom models. Secondly, our comparisons of the interatomic potentials for different molecules at different temperatures show that potentials for nonpolar CG sites tend to become less attractive as the temperature increases, while the potentials for polar CG sites tend to become more attractive as the temperature increases. The attractiveness of the CG potentials is also a function of the CG model resolution, the molecular mass, and the density. Finally, based upon this work, we anticipate developing quantitative methods for predicting the state-point dependence of CG potentials.

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First-principles Study of Energy Transfer Processes of the Open and Closed Quaternary Structures of Light-Harvesting Complexes in Cryptophyte Algae

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Abstract:

In this work, energy transfer processes in four closely-related light-harvesting complexes found in unicellular algae species are presented. The underlying ensemble of system-bath Hamiltonians that have been computed from first-principles are discussed. The computed linear absorption and excitonically-coupled circular dichroism spectra are compared against experimental measurements to assess the reliability of the parameterized models. The differences in the roles played by the low- and high-frequency vibrational modes of the system are elucidated in the non-adiabatic dynamics simulation computed from the path-integral based Partial Linearized Density Matrix (PLDM) method.

Towards Black Box Projection-based Embedding

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Abstract:

Projection-based WF-in-DFT embedding can be used to retain the high accuracy of wavefunction methods while still benefitting from the low cost of DFT. However, a number of challenges still remain to make projection-based embedding a truly black box method capable of describing of large complex systems. One challenge is to use a mixed basis set to describe our system because it provides a good balance between cost and accuracy. However, there are cases when using a mixed basis set introduces large amounts of error. Here we systematically analyze the possible sources of this mixed basis error by using the framework of embedding. Specifically, we determine if artificial charge flow occurs between subsystems, and if a minimal basis set in the environment gives rise to significant density errors. Another challenge is the derivation and implementation of analytical gradients. Here, we present recent work on analytical gradient theory for the projection-based embedding method, which will enable us to explore the potential energy surface so we can perform tasks such as geometry optimizations and study reaction pathways.

Many-body perturbation theory analysis of GaN defects

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Abstract:

Gallium nitride (GaN) and related alloys form a class of wide bandgap semiconductors that have broad applications as components in optoelectronic devices; in particular, power electronics and blue and ultraviolet optical devices. Nitride films grow with high defect densities, and understanding the relationship between structural defects and optoelectronic function will be central to the design of new high-performance materials. Here, we take a first-principles density functional theory (DFT) and many-body perturbation theory (MBPT) approach to quantify the influence of defects on the electronic properties of GaN, taking the nitrogen vacancy as an example. We predict that introduction of a charged nitrogen vacancy results in significant modification of the quasiparticle properties of GaN, which is partially captured by standard DFT. This work was partially supported by the Army Research Office.

Driven Similarity Renormalization Group Multireference Perturbation Theory

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Abstract:

The driven similarity renormalization group (DSRG) approach provides a simple and numerically robust way to formulate both single-reference [1] and multireference (MR) [2] theories. There are two key ingredients in the DSRG ansatz: a) the Hamiltonian is partially diagonalized via a unitary transformation and b) the excitation amplitudes are determined by a set of operator many-body conditions [3]. Recently we performed a perturbative analysis of the MR-DSRG equations up to third order [4,5]. The resulting multireference perturbation theory (MRPT) is intruder-free, size-consistent, non-iterative, and it also includes reference relaxation effects. The accuracy of second- and third-order DSRG-MRPT is benchmarked on the potential energy curves of F2, H2O2, C2H6, and N2 along the F—F, O—O, C—C, and N—N bond dissociation coordinates, respectively. The nonparallelism errors (NPEs) of DSRG-MRPT2 are found comparable to other MRPT2 methods including CASPT2 and NEVPT2, while the DSRG-MRPT3 method significantly reduces the NPEs over DSRG-MRPT2. We also compute the adiabatic singlet-triplet splitting (□ST) of 9,10-anthracyne. Our best estimate of □ST at the CASSCF(16,16)-DSRG-MRPT3/cc-pVTZ level of theory is 3.9 kcal/mol, a value that is within 0.1 kcal/mol from that obtain by Mukherjee multireference coupled cluster theory.

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Modeling of Proton-Coupled Electron Transfer in Soybean Lipoxygenase: QM/MM Free Energy Surfaces and Nonadiabatic Rate Constants

Pengfei Li, Alexander V. Soudakov, and Sharon Hammes-Schiffer

Abstract:

Soybean lipoxygenase is a prototype for proton-coupled electron transfer (PCET) in biological systems. The concerted PCET reaction catalyzed by this enzyme corresponds to proton transfer from a carbon atom of the linoleic acid substrate to an oxygen atom of a hydroxide ligand of the iron cofactor, as well as electron transfer from the pi backbone of the substrate to the iron center. This PCET reaction has a remarkably high kinetic isotope effect of ~80 at room temperature. We calculated the adiabatic free energy surfaces for this PCET reaction using mixed quantum mechanical/molecular mechanical (QM/MM) free energy simulations based on the finite temperature string method with umbrella sampling. Analysis of the free energy surfaces provided insights into the conformational sampling of the proton donor-acceptor (C-O) distance, which plays an important role in gating the PCET reaction. The roles of electrostatic and van der Waals interactions in the gating motion were also analyzed. In addition, the properties of the QM/MM free energy surface were used to compute input quantities to the vibronically nonadiabatic rate constant expressions for PCET. The resulting kinetic isotope effects for wild-type and mutant soybean lipoxygenases were compared to experimental values. This work provides a deeper understanding of the roles of electrostatics, conformational motions, and hydrogen tunneling in enzymatic PCET reactions.

An Ab Initio Exciton Model Including Single and Double Excitations: Energies, Gradients, Couplings, and Dynamics

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Abstract:

The Frenkel exciton model is a useful tool for coarse-graining electronic structures of multichromophoric systems. Focusing on singly-excited exciton states, we recently reported an *ab initio* exciton model for nonadiabatic dynamics simulations of large multichromophoric complexes [1,2]. Subsequently, we incorporated charge-transfer excited states in the exciton model [3], and demonstrated the robustness of the model in predicting reliable charge-transfer excitation energies and asymptotic behavior. In this work, we further expand the exciton model by incorporating the singlet-coupled pair of triplets, a doubly-excited exciton state that emerges in singlet fission, and derive analytical derivatives of the excitonic energies and couplings based on the Z-vector approach. Comparison with higher-order methods confirms that our model provides consistent energies and couplings. In addition, we show the possibility of carrying out molecular dynamics simulations on adiabatic energy surfaces as well as non-adiabatic dynamics simulations to properly model population transfer between electronic states.

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Towards Understanding the Electronic Structures of Iron-Molybdenum Cofactor in Nitrogenase with ab initio DMRG and Spin Projections

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Abstract:

Polymetallic transition metal compounds such as iron-sulfur clusters in biology have fascinating chemical and physical properties due to the presence of a large number of unpaired *d* electrons. Such systems are beyond the scope of the density functional theory (DFT) due to the strong correlation among different transition metal centers. The density matrix renormalization group (DMRG) is a powerful tool for strongly correlated systems. For iron-sulfur clusters, two problems need to be addressed: 1. Different spin states need to be resolved; 2. Local minimums are to be avoided. In this work, we present a combined approach using ab initio density matrix renormalization group (DMRG) with spin-projection to tackle these problems. The underlying wave function ansatz, spin-projected matrix product states (SP-MPS),[1] allows to initialize physically important states from broken-symmetry determinants, and is systematically improvable by gradually increasing the bond dimension in the underlying MPS. Some pilot applications to the iron-molybdenum cofactor in nitrogenase with eight transition metal atoms will be presented.

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Atomistic Modeling of Electromechanical Spectroscopies in Molecular Junctions

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Abstract:
In this poster, we present theoretical and computational advances in the Franco group toward the atomistic understanding of the electric and mechanical properties of single molecule junctions. At the methodological level, we introduce an accurate and computationally efficient strategy to capture non-reactive metal-molecule interactions that adapts the Tkatchenko-Scheffler scheme for van der Waals interactions into a simple and transferable classical force field. The force field is then used to quantitatively model experiments that measure the conductance of a conjugated polymer as a continuous function of its length. This strategy allows classical molecular dynamics simulation (MD) of molecules on surfaces with 10^6 atoms on microsecond timescales with the accuracy of high-level electronic structure methods. We also introduce well-defined criteria to determine when the Landauer steady-state approximation can be safely used to capture time-dependent currents in thermally fluctuating junctions, as is required to model experiments. Building upon these developments, we present advances toward the modeling of molecular electronics experiments with statistics, and studies that test the utility of force-conductance measurements in junctions as a platform to develop highly discriminating multidimensional single-molecule spectroscopies.

Triplet Tuning – A New “Black-Box” Construction Scheme for System-Dependent Density Functionals

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Abstract:
Density functional theory (DFT) is an efficient computational tool that plays an indispensable role in the design and screening of π-conjugated organic molecules with photochemical significance. However, due to intrinsic problems in DFT such as self-interaction error, the accurate prediction of energy levels is still a challenging task.[1] Functionals can be parameterized to correct these problems, but the parameters that make a well-behaved functional are system-dependent rather than universal in most cases. To alleviate both problems, optimally tuned range-separated hybrid functionals were introduced, in which the range-separation parameter, ω, can be adjusted to impose Koopman’s theorem, $\varepsilon_{\mathrm{HOMO}} = -I$. These functionals turned out to be good estimators for asymptotic properties like $\varepsilon_{\mathrm{HOMO}}$ and $\varepsilon_{\mathrm{LUMO}}$.[2,3] In the present study, we propose a “black-box” procedure that allows an automatic construction of molecule-specific range-separated hybrid functionals following the idea of such optimal tuning. However, instead of focusing on $\varepsilon_{\mathrm{HOMO}}$ and $\varepsilon_{\mathrm{LUMO}}$, we target more local, photochemistry-relevant energy levels such as the lowest triplet state, T_1. In practice, we minimize the difference between two $E(T_1)$’s that are obtained from two DFT-based approaches, Δ-SCF and linear-response TDDFT. We achieve this minimization using a non-empirical adjustment of two parameters in the range-separated hybrid functional – the above-mentioned ω, and the percentage of Hartree–Fock contribution in the short-range exchange, c_{HF}. We apply this triplet tuning scheme to a variety of organic molecules with important photochemical applications, including laser dyes, photovoltaics, and light-emitting diodes, and achieved good agreements with the spectroscopic measurements for $E(T_1)$’s and related local properties.[4]

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Derivation and Implementation of Analytical Derivatives of the Individual State Energies in the SA-REKS Method

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Abstract:

The state averaged restricted ensemble averaged Kohn-Sham method (SA-REKS) is a computationally efficient alternative to high-level multi-reference methods to provide both dynamic and static electron correlation in a balanced way. However, the analytical derivatives of the individual state energies was previously unavailable, because the energy is not obtained by self-consistent optimization of the energy functional. Here we derived the analytic energy derivatives formalism for (SI)-SA-REKS method with the Z-vector approach, and implemented the method effectively on graphic processing units (GPUs). We tested the performance of the implementation on a trans-PSB3 molecule embedded in water clusters of increasing size by making comparison with CASPT2. Our implementation has a speedup of 3X - 53X for systems with 14 to 116 atoms. The scaling, O(N1.77), is also superior to O(N3.00) of CASPT2, making (SI)-SA-REKS capable of handling excited state dynamics studies of large molecular systems.

Single-Molecule Imaging Using Atomistic Near-Field Tip-Enhanced Raman Spectroscopy

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Abstract:

Advances in tip-enhanced Raman spectroscopy (TERS) have demonstrated ultrahigh spatial resolution so that the vibrational modes of individual molecules can be visualized. The spatial resolution of TERS is determined by the confinement of the plasmon-induced field in the junction; however, the conditions necessary for achieving the high spatial confinement required for imaging individual molecules are not fully understood. Here, we present a systematic theoretical study of TERS imaging of single molecules, using a hybrid atomistic electrodynamics-quantum mechanical method. This approach provides a consistent treatment of the molecule and the plasmonic near field under conditions where they cannot be treated separately. In our simulations, we demonstrate that TERS is capable of uniquely resolving intricate molecule vibrations with atomic resolution, although we find that TERS images are extremely sensitive to the near field in the junction. Achieving the atomic resolution requires the near field to be confined within a few ångstroms in diameter and the near-field focal plane to be in the molecule plane. Furthermore, we demonstrate that the traditional surface selection rule of Raman spectroscopy is altered due to the significant field confinement that leads to significant field-gradient effects in the Raman scattering. This work provides insights into single-molecule imaging based on TERS and Raman scattering of molecules in nanojunctions with atomic dimensions.

Quantum Thermodynamic Entropy and the Second Law

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Abstract:

The quantum von Neumann entropy of an isolated universe is constant in time, in contradiction to the standard meaning of entropy in the second law: $\Delta S_{univ} > 0$. We propose an alternate definition of S_{univ} and test its behavior in calculations of a model oscillator system interacting with an environment in a spontaneous process of thermalization. Good agreement with the classical entropy change is observed in the limit of a large environment and negligible system-environment interaction. Outside this limit, quantum interactions lead to *excess quantum entropy production* above the classical value. The new entropy S_{univ} appears well founded for future explorations of quantum thermodynamics where excess entropy production may have physically significant effects on thermodynamic behavior.

Electrostatic effects on ionomer nano-structures

Boran Ma, Trung Dac Nguyen, Victor A. Pryamitsyn, Monica Olvera de la Cruz

Abstract:

Understanding electrostatic interaction in polymer with charged groups is crucial to better design shape memory polymers and ion conducting membranes for multiple energy storage and conversion applications. Here, we investigate the influence of the electrostatic interaction strength (represented by l_B) on the nanostructure of randomly charged polymers (ionomers) and their counter ions. Using coarse-grained molecular dynamics (CGMD) simulations, we found that variations in l_B remarkably affect the formation of ionic clusters for a range of charged monomer fractions (f_C). The structure factors of the charged species show a closely packed distribution of ionic clusters as l_B increases. The associated fractal dimension of ionic clusters is strongly dependent on both the value of l_B and of f_C . The analysis of cluster size distribution further reveals a percolation transition. Finally, a phase-space diagram of the different ionic structures is constructed by analyzing the distribution of ionic clusters. These findings provide insight into the role of electrostatics in governing the nanostructures formed in ionomer melts.

Approximate EOM-CCSD model for electron attached and ionized states.

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Abstract:

Equation-of-motion Coupled Cluster (EOM-IP/EA-CC) theory is a powerful tool for describing the electronic structure of electron attached and ionized states. EOM-CC with single and double substitutions (EOM-IP/EA-CCSD) is the most common approach among these models due to its advantageous balance of scaling and accuracy. However, even EOM-CCSD is prohibitively expensive to be applied to large molecular systems, having a scaling of O(N6) originating from the reference state CCSD calculation. Here, we propose an approximate EOM-CCSD model, which is similar to EOM-CCSD(2) (correlation perturbation at the second order) by Stanton and Gauss [1], yet provides a better accuracy without significantly increasing the computational cost. Similarly to EOM-CCSD(2), our method allows to skip the initial CCSD step and exploits MP2 amplitudes to approximate coupled-cluster T amplitudes. This dramatically reduces the overall computational cost and leads to the scaling with the system size of O(N5). The major difference between the proposed scheme and EOM-CCSD(2), comes from the disconnected terms in the similarity transformed Hamiltonian matrix [2]. Although the method formally no longer yields size-intensive energy gaps, the numerical results do not manifest any significant deviations from size-intensivity. We report a benchmark calculation for 96 molecules and a total of 3266 EE, EA, and IP energies. The proposed method is shown to be more accurate and as efficient as the related EOM-CCSD(2) model.

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Multiscale and structured interactions affect diffusion dynamics

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Abstract:
Diffusion dynamics in complex environments must properly address correlations at multiple scales. In many such environments, all-atom simulations would be too expensive, so coarse graining must be applied. In order to understand how a simple coarse-grained system behaves under multiple scales, we run simulations of a sphero-cylindrical tracer moving though a sea of hard scatterers while also being immersed in a Langevin bath. The scatterer background density and Langevin friction are manipulated so that both large and small differences in the correlation time between these two solvents can be addressed. The resulting multiscale dynamics of the tracer exhibits tunable and multiscale response. We observe how this response changes with system parameters and dimensionality.

This work has been partially funded by the National Science Foundation through grant number CHE 1700749. The computing resources necessary for this research were provided in part by the National Science Foundation through XSEDE resources provided by XSEDE-Stampede and XSEDE-Bridges under grant number TG-CTS090079.

Probing the Structural Properties of Small Clusters using the Diffusion Monte Carlo Method

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Abstract:
The ground states of small molecular clusters have long been of interest to theoretical chemists and physicists as their structures can be strongly influenced by quantum delocalization. We implement a popular method called diffusion Monte Carlo (DMC) to study the ground state energies, wavefunctions, and structural characteristics of small clusters from water to parahydrogen and their isotopologues. We assessed the performance of DMC with regard to sources of systematic error or bias (i.e. the random walker population size and the time step). In order to gain a more accurate, qualitative understanding of small water clusters in their ground states with 2-6 molecules, we employed an *ab initio*-based potential energy surface (PES) in conjunction with DMC to determine the minimum configurations/structures that substantially contribute to the wavefunction. More recently, our principle aim has been directed toward small parahydrogen clusters and their orthodeuterium isotopologues. Exploring these systems with DMC has proven to be nontrivial due to significant delocalization of the ground state over a vast configuration space that includes numerous local minima, many of which compete with each other for the ground state. We have performed a rigorous structural analysis of the aforementioned systems to probe phase transitions induced by quantum fluctuations and to identify the configurations that contribute appreciable amplitude to the ground state wavefunction. Consequently, we establish the physical properties of the ground state, which are either liquid- or solid-like depending on the extent of the quantum delocalization for the various isotopologues.

On the characterization of charge-transfer effects in non-covalently bound molecular complexes

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The charge-transfer (CT) effect is an important binding force in the formation of intermolecular complexes, which manifests itself by modulating the structural and vibrational properties of the binding moieties. Because of its key role, there have been a variety of approaches proposed to quantify the energetic magnitude of CT, typically relying on a definition of a fragment-charge-conserved (“CT-free”) state based on either Hilbert (orbital) space partitioning or real space partitioning.

In this work, we investigate two widely used definitions of the “CT-free” state: the absolutely localized molecular orbitals (ALMO) method, and the constrained density functional theory (CDFT) approach. Their performance on a broad range of model systems, including hydrogen-bonding dimers, water-ion complexes, Lewis acid-base adducts, and metal-carbonyl complexes, is compared. For the majority of the investigated systems, CDFT yields a significantly smaller CT contribution compared to that given by the ALMO approach. We then employ the adiabatic EDA approach to explore which definition better accounts for well-established observable consequences of CT. We find that fingerprints of CT, such as the “pyramidalization” of the borane molecule upon the formation of dative complexes, and the red shift of the OH stretch frequency of H_2O when it is bound to a proton acceptor, appear on the “CT-free” PES constructed with the CDFT definition.

These quantitative and even qualitative differences arise from the physical discrepancies between these two definitions: (i) the CDFT definition captures only the net charge flow between molecules, as opposed to the ALMO definition where forward and backward donations contribute to the resulting CT energy additively; (ii) the so-called constant density (ρ) charge-transfer effect is incorporated in the “CT-free” state prepared by CDFT. The former is most exaggerated in symmetric systems such as the formic acid dimer, where CT vanishes according to the CDFT definition despite the formation of double hydrogen bonds, while the ALMO approach indicates a significant contribution from CT in this system. These results suggest that although the CDFT definition has its merits (e.g., it provides the possibility to compare with net charge flow measured by experiments), it is less appropriate compared to the ALMO-based definition for characterizing the effects of CT in non-covalently bound molecular complexes.

Titanium nitride as a potential material for plasmonic assisted photocatalysis

Brendan Mattingly, Prof. David F. Coker, Prof. Bjorn Reinhard

Abstract:

Resonant interactions between incident light and coherent collective electronic oscillations, the so-called plasmons, provide new opportunities for chemical catalysis beyond their current utility in nano-optics. Plasmonic materials can produce excited ``hot'' electrons, generate strong local E-fields that can influence chemical transformations, and assist photocatalytic processes by promoting interfacial charge transfer in metal-semiconductor hybrids. Titanium-nitride and its doped-defect derivatives are such potential materials, proving more tractable over their more expensive noble metal counterparts. From first-principles calculations, we observe a dependence of the screened plasmon resonance on particular dopants and at specific concentrations. This controlled variance of the resonance frequency, therefore, spans a wide range of the visible spectrum which allows for potential use in photocatalytic reactions that rely on such a driving E-field. Moreover, the potential usage of ``hot'' electrons in titanium-nitride is investigated by the determination of their lifetimes via electron-electron and electron-phonon interactions.

Prediction of Optoelectronic Traits of Dyes for Photoelectrochemical Purposes

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Abstract:

In any solar energy-driven system, the number of photons harvested limits the amount of energy available. This makes it important to improve spectral coverage and ensure that the photons absorbed can actually be used. In this study, we computationally model spectral coverage as well as interfacial electron transfer in 54 dye-adsorbate model systems with the intention of creating a model capable of predicting solar cell efficiencies with confidence, in turn allowing systematic improvement of such systems.

Light-harvesting molecules that absorb across the entire visible region are known as panchromatic dyes, which maximize solar photon absorption yield. Here we have systematically studied the absorption properties of a series of porphyrin–linker–phenazine molecules using TD-DFT to calculate optical transitions. The porphyrin–ethyne–phenazine system shows excellent spectral coverage and a first-pass screening procedure based on its calculated ΔGoxidation and the outer-sphere reorganization energy indicates that the system has great promise as a sensitizer for photoelectrochemical cells.

We have examined our series of sensitizers using differing chromophoric cores but linked to a TiO2 surface via the same carboxylate linker moiety. Density functional theory was used to verify the character of orbitals calculated with semiempirical Extended Hückel (EH) calculations which were then used for electron-injection dynamics calculations. A regression analysis using the parameters obtained from TD-DFT and EH dynamics calculations were used to predict the likelihood of a dye beating a benchmark in a typical dye-sensitized solar cell setup.

Towards Understanding the Interactions of Aromatic Dipeptide Nanotubes

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Abstract:

The self-assembly of peptides has numerous potential applications in the fields of energy, nanobiotechnology, and nanomedicine. Peptides serve as excellent building blocks because they offer a great diversity of chemical and physical properties, can be synthesized in large amounts, and can be easily functionalized. Aromatic peptides have the tendency to form dipeptides which then self-assemble into nanotubes. However, there is still a lack of fundamental understanding between structures and properties of these materials. In this study, quantum-chemical computational methods were used to investigate linear and cyclic dityrosine and tryptophan-tyrosine, the building blocks of four different aromatic dipeptide nanotubes. First the numerous conformations of the three dipeptides were screened to find the most sterically and energetically stable forms. The structure, energetics, thermodynamics, and spectra of the lowest energy conformers were then studied further. Additionally, the effects of solvation were investigated. Based on these work, it is possible that the growth of fibers involved π-stacking and hydrogen bonding interactions between planar diketopiperazine rings resulting in a tubular fiber-like morphology. We are currently working on understanding and predicting peptide-based nanotube-TiO_2-porphyrin interactions, size effects, interfacial effects, and electron transfer mechanisms.

Revealing Substrate Positioning Dynamics in Aliphatic Halogenase SyrB2 through Spectroscopically-Guided Simulation

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We explore the role of substrate positioning in reaction selectivity exhibited by SyrB2, which belongs to a class of mononuclear, non-heme Fe(II), alpha-ketoglutarate dependent biosynthetic enzymes. These enzymes have the ability to activate C-H bonds and catalyze a variety of reactions such as hydroxylation, halogenation and stereoinversion, making them crucial to the synthesis of valuable natural products. A deeper understanding of the factors that bias the enzymes towards a particular reaction is crucial for deeper understanding of natural product biosynthesis and, ultimately, for enzyme engineering in therapeutic drug development. SyrB2 reacts only with substrates delivered via a prosthetic phosphopantetheine (PPant) arm delivered from a carrier protein. Depending on the loaded substrate, SyrB2 either exclusively chlorinates its native substrate L-Threonine or predominantly hydroxylates non-native substrates that differ only by absence of a hydroxyl group (L-Aminobutyric acid) as well as an added methylene group (L-Norvaline), which differs by an added methylene group. This subtle difference in substrate difference altering reaction outcomes thus enables us to identify how the greater SyrB2 protein environment biases selectivity for halogenation. Recent hyperfine sublevel correlation (HYSCORE) spectroscopy has provided some insight into average positions and angles of substrates to the iron center in SyrB2, but a more complete nanoscale picture of SyrB2 dynamics is needed to fully understand its reaction selectivity. Here we use long-time (i.e., multi-microsecond) classical molecular dynamics (MD) and large-scale QM/MM to explain trends in HYSCORE substrate orientations and rationalize reaction specificity. We resolve uncertainty regarding the three possible coordination isomers of Fe(II) active site by comparing interactions sampled during MD runs in each configuration and identify the most plausible coordination orientations to explain both reactivity and the reported experimental distances and angles. Hydrogen bonding, energy decomposition analysis, and large-scale electronic structure calculations provide further rationalization of protein-substrate and protein-protein interactions. Beyond selectivity in SyrB2, this approach is expected to be of value to provide insight into active-site dynamics in multi-protein biosynthetic assemblies, ultimately enabling their rational design.

Significant enhancement of polyene light absorption induced by electrostatic fields.

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Abstract:

The development of solar energy devices based on molecular materials critically depends on the effectiveness of the absorbing molecular layer. The Thomas-Reiche-Kuhn sum rule equals the total (electronic) oscillator strength of a molecule to its total electron number. However, in known molecular absorbers the excitations in the UV-visible spectral region are associated with only about 1% of the overall oscillator strength, thus limiting the performance of organic solar cells.1 In this theoretical study, we show that electrostatic fields can be used to alter the electronic structure of polyenes so as to enhance their absorption in the UV-visible region. Our TDDFT calculations on single molecules (either in gas phase or absorbed on gold) indicate that the integrated oscillator strength for electronic transitions in the UV-visible can be increased by an order of magnitude depending on the strength of the applied field. This enhancement and its dependence on the field intensity are rationalized by means of a one-dimensional piecewise constant potential model. Our analysis prompts future experimental studies on the use of electric fields to modulate the absorption properties of materials based on linear molecules.

[1] Zheng, L.; Dave, A. R., Polizzi, N. F.; Migliore, A.; Beratan, D. N. Where Is the Electronic Oscillator Strength? Mapping Oscillator Strength across Molecular Absorption Spectra. *J. Phys. Chem. A* **2016**, *120*, 1933-1943.

Molecular-Level Spectroscopic Studies of Ice Using a Many-Body Potential

Daniel R. Moberg, Shelby C. Straight, Christopher Knight, and Francesco Paesani

Abstract:

Ice plays a central role in several processes of relevance to a broad range of disciplines, including climate research, atmospheric and environmental chemistry, materials science, and engineering. However, an unambiguous assignment of the vibrational spectra of hexagonal ice (I_h) remains a matter of debate. The use of an accurate representation of many-body interactions between water molecules, combined with an explicit treatment of nuclear quantum effects through many-body molecular dynamics (MB-MD), leads to an interpretation of the ice I_h spectrum in terms of the structure and dynamics of the underlying hydrogen-bond network. The features of the infrared and Raman spectra in the OH stretching region can be assigned by taking into account both the symmetry and the delocalized nature of the lattice vibrations as well as the local electrostatic environment experienced by each water molecule. The high level of agreement with experiment raises prospects for predictive MB-MD simulations to provide molecular-level insights into fundamental processes taking place in bulk ice and on ice surfaces.

Protein-protein binding in solution and on the membrane using CG-Metadynamics:
a case study of LSP1 homodimerization

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Abstract:

Successful protein-protein association first requires that component proteins search through space to encounter one another before overcoming energetic barriers to complex formation. The vast majority of protein-protein equilibrium constants are experimentally characterized in solution, where proteins engage in a 3D search to contact. Critically, many proteins can also associate after restriction to the membrane surface, thus performing now a 2D search to contact characterized by a new, 2D equilibrium constant that is rarely measured. Here, we study the LSP1 homodimerization in solution and on the membrane to quantify how membrane restriction alters binding equilibrium between dimers. LSP1 is a BAR-domain containing cytosolic yeast protein that is central to eisosome formation at the plasma membrane and can thus dimerize both in solution and on the surface. We employed coarse-grained (CG) model based on MARTINI force field and metadynamics (standard and well-tempered) to study the free energy landscape of LSP1-LSP1 interactions in 2D and 3D. We use two distances (d_1 and d_2) as collective variables to characterize the bound state based on the known PDB structure. Our results indicate that the bound state is relatively weakly stabilized in solution, with the contacts at one end of the protein (d2) being significantly more important for stabilizing the complex than the other site (d1). On the membrane, our results thus far indicate a strong interaction with the membrane and potentially a larger energetic barrier to complex formation. These simulations will provide one of the few computational calculations of 2D equilibrium constants (extracted from our free energy calculations), and the first to use high resolution proteins and membranes.

Perturbative Approach to Ultrafast Intersystem Crossing in Nonadiabatic Molecular Dynamics

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Abstract:
Ultrafast intersystem crossing (ISC) competing with spin-conserving deactivation pathways is common - in transition metal compounds such as tris-(bipyridine)ruthenium2+; and even some molecules containing only first- and second-row elements such as benzophenone. Nonadiabatic molecular dynamics (NAMD) is the method of choice to investigate and predict the effects of ultrafast ISC computationally. We present a perturbative scheme for including this ISC through spin-orbit coupling in NAMD simulations within the time-dependent density functional theory (TDDFT) framework. The spin-orbit coupling strength is obtained from the trace of the one-electron mean field Breit-Pauli spin-orbit coupling operator with the transition density matrix. We report benchmark applications to validate our approach, and discuss its scope and limitations.

Electronic excitations in thermal heterogeneous catalysis

Matthew M. Montemore, Robert Hoyt, Grigory Kolesov, Efthimios Kaxiras
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Abstract:

Metal nanoparticles are used as catalysts in large-scale chemical processes and in potential new clean energy technologies. Most computational studies of these catalysts assume that the system remains in the electronic ground state. However, electronic excitations are easily induced in metal surfaces, due to the lack of a band gap. Here, we use high-quality nonadiabatic simulations to show that chemical processes on catalytic nanoparticles can induce electronic excitations, and we examine the possible effects of these processes on surface chemistry. These simulations show that ground-state calculations do not fully capture surface processes on catalytic surfaces.

We performed nonadiabatic dynamics using real-time, time-dependent density functional theory, propagating the nuclei using Ehrenfest dynamics. We study many trajectories of H2 and N2 molecules interacting with Ru nanoparticles ranging in size from 13 to 147 atoms. These simulations show that, during the adsorption and dissociation processes, a significant amount of energy can be dissipated into electronic degrees of freedom, often at least as much or more than the amount of energy dissipated into ionic vibrations. This suggests that the electronic structure of catalytic surfaces may, transiently, be quite different from the ground state. We characterize the electronic structure and spatial character of the excitations as a function of time. We also show that these excitations can affect barriers and can influence the surface chemistry of other species reacting on the nanoparticle. Therefore, nonadiabatic effects need to be accounted for in order to get quantitatively correct predictions of processes on metal nanoparticles.

Unifying quantum master equations and quantum-classical trajectories for photochemistry and electrode processes

Andrés Montoya-Castillo, Aaron Kelly, Lu Wang, David R. Reichman, and Thomas E. Markland

Abstract:

The development of accurate, efficient, and broadly applicable quantum dynamics methods is essential for our understanding of processes ranging from the relaxation to equilibrium of photoexcited chromophores to electric and thermal transport across driven nanojunctions. Generalized quantum master equations (GQMEs) have provided invaluable intuition about these chemical and physical processes, although they are often applied in perturbative limits. However, it has recently been shown that GQMEs can also be used to make quantum-classical dynamics methods dramatically more efficient and accurate for a large number of problems. Here I will show how one can create a framework that explicitly unifies and clarifies the connections between the Nakajima-Zwanzig treatment of reduced density matrix dynamics and the more general Mori approach to GQMEs. I will then demonstrate that this approach can be used to dramatically improve the accuracy of the nonadiabatic dynamics of even crude quantum-classical trajectory-based approaches, such as mean field theories. In particular I will show how we can extend this formalism to treat interfacial electrochemistry, including electron transfer and proton-coupled electron transfer at an interface.

Structural origin of the temperature-dependent Raman and infrared spectra of liquid water

Tobias Morawietz, Ondrej Marsalek, and Thomas E. Markland

Department of Chemistry, Stanford University

Abstract:

Raman and infrared spectroscopies provide a window on the properties of water's hydrogen bond network over a broad range of frequencies. However, the interpretation of the resulting spectroscopic features and their variation with temperature across the entire spectral range remains a subject of ongoing debate. Here we show that ab initio simulations accelerated by machine-learning potentials are able to accurately describe the structural and spectroscopic properties of liquid water from its freezing to boiling point. We then demonstrate that the temperature-dependent shifts and isosbestic points in the Raman and infrared spectra can be directly linked to contributions arising from several distinct hydrogen bonding motifs which can be grouped into two main classes.

The Electronic Structure of Biologically-Inspired Perylene Diimide Arrays from First-Principles

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Abstract:

Perylene-3,4,9,10-tetracarboxylic diimide (PTCDI) based materials have excellent electrochemical, electrical, and photophysical characteristics, with promise as components in organic optoelectronic devices such as light-emitting diodes and solar cells. Here, we study the electronic and optical properties of a series of recently synthesized PTCDI DNA base surrogates with first-principles density functional theory (DFT) and many body perturbation theory (MBPT). By stacking the molecules along a DNA-inspired backbone and varying the number of stacked molecules, we determine the role of inter-molecular interactions on the excited-state energetics, as well as vibrational excitations within the molecules. We demonstrate that strong inter-molecular interactions lead to distinct vibrational, electronic, and optical properties for design of new electronic and optoelectronic nanowires.

Reaction rate constants of noisy systems obtained on the transition state trajectory

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Abstract:

Kramers theory has been derived and advanced in multiple ways since it was first introduced. In transition state theory frameworks, the rates are invariably approximate because of the recrossings of the dividing surface. In particular, the flux for nontrivial dissipated barrier problems has not yet been obtained directly on a non-recrossing dividing surface. In this poster, we obtain reaction rates across the dividing surface emerging from distributions initially on a saddle of a barrier in a Langevin bath. As previously observed, the non-recrossing dividing surface is time-dependent and must be obtained for each noise realization. The challenge is the determination of a well-defined phase-space transformation of the flux from the fixed coordinate system to the moving frame. We show that trivial choices of the flux do not lead to the Kramers result, and conjecture a more accurate rate formula.

This work has been partially funded by the National Science Foundation through grant number CHE 1700749.

Decoding spectroscopic features and time-scales of aqueous proton defects

Joe Napoli, Ondrej Marsalek, Thomas E. Markland

Department of Chemistry, Stanford University

Abstract:

Concentrated acid solutions exhibit complex structural and dynamical features arising from the presence of multiple interacting reactive proton defects and counterions. Here we exploit recent developments to efficiently perform simulations treating the quantum nature of both the electrons and nuclei to uncover how proton defect structures and their interconversion manifest spectroscopically. Specifically, we propose a physically transparent proton solvation coordinate and demonstrate how one can use it to understand observed spectroscopic features and recent 2D-IR experiments.

The effect of channel shape, size, and functionality on directed hydrogen bonding networks

Duong Nguyen, Mai Huynh, Truc Huynh, Lana Patel, Mai-Anh Ha and Maria A Gomez

Department of Chemistry, Mount Holyoke College

Abstract:

Proton conduction through a water channel plays an important role in both biochemical and engineered systems. In influenza A virus, the proton conduction through an M2 protein channel is crucial to the viral pathogenesis. Engineered materials such as the polymer membrane of fuel cells also require a good proton conductivity. This study investigates how the shape and functionality of a channel affect hydrogen bonding networks. Three different shapes of water channel are considered: a cylinder, a cylinder with sinusoidal protrusions, and the open-state AM2 protein channel. Monte Carlo is used to find the equilibrium distribution of water molecules within the first two shapes, whereas molecular dynamics (MD) is performed for the AM2 channel. After the final coordinates of waters inside the channels are extracted, all hydrogen bonding networks that extend throughout the length of the channels are found using graph theory. The sinusoidal protrusions in the cylinder narrow down the distribution of networks. The distinct shape of the AM2 protein pore also has an effect on the networks found; at the final step of the MD movie, the two Val 27 and His 37 gates only allow one water to pass through; however, during the process of MD, the gates can actually become fully open and allow a large amount of water molecules inside. This difference affects the number of hydrogen bonding networks found; and since the protein's hydrophilic functional groups at the inner core can possibly participate in hydrogen bonding, they need to be taken into consideration as well.

Plasmon-exciton energy transfer in nanoparticle-molecule aggregates

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Abstract:
We investigate the effect of molecular systems on the energy absorption and transfer between plasmon excitations in neighboring nanoparticles within a semiclassical model. In particular we focus on the effect of molecular relaxation and dephasing on the inter-plasmon interaction as expressed by lineshape for the scattered radiation and the heat rate. The relative importance of energy transfer via the excitonic subsystem and that associated with direct plasmon-plasmon interaction is studied as well. We find that coupling through the molecule is important for molecules on resonance with the nanoparticle dimer plasmon frequencies, but sensitive to relaxation and dephasing in the molecular subsystem. We rationalize this observation by obtaining an expression for the effective rate of energy transfer from the molecule to the plasmon and by numerically evaluating its dependence on molecular relaxation and dephasing.

Crystal orientation dependence of heterogeneous nucleation at the Cu-Pb solid-liquid interface.

J. Pablo Palafox-Hernandez and Brian B. Laird

Abstract:

In this work, we examine the effect of surface structure on the heterogeneous nucleation of Pb crystals from the melt at a Cu substrate using molecular-dynamics (MD) simulation. In a previous work [Palafox-Hernandez et al., Acta Mater. 59, 3137 (2011)] studying the Cu/Pb solid-liquid interface with MD simulation, we observed that the structure of the Cu(111) and Cu(100) interfaces was significantly different at 625 K, just above the Pb melting temperature (618 K for the model). The Cu(100) interface exhibited significant surface alloying in the crystal plane in contact with the melt. In contrast, no surface alloying was seen at the Cu(111) interface; however, a prefreezing layer of crystalline Pb, 2-3 atomic planes thick and slightly compressed relative to bulk Pb crystal, was observed to form at the interface. We observe that at the Cu(111) interface the prefreezing layer is no longer present at 750 K, but surface alloying in the Cu(100) interface persists. In a series of undercooling MD simulations, heterogeneous nucleation of fcc Pb is observed at the Cu(111) interface within the simulation time (5 ns) at 592 K—a 26 K undercooling. Nucleation and growth at Cu(111) proceeded layerwise with a nearly planar critical nucleus. Quantitative analysis yielded heterogeneous nucleation barriers that are more than two orders of magnitude smaller than the predicted homogeneous nucleation barriers from classical nucleation theory. Nucleation was considerably more difficult on the Cu(100) surface-alloyed substrate. An undercooling of approximately 170 K was necessary to observe nucleation at this interface within the simulation time. From qualitative observation, the critical nucleus showed a contact angle with the Cu(100) surface of over 90◦, indicating poor wetting of the Cu(100) surface by the nucleating phase, which according to classical heterogeneous nucleation theory provides an explanation of the large undercooling necessary to nucleate on the Cu(100) surface, relative to Cu(111), whose surface is more similar to the nucleating phase due to the presence of the prefreezing layer.

"Role of cholesterol in ternary lipid membrane phase separation observed via coarse-grained simulations"

George A. Pantelopulos and John E. Straub

Abstract:

Formation of micro- and macroscale lipid domains is of great interest to understanding membrane protein structure and function. The formation of domains on the membrane surface has been the study of much experimental, theoretical, and simulation work. Cholesterol (CHOL) is understood to play an essential role in the formation of micro- and macroscale lipid domains. We present a study of the micro- and macroscopic domain structures observed in the phase-separating mixture of DPPC:DIPC:CHOL at equimolar lipid and various CHOL concentrations. We find CHOL to modulate the domain formation mechanism and cause formation of anti-registered domains at high concentration. Additionally, the formation of CHOL "threads" at high concentration cause for loss of membrane mobility and undulation of the membrane surface while forming a ordered liquid co-crystal with DPPC. These findings offer new insights to the effect of cholesterol on lipid domain formation mechanism, size, and structure and are suggestive of the structural environment in which CHOL-binding proteins may exist.

Lightspeed: A Simple, Flexible, and Highly-Optimized Library for the Rapid Development of Production-Level Electronic Structure Theory

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Stanford, CA and SLAC National Accelerator Laboratory, Menlo Park, CA

Abstract:

We discuss the architecture and developments in "Lightspeed," a C++/CUDA/Python library designed to enhance the ease of development of production-level electronic structure methods. Lightspeed does not do electronic structure theory – Lightspeed helps you do electronic structure theory. To that end, Lightspeed provides simple C++ and Python interfaces to such primitive operations as molecular integrals, Coulomb (J) and exchange (K) matrix builds, density functional theory (DFT) potentials, complete active space matrix-vector products, and gradients for all of the above. Additional utility libraries provide access to tensor operations, large-scale optimization algorithms (e.g., DIIS and Davidson methods), and several types of electronic structure analyses (e.g., orbital localization, grid properties, etc). These operations are implemented for CPU and/or GPU hardware, depending on the resources available at runtime. Lightspeed enables students as young as undergraduates to implement production-level codes for such methods as Hartree-Fock/density functional theory, configuration interaction singles/time-dependent density functional theory, complete active space self consistent field, including gradients. Moreover, Lightspeed enables rapid development of new electronic structure methods, as demonstrated herein with the "Parsec" fragment-based model, which is capable of single point and gradient evaluations for systems with >1 million atoms, and dynamics simulations for systems with > 1 thousand atoms.

Sodium chloride cluster formation in methanol and water

Lara A. Patel and James T. Kindt

Abstract:
Sodium chloride cluster formation has been studied extensively and in recent years, it has been observed that clusters transition through a pre-nucleation phase where the ions form amorphous clusters. Once these clusters exceed a given size, they transition to an ordered cluster. We shall present the results of applying the “Partition-Enabled Analysis of Cluster Histograms” (PEACH) approach to extracting equilibrium association constants and thereby the free energy surface for small NaCl clusters in three solvation environments: pure methanol, a methanol and water mixture, and pure water. We will show that changing the solvation environment changes the relative stabilities of the ordered and amorphous clusters. This shift in relative stability is reflected by the cluster size at which a transition to the ordered cluster structure occurs.

Raman Signatures of Pt-Au Interactions in Quasi-One Dimensional Metal-Organic Nanowires

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[3] Materials Science and Engineering Division, Boston University
[4] Department of Physics, Boston University

Abstract:

We present a study of the vibrational properties of tunable quasi-one-dimensional metal-organic chains that are promising as electronic and spintronic materials. These structures consist of single chains of the form [Pt(tpy)X][AuY2] that self-assemble as weakly bound wires within an anisotropic crystal in the solid-state, forming salts of alternating Pt^+ and Au^- atoms embedded in organic matrices. Here, we utilize density functional theory (DFT) and Raman spectroscopy in order to probe their structural and vibrational properties. By comparison of prediction with measurements, we determine the optical signatures of intra-chain, specifically Au-Pt, interactions and how these interactions influence the electronic and magnetic properties of the quasi-one dimensional crystals.

Quantum Mechanical studies of catalytic effects on water splitting

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Abstract:

Fossils are the world's outstanding fuel source. As the world's population increases, fuel usage is also increased. The problem is fossil fuel is not renewable. Also the combustion of fossil fuel produces pollutants like CO2, which increases environmental pollution. Even though there are alternative energy sources like wind, hydropower, geothermal and solar; it is essential a produce clean and renewable energy source. Hydrogen is considered as the fuel for the future as it is environmental friendly and clean. Numerous studies have been developed to produce hydrogen by splitting water after Fujishima and Honda first showed photocatalytic water splitting in the presence of a TiO2 catalyst1 in 1972. Experiments have shown that H2 evolution is 1.9 times more efficient when TiO2 is absorbed on a graphene oxide (GO) sheet than from pure TiO2.2 This is because TiO2 can form a p-n heterojunction with GO for visible light absorption. ZnO also can form a p-n heterojunction with GO2. ZnO is a semiconductor, which has a wide band gap (3.4 eV).

This study is mainly focused on density functional theory calculations of water splitting on GO-ZnO surface. Initial studies were carried out using (ZnO)n, with n=1, 2 and 3, ZnO monolayer and (ZnO)3 cluster absorbed on Graphene Oxide.Preliminary calculations of the structures were optimized with density functional theory (DFT) using the B3LYP exchange functional and STO-3G and 3-21G basis sets in the GAUSSIAN 09 quantum chemistry package, to be followed by calculations on larger clusters adsorbed on a sheet of graphene oxide with more accurate basis sets at the DFT and MP2 levels.

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2. Yeh, T.; Cihlar, J.; Chang, C.; Cheng, C.; Teng, H. Roles of graphene oxide in photocatalytic water splitting 2013, 1369-7021/06
3. Fang, Z.; Dixon, D. Computational study of H_2 and O_2 production from water splitting by small $(MO_2)_n$ Clusters (M=Ti,Zr,Hf). J.Phys.Chem.A 2013,117,3539-3555

Molecular Simulation of Gas-Expanded Liquids: Phase Equilibrium and Structure of CO2-Expanded Ethylene Oxide and Methanol

Ezekiel A. Piskulich, Brian B. Laird, and Ward H. Thompson

Abstract:
Ethylene oxide is an industrial commodity chemical used in large quantities as a precursor for the manufacture of an assortment of common products, such as solvents, antifreezes, textiles, detergents, adhesives, pharmaceuticals, polyurethane, and poly-carbonates. In the last example, ethylene oxide is carboxylated to produce ethylene carbonate, which can be transesterificated to produce dimethyl carbonate, a key ingredient in the production of poly-carbonates. Additionally, when mixed with dimethyl carbonate, ethylene carbonate can be used to create an organic electrolyte solution for applications to batteries and supercapacitors. It has been demonstrated experimentally that using carbon dioxide-expanded solvents can improve the kinetics of the carboxylation process; however, the phase behavior of the reaction mixture is not well understood. We are using Gibbs Ensemble Monte Carlo and Molecular Dynamics to study the effects of gas-expansion on the chemicals involved in this reaction. Phase equilibria, volume expansions, transport properties and liquid structure are calculated for each of these gas-expansions to fully characterize the chemicals within this process, and trends for temperature and pressure dependence of these properties are compared between mixtures. A full understanding of these properties is needed to discern the effect of mixture composition on both its dynamical properties and phase behavior, allowing us to tune these liquids to favor specific properties. Furthermore, a molecular-level insight is gained into the dynamics and structure of these gas-expanded liquids, which is crucial for optimizing the productivity of this reaction. Additionally, the effect of gas-expansion on the formation of hydrogen bond networks within a hydrogen bonding liquid is considered.

Multi-scale simulations of a high-temperature diatomic reactive gas

Alexander Popov and Rigoberto Hernandez

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Abstract:

A multi-scale integrator has been developed in order to model the steady state and equilibrium behavior of a reactive nitrogen (or oxygen) gas contained within a microscale pore. This integrator combines a short-time scale eXtended Particle Dynamics (XPD) algorithm and longer-time scale Computational Fluid Dynamics (CFD) tools, through the implementation of an analogue of the replica-exchange (RE) method. It is capable of simultaneously characterizing detailed dynamics at molecular and material length scales. The XPD algorithm is a combination of MD simulations and a simple reactive force field which is constrained in a way to allow molecules to dissociate/associate. The RE is generalized to capture important variables (such as energy, temperature, reaction rates and composition) and convert them between particle and purely coarse-grained scales.

The computing resources necessary for this research were provided in part by the National Science Foundation through XSEDE resources provided by Stampede and Maverick under grant number TG-CTS090079.

Partial Linearized Density Matrix Dynamics for Nonlinear Electronic Spectroscopy

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Abstract:

Recent progress in experimental techniques such as two-dimensional electronic spectroscopy and broadband pump-probe spectroscopy, that are capable of probing the ultrafast dynamics of excited-state wavepackets, have highlighted the existence of long-lived vibronic coherence in light-harvesting complexes. These findings have motivated the reconsideration of coherent phenomena playing an important role in the early-time non-equilibrium relaxation processes and energy transfer efficiency in these complex systems. However, detailed interpretation of experimental spectra can be troublesome due to highly convoluted signals from competing energetic pathways. The ability to independently control each degree of freedom (DOF) makes theoretical analysis of these spectroscopic features a necessity.

In this work, we propose Partial Linearized Density Matrix (PLDM) path integral propagation as a method for computing nonlinear electronic spectra. The PLDM propagation method involves treating subsystem DOFs semi-classically (within the Meyer-Miller mapping formalism) while bath DOFs are treated within a truncated Wigner approximation. This method provides accurate density matrix dynamics for non-Markovian open quantum systems, from which nonlinear optical response functions can be extracted.

Explaining unexpected interactions in the structurally characterized proteome with large-scale electronic structure modeling

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Abstract:
Since the advent of X-ray crystallography, knowledge of a protein's crystal structure has provided critical new insight into protein function, either inferred from interatomic distances or as a starting point for atomistic simulation of dynamics and reactivity. Unusually short, non-bonded distances in protein structures, *i.e.* close contacts, arise in even the highest-resolution (*i.e.,* sub-2.0 Å) crystal structures available. These close contacts are expected to correspond to unusually energetically strong interactions, such as strong hydrogen bonds exhibiting charge transfer, or other interactions that are otherwise not fully understood and cannot be well characterized by commonly employed molecular mechanics force fields. First-principles simulation can provide valuable insights in the nature of these interactions, particularly bolstered by recent advances that have made possible the large-scale electronic structure modeling of thousands of atoms. Here, we take a bird's eye view of the structurally characterized proteome to identify the overall nature of all unusually short intra-protein residue-residue interactions in high-resolution crystal structures. We i) resolve the residue and secondary-structure dependent nature of these unusually short interactions; ii) quantify the extent to which components from energy decomposition (*i.e.,* electrostatic versus van der Waals) in a classical and first-principles picture differ; and iii) validate and explain representative newly discovered interaction motifs through large-scale simulation of the effect of the greater protein environment. These newly discovered interactions will provide key new insights into established protein structure-function relationships.

Nano-bio interface between polyelectrolytes and bacterial lipopolysaccharides

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Abstract:

Lipopolysaccharides (LPS) on gram negative bacteria are critical mediators of the interaction between nanoparticles and bacteria surfaces. We demonstrate the relevance of computational simulations of LPS molecules with polyelectrolytes for providing insight into the corresponding interactions in the bacteria. The relative attachment of free polyelectrolytes to representative model structures of the LPS molecules found on the surface of Pseudomonas aeruginosa, Salmonella typhimurium, and Escherichia coli bacteria have been determined from simulations. The association energies are obtained from the difference between the average interaction energy and that from water-ion and water-water pairs. The results indicate that the number of phosphate groups in the core region of the LPS molecule can play an important role in the attachment of the polyelectrolyte to the LPS molecule. The degree of polyelectrolyte association to the rough LPS was also compared to that of the smoother constructs. In general, these traces suggest that polyelectrolyte associates to the rough LPS molecules more strongly than to smooth LPS molecules.

This work has been partially funded by the National Science Foundation through a grant to Center for Sustainable Nanotechnology under grant number CHE-1503408. The computing resources necessary for this research were provided in part by the National Science Foundation through XSEDE resources provided by Bridges under under grant number TG-CTS090079.

Proton transfer and recombination of the H+ and OH- ions In bulk water and water wires from a dissociating water model

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Abstract:

Molecular dynamics (MD) simulations of a dissociating water model based on a rescaled interatomic potential (s-OSS2) derived by Ojäme, Shavitt and S. Singer1 from ab-initio calculations at the MP2 level were used to calculate the ion motilities of H+ and OH- ions in bulk water. The diffusion coefficient of the H+ ion is greater than that of OH_ ions by nearly a factor of two, and in excellent agreement (after correction to infinite dilution) with experimental values from 0 to 50C2. The same model applied to ion transport along an open single-chain water3 wire agrees with the theoretical dipole-lattice model of Dellago et al and extended EVB calculations4, 5. Unlike liquid water, the diffusion coefficients of H+ and OH_ are nearly the same in the open water wire4, in qualitative agreement with Bankura and Chandra QM/MM simulations in long water-filled nanotubes5. Recombination (neutralization) of H+ and OH- in the nanotube is accompanied by compression along the wire and a synchronized jump of two protons at the final stages of neutralization7, similar to the neutralization in bulk water observed by Hassanali et al7 in QM/MM simulations8. Proton transfer and neutralization of H+ and OH- ions in 2D water sheets is more complicated.

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Binding, Folding, and Insertion of a β-Hairpin Peptide at a Lipid Bilayer Surface: Insights from Molecular Dynamics Simulations and Experiment

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Abstract:

Antimicrobial peptides (AMPs) are common in many biological systems and act as host defenses against microbial pathogens. In our current study, we investigate the interactions of SVS-1 (KVKVKVKV-PDPL-TKVKVKVK), an anti-cancer β-hairpin peptide (ACP), with lipid bilayers using atomistic molecular dynamics (MD) simulations and spectroscopic studies. In agreement with experimental work conducted by the Schneider group (Sinthuvanich, 2012), simulated peptides bind favorably to anionic but not neutral bilayers in the absence of tension. Unfolded peptides at the anionic surface were observed to undergo several folding and misfolding pathways, whereas SVS-1 underwent partial folding in solution when placed in the presence of a neutral surface. Folded peptides at the negatively charged surface did not spontaneously insert their hydrophobic faces into the bilayer on the 1 μs timescale, but kept their Lys-rich face downward toward the lipid headgroups. Upon the application of sufficient surface tension, peptide was observed to partially insert or “flip and dip” into the anionic bilayer within ~200 ns. Fluorescence studies of a Trp-substituted SVS-1 analog indicate that it binds to a neutral DPPC bilayer only under high-curvature conditions. Simulations similarly show binding of SVS-1 to a neutral surface under conditions that favor hydrophobic exposure.

Bootstrap Embedding: A low-scaling, fragment-based method for strong correlation

Nathan D. Ricke, Hong-Zhou Ye, Matthew Welborn, Troy Van Voorhis

Fragment embedding approaches offer the possibility of accurate description of strongly correlated systems with low-scaling computational expense. In particular, wave function embedding approaches have demonstrated the ability to subdivide systems across highly entangled regions, promising wide applicability for a number of challenging systems. Bootstrap Embedding is a wavefunction embedding method that has shown promise for accurately embedding across covalent bonds with low-scaling and robust convergence properties. We show here that Bootstrap Embedding successfully describes the energetics of the Pariser-Parr-Pople and 2D Hubbard models, as well as hydrogen rings. We further investigate the accuracy of this method for varying fragment size, shape, and applied constraints.

Generalized coupled-cluster approaches for quantum simulation of strongly correlated system.

Jhonathan Romero, Hannah Sim, Libor Veis, Gian Giacomo-Guerreschi, Alán Aspuru-Guzik

Abstract:

Quantum computers are becoming large enough to perform tasks beyond the capabilities of the biggest quantum supercomputers. The first generation of quantum machines are expected to have between 50 to 100 qubits and being able to execute thousands of quantum operations, however, they will lack error-correction. To exploit these "pre-threshold" machines as quantum simulators for chemistry, we need algorithms that are relatively robust to machine noise and can be run using fewer gates. One example of such algorithms is the variational quantum eigensolver (VQE) [1,2]. In this approach, quantum states are prepared based on a given ansatz followed by the measurement of the energy on the quantum computer. The information of the energy is then used to optimize the variational parameters associated to the ansatz using a classical optimization routine. Traditionally, single-reference unitary coupled cluster [1-4] has been used as the canonical ansatz for chemistry simulations. In this work, I present an extension of the unitarity coupled cluster approach to multireference cases. Our method is based on the preparation of an entangled initial state, obtained using classical density matrix renormalization group (DMRG) approaches, followed by the application of a generalized unitary coupled cluster implementation (GUCCI), where all the possible excitation operators are considered. We present numerical simulations of the quantum algorithm for the Hubbard model and a variety of strongly correlated molecular systems.

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Nitrous Oxide as a Probe of Aqueous Cation Solvation Environments: Ultrafast Mid-IR Pump-Probe Measurements and Molecular Dynamics Simulations

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Abstract:

The long-range effects of ions in water continue to be a subject of great debate in theory and experiment. We summarize recent ultrafast mid-IR pump-probe spectroscopic measurements of the N2O asymmetric stretch vibrational lifetime and the rotational time constants of gas probe N2O in aqueous MClx salt solutions (M=Mg2+, Ca2+, Na+, K+, Cs+) at room temperature. These studies measure the vibrational population lifetime of the v3 asymmetric stretch of N2O in the salt solutions, as well as reorientational dynamics. Relative to pure H2O, the vibrational population lifetimes increase for Cs+ and K+, and decrease for Mg2+ and Ca2+, and follow a phenomenological Hofmeister series trend (Mg2+ > Ca2+ > Na+ > K+ > Cs+). The rotational dynamics show a similar trend, with the rotations of N2O retarded in Cs+ and accelerated in Mg2+. The key premise of these studies is that N2O does not interact significantly with the ions in solution because it cannot form hydrogen bonds and is weakly polar. Thus, we hypothesize that these spectroscopic measurements report the structure of water outside of the first solvation of N2O. To support this claim, we have performed all-atom molecular dynamics simulations for the aqueous salt solutions at experimental density to elucidate the location of the N2O reporter molecule with respect to the cations and to quantify the formation of ion clusters, which can play a significant role in vibrational and rotational dynamics.

Quinonile Photobasicity is Mediated by Hole Injection

Saswata Roy and Filipp Furche

Photoacids and photobases drive acid-base reactions by photon energy. Although known since 1940, the large-scale development of photoacids and photobases into efficient molecular light harvesting devices has been confounded by a lack of mechanistic understanding. A new mechanism explaining the photobasicity of quinolines is proposed based on nonadiabatic molecular dynamics simulations using time-dependent density functional theory (TDDFT). Rather than changing the basicity of the quinoline, photoexcitation is found to induce oxidation of adjacent water molecules. We develop a mechanistic understanding of the process in the molecular orbital theory framework, and discuss the limitations of our methods arising from using TDDFT to simulate excited state. Further support for the proposed mechanism is provided by comparison to experimental time-resolved fluorescence spectroscopy and correlated wavefunction calculations. These results suggest that the conventional picture of excited acid-base equilibrium may need to be revisited.

Regimes of electron transfer in Geobacter Sulfurreducens pili

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Abstract:

The electrically conductive pili of G. sulfurreducens have both environmental and practical significance with their importance in facilitating extracellular electron transfer (EET) to insoluble minerals for cellular respiration, to other microbial species in direct interspecies electron transfer (DIET) mechanism to sustain growth in syntrophic communities, and through conductive biofilms for bioenergy and bioelectronic applications. Debates hold on the electron transfer mechanism of G. sulfurreducens pili: incoherent hopping or coherent metallic-like transport. Here in this poster we examine electron transfer of G. sulfurreducens pili in regimes ranging from purely incoherent to purely coherent transport through pre-defined closely packed aromatic amino acid residues, and results indicates that in a biological reasonable zone of ET parameters including the nearest-neighbor electronic interaction, reorganization energy, and reaction free energy, electron transfer in G. sulfurreducens pili is dominated by incoherent hopping between the delocalized electronic states among PHE. The electronic delocalization is supported by the strong PHE-PHE □-□ interaction arising from their spatially closed packing structures. We further examined physical and mechanistic requirements for ET rates that will sustain the typical biological respiration rate. We found that incoherent dominated mixed regimes with ET rates on the order of 108/s and conductivity on the order of mS/cm support ET rates in accordance to experimental conductivity measurement and regular microbe respiration rate, whereas purely coherent produce almost no ET rate to support microbial respiration. These findings provide a better understanding of long-range electronic transport in protein-based material.

Determination of Orientation of Bipyridine Re(I) fac-tricarbonyl Electrocatalysts on Au, on SrTiO3, and on TiO2 Surfaces through Computational and Experimental SFG Spectroscopy.

Benjamin Rudshteyn,[1] *Aimin Ge,*[2] *Melissa L. Helm,*[3] *Brian T. Psciuk,*[1] *Clifford P. Kubiak,*[3] *Tianquan Lian,*[2] *Victor S. Batista,*[1,*]

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Fundamental studies of CO_2 reduction catalysts bound to electrode surfaces rely upon the structural characterization and catalyst orientation relative to the electrode-electrolyte interface. Here, we focus on the analysis of a highly efficient $Re^I(R_2$-bpy)$(CO)_3Cl$ electrocatalysts for CO_2 reduction bound to Au, $SrTiO_3$, and TiO_2 electrode surfaces. We combine DFT, cyclic voltammetry, and infrared-visible sum frequency generation (IR-SFG) spectroscopy to resolve the arrangement of the electrocatalyst at the electrode interface as reported by specific SFG vibrational modes.

In one case (R = CN/H or SH), the cyano- and thiol- substituted molecule have been adsorbed on Au surfaces and found to bind through one of the anchoring groups in an orientation that exposes the labile Cl group and allows for vibrational relaxation via the axial C=O group. In another case (R=COOH), the carboxyl-substituted molecule has been adsorbed to the perovskite, $SrTiO_3$. In the final case (R = COOH), it has been found that the SFG signal shows an anisotropic distribution (Figure 1) for the (110) surface of rutile TiO_2, but not for the (001) surface, which is explained by preferential binding along one crystal axis due to additional favorable hydrogen bonding between the carboxylate groups and surface waters.

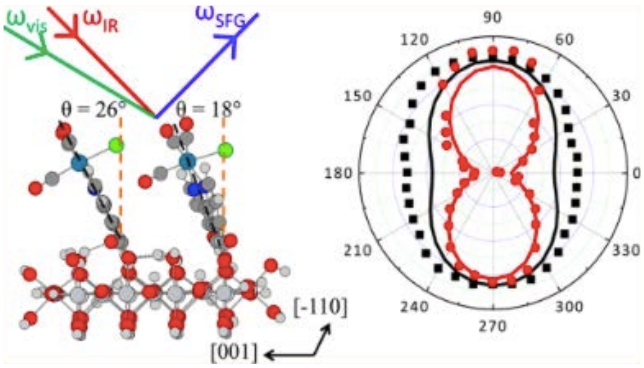

Figure 1. Left: Equilibrium structures determined for the dicarboxyl Re(I)-bpy *fac*-tricarbonyl electrocatalyst bound to a slab of anisotropic (110) rutile TiO_2. Right: The corresponding SFG amplitudes given for two normal modes with the theoretical amplitudes (solid) overlaid on the experimental (dotted). Black indicates the completely symmetric stretch and red indicates the out of phase symmetric stretch.

Fine tuned generation of Molecules with Objective-Reinforced Generative Adversarial Networks (ORGAN)

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Abstract:

In molecular discovery, we often seek to generate chemical species tailored to very specific needs. To this aim, different criteria, often encoded as heuristics, are applied; some typical examples include synthesizability[1], symmetry, and stability under normal conditions, as well as diversity[2] and the sometimes vague notion of 'performance'.

Here, we present Objective-Reinforced Generative Adversarial Networks (ORGAN)[3], a method that combines two well-established techniques from the Machine Learning field: Generative Adversarial Networks[4,5,6] (GANs) and reinforcement learning (RL), in order to accomplish this particular goal. In this way, while RL biases the molecular generation process towards arbitrary metrics, the GAN component of the reward function ensures that the model still remembers information learned from previously observed data.

We build upon previous results that incorporated GANs and RL in order to generate sequence data and test this model in several settings, for the generation of molecules encoded as text sequences (SMILES)[7]. We explore several applications that would benefit from this approach, including drug design[8] and organic photovoltaic materials discovery[9]. For each each case we show that we can effectively bias the generation process towards the desired properties.

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TDDFT in Regions of Strong S_0 and S_1 Coupling: A Nonadiabatic Moecular Dynamics Study of Cyclohexadiene and 7-Dehydrocholesterol

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Abstract:
Understanding the mechanism describing the photo-induced ring-opening of 1,3-cyclohexadiene (CHD) is a critical first step towards revealing the photobiological synthesis of 7-Dehydrocholesterol (PRO-D) in the epidermis. CHD and PRO-D were thoroughly analyzed by using time-dependent density functional theory (TDDFT) and complete active space self-consistent field theory (CASSCF) along with ab initio multiple spawning (AIMS). We show that TDDFT is unable to effectively describe the nonadiabatic dynamics of CHD and PRO-D upon photoexcitation due to over-estimating the dimensionality of the S_0/S_1conical intersection (CI). Describing the ground and excited state intersection for CHD and PRO-D as a degenerate seam, results in far too short computed excited-state lifetimes of 58fs and 297fs, respectively when compared to experiment. In addition, TDDFT is unable to capture the biexponential decay for both CHD and PRO-D due to its inability to effectively describe the S_2 charge transfer surface, which participates in considerable population transfer upon relaxation of CHD and PRO-D to the S_0 surface. Computed CASSCF excited state lifetimes for CHD and PRO-D agreed well with the experimentally determined biexponential S_1 population decay and 110fs and 340-900fs excited-state lifetime for CHD and PRO-D, respectively.

Designing a single-molecule exciton transistor.

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Abstract:

The ability to precisely control the movement of electronic excitations can aid in the design of excitonic circuits, with potential applications in bioimaging, microscopic signaling, or new forms of solar energy capture. Here, we demonstrate theoretically that an organic single-molecule exciton "transistor," or exciton gate, can be designed through the careful use of second excited singlet states (S2 states). This design makes it possible to control the direction and distance that an exciton travels, by using either an external light source or an auxiliary exciton source for switching the gate on and off. We demonstrate how to overcome the two main obstacles for the strategy to be viable. First, molecules with long-lived S2 states must be used, which limits the design to a small subset of organic molecules. Second, exquisite control of the relative orientations of molecules is required to properly align transition dipole moments, necessitating the use of a nanodesign method such as DNA origami. We introduce a rate model that relates decay rates and orientational errors to the probability that the exciton gate produces false positives and false negatives. Finally, in analogy to traditional transistors, we show how a universal set of logical binary gates may be constructed with these exciton gates, demonstrating that universal computation becomes possible.

Building active spaces automatically and systematically from atomic valence orbitals

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Abstract:

Quantum chemical modelling of systems with strong electron correlation usually requires a multiconfigurational and multireference treatment. A major challenge in applying these methods in practice is that a suitable active space needs to be chosen. The selection of the active space is accompanied by several problems, ranging from the necessity to manually select active orbitals to difficulties with clearly identifying molecular orbitals responsible for the principal chemical properties. In this work we describe a new method of constructing multireference active spaces automatically and systematically from a single-reference wavefunction and atomic valence orbitals, based on a linear transformation of the occupied and unoccupied orbital spaces. To demonstrate the capabilities of this approach, we performed calculations of electronic spectra for a variety of transition metal complexes and computed the potential energy surface for the homolytic dissociation of hydrogen peroxide catalyzed by aqueous ferrous ion (Fenton reaction).

Modelling Photoinduced Events and Non-Linear Spectroscopy in Complex Multichromophoric Systems

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Light-Harvesting (LH) Pigment-Protein Complexes in plants and photosynthetic bacteria, constitute the fundamental units through which sunlight is collected. The high complexity of such systems, where multiple interacting chromophores are embedded in a fluctuating protein matrix, makes it extremely difficult to study their response to external excitations. In this respect, advances in non-linear electronic spectroscopy with femtosecond time resolution, such as the Two-Dimensional Electronic Spectroscopy (2DES), have provided new insight on the energy transfer (ET) processes activated by light, allowing to decongest the overlapping transient spectra [1]. High density of information is obtained, but to accurately disentangle all the measured signals and reach a detailed and reliable map of the ET routes, it is mandatory to integrate the experimental measurements with theoretical models [2].

Here we introduce a fully Quantum-Chemistry based protocol to simulate and interpret linear and non-linear spectroscopy (2DES) of complex multichromophoric architectures of known structure. The proposed scheme relies on a QM/MM multi-scale approach [3,4], able to link single chromophore units with the entire molecular aggregate via a so called Frenkel Exciton Hamiltonian. This includes molecular vibrations and environmental fluctuations, eventually delivering the system’s manifold of states and their relaxation pathways with very high accuracy. Application to the LH2 test case, employed here as a challenging playground, gives an unprecedented insight into the interpretation of the spectral signatures of the measured 2DES signals.

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Ab Initio Interactive Molecular Dynamics: A Hands-On Experience with Quantum Chemistry

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Abstract:
In this work, we present a hands-on portable demo of our *ab initio* interactive molecular dynamics (AI-IMD) visualizer on a single laptop workstation. In previous work, we have shown how it is possible to use graphics processing units (GPUs) to achieve real-time AI-IMD simulations for molecules containing dozens of atoms. These AI-IMD simulations can become a powerful exploratory tool for computational chemists by allowing us to guide the simulation to chemically relevant regions of phase space. Additionally, this paradigm provides new avenues for education and increases the accessibility of chemistry to the public by allowing non-experts to interact with chemical systems and drive chemical reactions without needing to fully understand the underlying quantum mechanical principles. While AI-IMD simulations show promise, there are still several technical challenges to address before this technique can be applied broadly, including intuitive user control. Our current implementation uses a haptic device and a 3D display to allow accurate manipulation of the simulation, tools which are common in visualization labs today. We also present preliminary work in porting our visualizer to virtual reality (VR) and augmented reality (AR) devices to increase the impact of AI-IMD simulations as these technologies proliferate among the public.

Chemical Transformations Approaching Chemical Accuracy via Correlated Sampling in Auxiliary-Field Quantum Monte Carlo

James Shee, Shiwei Zhang, David R. Reichman, and Richard A. Friesner

Abstract:
The exact and phaseless variants of Auxiliary-Field Quantum Monte Carlo (AFQMC) have been shown to be capable of producing accurate ground-state energies for a wide variety of systems including those which exhibit substantial electron correlation effects. The computational cost of performing these calculations has to date been relatively high, impeding many important applications of these approaches. Here we present a correlated sampling methodology for AFQMC which relies on error cancellation to dramatically accelerate the calculation of energy differences of relevance to chemical transformations. In particular, we show that our correlated sampling-based AFQMC approach is capable of calculating redox properties, deprotonation free-energies, and hydrogen abstraction energies in an efficient manner without sacrificing accuracy. We validate the computational protocol by calculating the ionization potentials and electron affinities of the atoms contained in the G2 Test Set, and then proceed to utilize a composite method, which treats fixed-geometry processes with correlated sampling-based AFQMC and relaxation energies via MP2, to compute the ionization potential, deprotonation free-energy, and the O-H bond disocciation energy of methanol, all to within chemical accuracy. We show that the efficiency of correlated sampling relative to uncorrelated calculations increases with system and basis set size, and that correlated sampling greatly reduces the required number of random walkers to achieve a target statistical error. This translates to CPU-time speed-up factors of 55, 25, and 24 for the the ionization potential of the K atom, the deprotonation of methanol, and hydrogen abstraction from the O-H bond of methanol, respectively.

Multiscale Quantum Mechanics / Molecular Mechanics Simulations with Neural Networks

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Abstract:

Molecular dynamics (MD) simulation with multiscale quantum mechanics / molecular mechanics (QM/MM) methods is very powerful to understand the mechanism of chemical and biological reactions in solution or enzymes but intensely time consuming for many systems because of the great number of ab initio QM calculations. Semi-empirical QM/MM simulations have much higher efficiency, and the accuracy can be improved with a correction to achieve the ab initio QM/MM level. Herein we developed a neural network (NN) method for QM/MM calculation as an extension of the high-dimensional NN representation reported by Behler and Parrinello. With this approach, the potential energy of any configuration along the reaction path for a given QM/MM system can be predicted at the ab initio QM/MM level based on the semi-empirical QM/MM calculations. We further applied this method to the free energy calculation on chemical reaction systems in solution. The potentials of mean force at the ab initio QM/MM level are reproduced excellently based on the semi-empirical QM/MM simulations and the NN-predicted potential energies. The saving in computational cost is about 1 or 2 orders of magnitude compared to the ab initio QM/MM MD simulation or the correction using ab initio QM/MM potential energies. The direct MD simulations with the self-adaptive NN predictions are also under research to approximate ab initio QM/MM MD with higher efficiency.

Critical Micelle Concentrations and Critical Aggregation Numbers Predicted by a Thermodynamic Model and Molecular Dynamics Simulations

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Abstract:

A thermodynamic model, based solely on calculated chemical potentials without any empirical parameters, is proposed to predict the critical micelle concentration (CMC) and critical aggregation number of a surfactant in solution. In the model, the chemical potential of an aggregate is expressed in terms of ideal and excess contributions. The ideal contribution is calculated analytically and the excess contribution is decomposed into the chemical potential of a surfactant molecule in solution and in aggregates, both calculated using molecular dynamics simulations and the thermodynamic integration (TI) method. The method is tested by predicting CMCs and aggregation numbers of nonionic surfactants ($C_{12}EO_{12}$ and $C_{10}EO_6$). The model's predictions agree very well with the experimental data.

Three-body molecular interactions mediate the polarization and polarizability of the liquid water-vapor interface

Sucheol Shin and Adam P. Willard

Abstract:

Here we highlight the fundamental relationship between hydrogen bonding and molecular structure of water interface. We describe this relationship, and how it is mediated by the density profile of water interface, in terms of a mean field model of interfacial hydrogen bonding. Specifically the model can predict the orientational distribution of interfacial water molecules based on the anisotropic local density and given hydrogen bond geometry. We demonstrate that the fluctuation in bond geometry at the interface appears fairly different from that in the bulk environment and thus accounts for the mean polarization and its mean fluctuation observed at the interface. More interestingly, our simple model reveals that the interactions involving three water molecules are the key physical elements for the modulation of the interfacial polarization and polarizability, as they can bring about large deviations from the tetrahedral geometry in hydrogen bond network.

Dual-Functional Tamm-Dancoff Approximation: A Convenient Density Functional Method that Correctly Describes S_1/S_0 Conical Intersections

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The accurate computation of the electronic structures of multiple states is the base of direct and indirect simulations of molecules and materials under excitation. This requires sophisticated electronic structure theories that have the capability of describing the complex wavefunctions or densities in different regions of the potential energy surfaces (PESs). Conical intersections (CIs), points where two or more PESs degenerate, facilitating the population transfer from one state to the other, play an important role in the non-adiabatic processes. Near CI geometry, the PESs are lifted up linearly by two directions and form the branching plane.[1-2] Hence, efficient and accurate electronic structure theories should have the capability of describing the double cone topology of the PESs near CI. The current state of the art theories that can correctly describe the CI regions of the PESs are mostly based on the multi-reference electronic structures, for example, state-averaged complete active space self-consistent field (SA-CASSCF) theory and complete active space configuration interaction (CASCI) methods. However, the computational cost of the multi-reference methods grows exponentially when the active space increases. On the other hand, linear response (LR-) time-dependent density functional theory (TDDFT) is both efficient and accurate. LR-TDDFT has been applied to various photochemical problems of large molecules. However, LR-TDDFT is unable to describing the CIs between ground and excited states.[3] Hence the applications of LR-TDDFT in the non-adiabatic processes are limited. In this presentation, we will introduce a novel theoretical method based on LR-TDDFT, named dual functional Tamm-Dancoff approximation (DF-TDA) that has the capability of providing the correct double cone topology of the PESs near CI and can be accurate as LR-TDDFT. DF-TDA does this without explicitly employing double excitations and the first step is a Kohn-Sham calculation, so there are no complications due to active space selection in multi-reference methods. Furthermore, it involves only a particularly simple modification of the conventional procedure.

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Going beyond the perturbative regime: Post-Marcus methods based on the Generalized Quantum Master Equation

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Abstract:

Electron transfer reactions play an important role in various biological systems and optoelectronic devices. Commonly used perturbative methods, such as the semi-classical Marcus theory or the fully quantum-mechanical Fermi's Golden Rule approach, provide a simple and efficient framework to calculate transfer rates of such processes based on an intuitive picture. However, in many photophysical and photochemical processes in the condensed phase, coupling to nuclear degrees of freedom reaches the same magnitude as the electronic coupling so that nuclear reorganization effects exceed the weak coupling limit. The Generalized Quantum Master Equation (GQME) provides for these situations an exact, i.e. non-perturbative, equation of motion for the system of interest while reducing all remaining degrees of freedom to their effect on the system within the so-called memory kernel.

In this work, we examine various techniques to calculate the memory kernel numerically using a projection-free formulation based on correlation functions. Thus, an expression is obtained which allows for the calculation of the short-lived memory kernel by means of mixed quantum-classical methods, such as the Ehrenfest mean-field method (MF-GQME). The GQME is then numerically integrated cost effectively, which allows for the simulation of long-time dynamics beyond the perturbative regime at low computational costs.

eGFP-based motion sensor via electrochemical control of fluorescence

*Lena Simine, Heiko Lammert, Jose N. Onuchic, and Peter J. Rossky**

Abstract:

The rational design of genetically encoded fluorescent bio-sensors, which detect rearrangements of target proteins via interdomain allostery, is hindered by the absence of mechanistic understanding of the underlying photo-physics. Here, we investigate the mechanism for electrochemical control of fluorescence quantum yield in a model system: enhanced Green Fluorescent Protein (eGFP), using a combination of molecular dynamics (MD) and quantum chemistry simulations. Specifically, we uncover the mechanism of the modulation of fluorescence brightness by mild mechanical perturbations, and report a map of fluorescence quantum yield as a function of a 2D electric field imposed by the protein environment on the fluorophore; this map allows to assess the relative brightness of GFP homologues, or different conformants of thereof, directly from MD simulations. Our results are expected to expedite the discovery and optimization of fluorescent bio-sensors, e.g., genetically encoded voltage indicators.

Stochastic hard collision model for coarse-graining complex solvent dynamics

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Abstract:
In computer simulation studies, sluggish dynamics of model soft colloidal systems often deter us from gaining deeper understanding of the behavior of these complex systems at higher packing fractions. To overcome this difficulty, we recently introduced stochastic hard collision (SHC) dynamics [Craven et al., J. Chem. Phys., 2013, 138, 244901]. It includes the effects of inter-penetrability of soft particles while retaining the computational efficiency of hard collision dynamics. Here, we extend the earlier SHC model to coarse-grain an important class of soft matter system: hard-core soft-shell (HCSS) colloids. The HCSS colloids are characterized using two parameters: overlap probability (a measure of the propensity toward interpenetration), and inner core diameter. In both molecular dynamics and Monte-Carlo simulations, the overlap probability is seen to affect the packing fraction and the thermodynamic behavior of the system. We also find that the local structure and two-body correlation functions strongly depend on the overlap probability at a given packing fraction of the system.

This work has been partially funded by the National Science Foundation through grant number CHE 1700749. The computing resources necessary for this research were provided in part by the National Science Foundation through XSEDE resources provided by XSEDE-Bridges under grant number TG-CTS090079.

Cavity Hydration Dynamics in Cytochrome c Oxidase and Functional Implications

Chang Yun Son, Arun Yethiraj, and Qiang Cui

Abstract:

Cytochrome c oxidase (CcO) is a trans-membrane protein that uses the free energy of O_2 reduction to generate the proton concentration gradient across the membrane. The regulation of competitive proton transfer pathways has been established to be essential to the vectorial transport efficiency of CcO, yet the underlying mechanism at the molecular level remains lacking. Recent studies have highlighted the potential importance of hydration level change in an internal cavity that connects the proton entrance channel, the site of O_2 reduction and the putative proton exit route. In this work, we use atomistic molecular dynamics simulations to investigate the energetics and time scales associated with the volume fluctuation and hydration level change in this central cavity. Extensive unrestrained molecular dynamics simulations (accumulatively ~ 4 μs) and free energy computations for different chemical states of CcO support a model in which the volume and hydration level of the cavity is regulated by the protonation state of a propionate group of heme a_3, and to a lesser degree, the redox state of heme a and protonation state of Glu 286. Markov state model analysis of ~2 μs trajectories suggests that hydration level change occurs on the time scale of 100-200 ns prior to the proton loading site being protonated. The computed energetic and kinetic features for the cavity wetting transition suggest that reversible hydration level change of the cavity can indeed be a key factor that regulates the branching of proton transfer events and therefore contributes to the vectorial efficiency of proton transport.

Multiscale modeling of poly(ethylene oxide) with ionic liquids : GPU enabled first-principles force fields

Chang Yun Son, Jesse G. McDaniel, J.R. Schmidt, Qiang Cui, and Arun Yethiraj

Abstract:

Ionic liquids [IL] have multiple advantages as a solvent material for polymers and the mixture have wide range of applications including use in fuel cells, batteries and gas separation. Experimental studies of polymer/IL mixture showed intriguing physical properties such as lower crystal solution temperature (LCST), but their molecular level understanding is still lacking. Numerous molecular dynamics (MD) studies have been taken for ILs and polymer/IL mixtures, but often have limited applicability either due to the implicit parametrization of the interaction potentials or due to the significant computational cost. Here, we present a multiscale simulation study of six different ILs and poly(ethylene oxide) (PEO) using two sets of physically motivated, first-principles force fields based on symmetry-adapted perturbation theory (SAPT) – a fully polarizable and atomistic force field and a coarse-grained non-polarizable united atom force field. Both of the force fields provide accurate description of the kinetics and thermodynamics of pure ILs and polymeric melts as well as the mixture while not relying on any implicit parameters. The GPU implementation of extended Lagrangian dynamics for the polarizable force field in the MD package OPENMM enabled polarizable MD simulations of sub-microsecond timescale (750 times speeds up compared to the self-consistent field treatment of the polarization in CPU), which disclosed the important role of polarization in the enhanced dynamics of the certain ILs. Coarse-grained simulations of PEO/IL mixture suggest an entropic mechanism of LCST that does not depend on the directional hydrogen bonding between the IL and the PEO. A multiscale approach – switching to polarizable all atom force field after obtaining the equilibrium structure of the mixture with united atom force field – clarified the contribution of each interaction components toward the phase behavior and the dynamic properties.

“Enhanced Sampling of Bilayers, Vesicles, and Lipid-Wrapped Nanoparticles”

David Stelter and Tom Keyes

Abstract:

Lipids undergo a characteristic chain-melting phase transition near physiological temperature. Non-planar lipid structures, such as lipid vesicles and lipid-wrapped nanoparticles are promising materials with uses in drug delivery, imaging, and energy applications.

However, the phase behavior of non-lamellar bilayers and the dependence on variables such as curvature, NP interaction, and membrane composition are not well understood. Using molecular simulations, with novel enhanced sampling algorithms based on generalized ensembles, a complete thermodynamic picture of these first-order phase transitions are obtained with molecular resolution.

Exploring the Role of the Third Active Site Metal Ion in DNA Polymerase Eta with Quantum Mechanical/Molecular Mechanical Free Energy Simulations

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Abstract:

Human DNA polymerase η (Pol η) is an enzyme involved in the repair of DNA mutations that cause skin cancer. Recent experimental work suggests that a third Mg2+ ion plays an essential catalytic role, in addition to two well defined Mg2+ ions that align the active site for catalysis. These experiments were interpreted to imply that this metal ion enters the active site prior to the phosphoryl transfer reaction. In addition, a specific hydroxyl group has been proposed to protonate the pyrophosphate leaving group. We investigate this reaction mechanism using quantum mechanical/molecular mechanical (QM/MM) free energy simulations that combine a finite temperature string method with umbrella sampling. Our simulations address these key issues by providing critical information regarding the impact of the transient third metal on the reaction mechanism and the proposed proton transfer. The results provide evidence that the third metal ion not only acts as a shuttle for the pyrophosphate leaving group, but also thermodynamically drives the phosphoryl transfer reaction. Moreover, the simulations suggest that the presence of this third metal ion prevents the proposed proton transfer reaction to this leaving group.

Predictions of the Temperature Dependent Structure of the Air/Water Interface with MB-pol

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Abstract:

The imaginary component of the nonlinear optical susceptibility of the the air-water interface is studied by way of Many-Body Molecular Dynamics with the MB-pol water model. The extent of the intermolecular coupling clearly relies on temperature, shown by the decrease in magnitude of the redshift of the Sum-Frequency Generation (SFG) spectra upon transitioning from the auto- to cross-correlation function formalisms at different external conditions. The depth of interfacial optical activity is studied as a function of frequency and temperature, which shows that under the dipole approximation, an SFG active chromophore must be no further than 9 angstroms away from the Gibbs dividing surface to contribute to the spectra. The optical activity of MB-pol at the interface is compared to the vibrational response of the bulk liquid, and differences between the two are rationalized by the fluctuations of the Willard-Chandler dividing surface.

Accurate Quasiparticle Spectra from the T-matrix Self Energy and the Particle-Particle Random Phase Approximation

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Abstract:
The GW self energy, especially G0W0 based on the particle-hole random phase approximation (phRPA), is widely used to study quasiparticle (QP) energies. Motivated by the desirable features of the particle-particle (pp) RPA compared to the conventional phRPA, we explore the pp counterpart of GW, i.e. the T-matrix self energy, formulated with the eigenvectors and eigenvalues of the ppRPA matrix. We demonstrate the accuracy of the T-matrix method for molecular QP energies, highlighting the importance of the pp channel for calculating QP spectra.

High-Throughput Virtual Screening of Flow Battery Electrolytes

Daniel P. Tabor and Alán Aspuru-Guzik

Abstract:

Aqueous flow batteries for grid storage represent a potential economic and technical solution for the intermittency problem of some renewable energy sources. Such flow batteries have already been deployed in a limited capacity using earth-rare vanadium electrolytes, which limits the potential global implementation of this technology. The development of new flow batteries and electrolyte materials requires the collaboration of experimental battery design, new electrolyte synthesis, and (*in silico*) materials screening. We present an overview of the materials screening aspect, focusing on the methods and results of a high-throughput virtual screen of organic and organometallic electrolytes. Several properties of a large library (~150,000) of quinones, viologen, and ferrocene derivatives are calculated. These properties include reduction potentials, solubility, and stability using various levels of theory, ranging from cheminformatics approaches to wavefunction theory. Recently, we have focused substantial efforts to minimize decomposition pathways. Finally, we will present efforts to characterize synthetic accessibility beyond cheminformatics methods and use machine learning methods to generate new electrolyte candidate without a reliance on fragment-based libraries.

Automatic differentiation in quantum chemistry

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Abstract:

Automatic differentiation (AD) is a tool that allows us to calculate derivatives of implemented functions with respect to all of their parameters up to machine precision, without having to add in any other explicit functions[1]. Since it is easy to use and accurate, AD has great potential in quantum chemistry, where accurate derivatives are required to compute molecular properties and optimizations[2]. However, implementing analytical derivatives of new electronic structure methods or response functions can be both time-consuming and non-trivial. First steps have already been taken toward including AD in quantum chemistry algorithms to circumvent these issues[3].

In this poster, we show how automatic differentiation can be used to compute arbitrary gradients throughout a complete quantum chemistry method with respect to any input parameter. We will describe an implementation of a fully autodifferentiable Hartree-Fock (HF) algorithm. We have selected HF for two reasons: (i) it is the starting point of many electronic correlation methods, and (ii) it features mathematical functions, including eigenvectors and special functions, which are also present in more accurate methods. Finally, we present results from embedding these gradient calculations within an optimization procedure to assemble a fully variational HF method. Using the floating Gaussian framework[4], this implementation minimizes the SCF-energy with respect to all parameters of the Gaussian basis functions and molecular geometries.

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Multi-level computational study of Photoinduced Charge Transfer in Cryptochromes

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Abstract:

Photoinduced electron transfer is ubiquitous in biological systems. Yet, a predictive and quantitative simulation of the electron transfer (ET) in biomolecules remains a challenge for the modern computational chemistry. Proper characterization of electron transfer requires (i) identifying the active players in the cascade of ET processes, i.e. establishing the efficient electron transfer channels, and (ii) quantifying thermodynamics and dynamics of ET events. Here we present the results of the multi-level computational study of the mechanism of the photoinduced ET in cryptochromes, photoreceptors involved in growth and development processes in plants and likely in the magnetosensoric machinery of migratory birds and insects.[1] We exploit multiple computational chemistry methods targeting different aspects of ET process at the different levels from empirical coarse-grained description to atomistic QM/MM simulations. Specifically, we use simple empirical analysis of the protein structure to identify existing chains of aromatic amino acid side-chains, co-factors, and metabolites that can serve for efficient hole transfer[2]. We then employ hybrid quantum mechanical/molecular mechanical (QM/MM) methods to explore ET energetics and timescales. The efficiency of the competing conventional and the alternative electron transfer pathways[3,4] is estimated based on the computed free energy changes, reorganization energies, and constrained density functional theory – configuration interaction[5] (CDFT-CI) electronic couplings. Classical MD simulations are performed to sample configurational space of the system. The energetic parameters are extracted from QM/MM electronic embedding simulations using density functional theory and recently developed extension of effective fragment potential approach to macromolecules taking into account the effect of environment polarization, crucial in charge transfer/separation processes.[6]The obtained results indicate that photoexcitation can initiate several competing ET channels, and contribute to understanding of complex electron transfer processes accompanying the formation of a photoactivated state of a protein *in vivo* and *in vitro* in diverse systems, including cryptochromes in birds and humans.

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Self-Assembly of Porous Polymer Gels

Paul E. Teichen and Adam P. Willard

Abstract:

Polymer gels can efficiently sequester organic pollutants from water if they exhibit extensive and stable porosity and can be regenerated under near-ambient conditions. The porosity and crosslinking in polymer gels are sensitive to the rate at which solvent and air are removed from the polymer solution, suggesting that optimal gelation may occur out of equilibrium. We model the complex polymer solution as a dense fluid and use a hierarchical renormalization of Lum-Chandler-Weeks theory to predict the optimal drying rate for solutions with different surface tensions. We also examine the viscoelastic properties of porous polymer gels under compression.

Title: From First Principles: Modulation of Hole Transfer Pathways in the p53 DNA-Binding Domain

Ruijie D. Teo, Agostino Migliore, David N. Beratan

Abstract:

Redox signaling has been shown in numerous studies to regulate protein-DNA interactions that control major cellular metabolic pathways. In particular, the role of the redox-active cysteine in mediating the DNA-binding capability of the tumor suppressor protein p53 has been experimentally demonstrated in seminal studies by Barton et. al. However, the mechanism and properties of the electron transfer between cysteine and DNA are still poorly understood at a molecular level. To gain understanding on this charge transfer from first principles, we have performed Car-Parrinello MD simulations combined with DFT electronic structure calculations on atomistic models of p53-DNA contact regions in representative protein-DNA complexes from the protein data bank. Our analysis suggests that the p53-DNA interaction is influenced by the DNA sequence of purines. In particular, the cysteine residue has different electronic couplings with nearby adenine and guanine, and this feature appears not to be erased by structural fluctuations, thus leading to accordingly different hole transfer efficiencies.

Diffusion Maps Speed Reaction Path Search

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and SLAC National Accelerator Laboratory, Menlo Park, CA

Abstract:
In theoretical chemistry a reaction is usually defined in terms of its Minimum Energy Path (MEP). The process of finding the optimised MEP can consume at least as many computer resources as a finite temperature reaction dynamics simulation. One way to look at this problem is that local optimisation (i.e., gradient following) is an expensive way to find global features on a molecular potential energy surface. Here we use Diffusion Maps to provide a natural bridge between reaction dynamics and the MEP. We find that using a dynamically sampled, data driven initial guess can speed convergence of Nudged Elastic Band calculations.

Dynamics of reactions fundamental to the origins of life

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Abstract:

Recently, several reactions have been proposed as a means to describe a mechanism for the origin of amino acids and nucleobases [1]. The reactions rely on the presence of hydrogen cyanide and hydrogen sulfide. The mechanism of many of these processes is not fully understood and the conditions which are optimal for the kinetics are also unknown [1]. Previously it was believed that the Urey-Miller reaction could explain the origin of many compounds but new evidence on the composition of the primordial atmosphere has excluded it. In this context, I have studied the Urey-Miller reaction as a test case. I have employed the powerful software TeraChem [2-5] to simulate the dynamics. TeraChem is a general purpose quantum chemistry software designed to run on NVIDIA GPU architectures. This design principle enables the rapid simulation of large molecular systems using ab initio methods. With this software and using the COSMO model for the solvent, multiple trajectories were propagated for various values of the dielectric constant. These trajectories have been refined to identify reactive events. Thus, a map of reactivity as a function of the dielectric constant of the solvent has been obtained. From this information one can understand the role of the solvent's dielectric constant on the discovery of reactions and how this can be used as a tool in the process of reaction discovery.

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Predicting Intersystem Crossing Rates: Nonadiabatic Molecular Dynamics vs. Statistical Theory

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Abstract:
Accurate prediction of the intersystem crossing rates is important for many different applications in chemistry, physics, and biology. We implemented the ab initio multiple spawning (AIMS) molecular dynamics method to describe the intersystem crossing processes, where nonradiative transitions between electronic states with different spin multiplicities are mediated by spin-orbit coupling. Our implementation of the direct AIMS dynamics uses the complete active space self-consistent field (CASSCF) or density functional theory (DFT) methods to describe multiple coupled electronic states on which multidimensional Gaussians wave packets are propagated. The AIMS-DFT and AIMS-CASSCF implementations are used to investigate the effects of electronic structure methods on the predicted intersystem crossing rate constants and the excited state lifetime in the GeH2 molecule. The convergence of the rate constants with respect to the simulation time, the number of trajectories, and the integration time step is analyzed. The AIMS dynamics rate constants and lifetime are compared with the ones predicted by the statistical nonadiabatic transition state theory using the local properties of the CASSCF and DFT potential energy surfaces at the minimum energy crossing between the ground and excited electronic states.

Planar Hypercoordinate Carbon Zoo

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Since the pioneer work of Hoffmann *et al.*[1] on the stabilization of planar tetracoordinate carbon (ptC) as a thermally accessible transition state, scientists have tried to design and understand these nonclassical structures. Later on, it was concluded that ptCs have a preference for 18 valence electrons due to bonding interactions between peripheral ligands in the molecule.[2,3] This rule has been used to find novel species having global minima structures containing a ptC[4] or also planar pentacoordinate carbons (ppC).[5]

In this work, a massive search at PBE0/def2-TZVP[6,7] level on the potential energy surface of systems with 18 valence electrons was done to find ptC and ppC. The clusters meet the following rules:

- i. They are comprised of C and other elements from the main group of the periodic table.
- ii. Systems are either pentaatomic or hexaatomic.
- iii. Charges are equal to 0, ±1 or ±2.

So, the PESs of 508 pentaatomic and 424 hexaatomic species were systematically explored. For each case, 150 singlets and 80 triplets initial motifs were considered. A total of 428720 optimizations were carried out.

Our computations show that the global minima of 156 pentaatomic clusters have a ptC. In hexaatomic species, 50 ptC and 18 ppC were found to be global minima. We also used statistical data analysis tools (Random Forests, Support Vector Machines) to rank and quantify the most important features that determine if a compound will be a global or local minima, with a prediction accuracy of 90%.

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Quantum Control at a Light-Induced Conical Intersection: Floquet Theory Applied to the Photoisomerization of Rhodopsin

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Abstract:

The development of ultrafast laser technology has opened the possibility to manipulate and control chemical reactivity with high precision. In the presence of strong electric fields, the topography of the potential energy surfaces can be altered giving rise to a variety of non-adiabatic effects. Light-Induced potentials, including Light-Induced Conical Intersections,[1] can open new reaction channels or modify the product yields of existing pathways. Here, we report a Floquet theoretical study of quantum control as applied to the ultrafast cis-trans photoisomerization dynamics of rhodopsin. We first analyze the performance of the Split Operator Fourier Transform (SOFT) methodology[2] in the (adiabatic) Floquet representation, using a 25-dimensional model potential[3] to describe the cis-trans isomerization according to the time-dependent self-consistent field propagation method.[4] Benchmark calculations for a variety of different pulses show that the Floquet-SOFT approach is computationally efficient and exhibits excellent agreement with exact results even with a single dressed-state for short-time propagation. Moreover, the Floquet representation provides valuable physical insights into the dynamical evolution of the wave-packet since the effect of the control pulse is naturally decoupled along the different channels. Based on these results, we analyze the effect of different control pulses on the dynamics of cis-trans isomerization, including changes in pulse duration and intensity. Results obtain with long (300 fs) pulses show that it is possible to 'trap' the wave-packet in the excited state and delay the excited-state isomerization, demonstrating the feasibility of ultrafast optical switches based on rhodopsin isomerization.

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Quantum-classical path integral calculations of ferrocene-ferrocenium charge transfer in solution

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Abstract:
It is well known that performing highly accurate quantum simulations of condensed phase reactions is exceedingly difficult, due to the exponential scaling of quantum mechanics. Quantum-classical path integral[1-6] (QCPI) is a recently developed methodology designed to efficiently and accurately simulate the dynamics of a quantum system immersed in a condensed phase environment. It combines a path integral representation of the system with a classical description of the environment. Unlike wavefunctions, quantum paths are local in space, and can thus be coupled to classical trajectories without approximation. In this manner, QCPI treats the system-environment interactions exactly. In this work, QCPI was used to investigate the charge transfer process of the ferrocene-ferrocenium pair in solution with unprecedented accuracy.

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Determining polarizable force fields with electrostatic potentials from quantum mechanical linear response theory

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Abstract:

We developed a new method to calculate the atomic polarizabilities by fitting to the electrostatic potentials (ESPs) obtained from quantum mechanical (QM) calculations within the linear response theory. This parallels the conventional approach of fitting atomic charges based on electrostatic potentials from the electron density. Our ESP fitting is combined with the induced dipole model under the perturbation of uniform external electric fields of all orientations. QM calculations for the linear response to the external electric fields are used as input, fully consistent with the induced dipole model, which itself is a linear response model. The orientation of the uniform external electric fields is integrated in all directions. The integration of orientation and QM linear response calculations together makes the fitting results independent of the orientations and magnitudes of the uniform external electric fields applied. Another advantage of our method is that QM calculation is only needed once, in contrast to the conventional approach, where many QM calculations are needed for many different applied electric fields. The molecular polarizabilities obtained from our method show comparable accuracy with those from fitting directly to the experimental or theoretical molecular polarizabilities. Since ESP is directly fitted, atomic polarizabilities obtained from our method are expected to reproduce the electrostatic interactions better. Our method was used to calculate both transferable atomic polarizabilities for polarizable molecular mechanics force fields and nontransferable molecule-specific atomic polarizabilities.

Multiscale Simulation of Proton Transport in the ClC Antiporter

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Abstract:
ClC-ec1, a prototype of the ClC family of proteins which are ubiquitous in nature and govern a wide range of physiological processes, enables the transmembrane exchange of Cl^- or NO_3^- ions for proton in opposite directions. Despite extensive investigation into the protein, the molecular mechanism though which the transported anion is related to the proton has not been fully elucidated. Herein, we have identified the indirect interaction between the transported ions at an atomistic scale through investigating the proton transport (PT) in the presence of various anions, with the help of multiscale simulations in which Grotthuss mechanism of PT is treated explicitly. We report, to our knowledge, the first free-energy profiles for PT across the channel comprising the central anion binding site occupied by a polyatomic anion, either NO_3^- or SCN^-. The proton conductance calculated from the free-energy profile recaptures the experimental observation of nitrate slowing PT and thiocyanate blocking PT. Our results also indicate that water is energetically unfavorable in the cavity unless the excess proton is present. Further analyzing the free-energy profile, we have unexpectedly discovered that the solvation of the cavity below the anion is a reasonably facile process. However, connecting the water network past the steric hindrance of the polyatomic anions contributes to their increased free-energy barrier. Hence, most relevant to the PT barrier is the water connectivity along the PT pathway in the presence of the excess proton, the latter of which is significantly dependent upon the property of the anion. The results presented here suggest both how water environment and PT are mutually affected and how we should control the functionality of the ClC family of proteins.

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Mechanism of Proton Transport in Influenza A M2 Mutant From Multiscale Simulations

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Abstract:

The influenza A virus M2 channel (AM2) is a homotetrameric acid-activated proton channel responsible for the acidification of the virus interior, a crucial step in the viral life cycle. One important feature of this channel is its asymmetric conductance—inward proton flux is allowed when the exterior pH is low and the viral interior pH is high, but reverse proton flux is prohibited under a reversed pH gradient. However, the mechanism of this asymmetry is not fully understood. It has been experimentally indicated that four tryptophan residues (Trp41) form a gate that results in asymmetric conduction, and another residue, Asp44, is critical for maintaining the stability of this gate. Here, multiscale computer simulations are used to characterize proton transport through an Asp44 mutant that exhibits both increased conduction and an altered asymmetric conductance. Classical, QM/MM, and reactive molecular dynamics methods are bridged in a multiscale fashion to determine explicit proton transport free energy profiles through the channel and to deduce the mechanism of asymmetric conductance. This work shows how this mutation results in different proton conduction behavior and the role of these critical residues.

First-principle time-dependent simulation of organic solar cells

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Abstract:

With the urgent need of new clean energy source and the rapid development of the photovoltaic industry, organic solar cells (OSCs) have attracted major academia attentions all over the world[1,2]. One of the most popular choice of OSC material is a blend of poly(3-hexylthiophene) (P3HT) and fullerene (PCBM). However, due to the ultrafast nature of its charge transfer mechanism, details of several critical steps lie beyond the reach of currently available experimental techniques, and a clear picture of the true mechanism still eludes us[3,4]. On the other hand, the exponentially increasing computational power becoming available each year opened up another gate in the realm of simulation.

In this work, first-principle simulation with the time-dependent density-functional tight-binding for (TDDFTB) algorism is carried out on a typical structure of P3HT and PCBM mixture, where details of the generation and separation of electron-hole pair near the interface are revealed. Compared to other simulation efforts, our TDDFTB algorism has the advantage of following a system's entire evolution trajectory with femtosecond resolution. Numerous trials of simulation with different P3HT/PCBM compositions and arrangements are carried out to confirm an experimental observation that exciton separation can be accelerated by the aggregation in PCBM. The hypothesized interfacial cascaded energy is also observed in our simulation where its exciton separation enhancement effects are also demonstrated. The effect of nuclei vibration is also investigated in combination with Ehrenfest dynamics, and charge transfer is found to be either increased or decreased in different scenarios.

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Size-Independent Machine Learning Based First-Principles Method for Accurate Prediction of the Heat of Formation of Fuels

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Abstract:

The first-principle-machine-learning combined algorism for small organic molecule heat of formation (HOF) prediction was previously demonstrated to be able to achieve chemical accuracy in a broad spectrum of target molecules1. However, its accuracy deteriorates with the increase of molecular size. A closer inspection revealed a systematic correlation between the prediction error and molecular size that appears correctable by further statistical analysis, calling for a more sophisticated machine learning algorism to be implemented. A size-independent multi-step MVLR-NN (Multivariable Linear Regression-Neural Network)-B3LYP algorism is developed in this work that successfully improved the overall prediction accuracy. The improvement in prediction power of the new algorism becomes more conspicuous for the large molecule dataset. More significantly, the trend of increasing error with respect to molecular size is successfully removed in the HOF values predicted by the new algorism. The current algorism is based on a 436-molecule database that consists of molecules made of elements H, C, N, O, F, S, and Cl. It is designed in the way that a future extension to a more diverse database appears automatic and natural. The training and testing sets are divided randomly while ensuring a consistent proportion of large molecules. 12 molecular descriptors were selected to encode molecule's characteristics among which raw HOF calculation from DFT(B3LYP) and molecular size are also included. Upon the size-independent machine learning correction, the mean absolute deviation (MAD) of the B3LYP/6-311+G(3df,2p) calculated HOF is reduced from 11.72 to 1.28 kcal mol−1 and 12.90 to 1.44 kcal mol−1 for the training and testing data sets, respectively. Furthermore, the MAD of big fuel molecules is reduced from 17.29 to 1.41 kcal mol-1.

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Pseudopotentials for hybrid-density functionals and SCAN

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Abstract:

Pseudopotentials play an important role in reducing the cost while simultaneously keeping the accuracy of plane-wave density-functional theory (DFT) calculations, and are essential for realistic atomic-scale simulations in chemistry and physics. It is known that a mismatch of density functionals used in constructing the pseudopotential and in the target DFT calculation can induce systematic errors. However, present-day pseudopotential DFT calculations have not kept pace with recent developments of new DFT functionals, often using pseudopotentials constructed from established older density functionals. Here, we use the pseudopotential generator, OPIUM (http://opium.sourceforge.net) to construct accurate pseudopotentials for modern DFT functionals such as hybrid functionals. In this talk, we present a scheme for generating PBE0 pseudopotentials, and benchmarking against the G2 dataset. The results show the reduction of errors on HOMO-LUMO gaps and formation energies. The presented approach for pseudopotential generation can also be applied to meta-GGAs, such as the recently developed SCAN functional.

Development of a Practical Multicomponent Density Functional for Electron-Proton Correlation to Produce Accurate Proton Densities

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Abstract:

Multicomponent density functional theory (DFT) enables the consistent quantum mechanical treatment of both electrons and protons. A major challenge has been the design of electron-proton correlation functionals that produce even qualitatively accurate proton densities. Herein an electron-proton correlation functional, epc17, is derived analogously to the Colle-Salvetti formalism for electron correlation and is implemented within the nuclear-electronic orbital (NEO) framework. The NEO-DFT/epc17 method produces accurate proton densities efficiently and is promising for diverse applications.

Environment-Perturbed Transition State Sampling and its Applications in Chemical and Biochemical Reactions in Condensed Media

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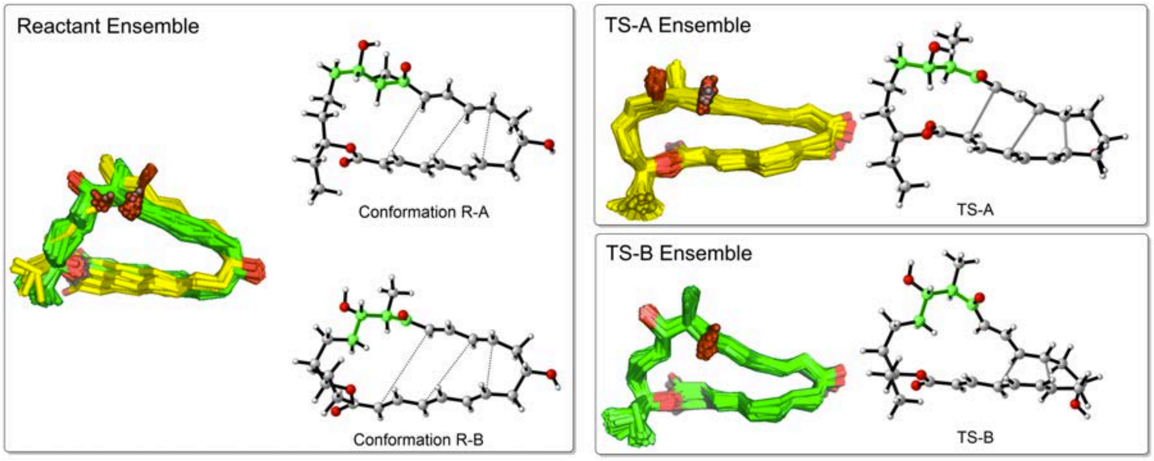
We developed a method, environment-perturbed transition state sampling, for exploring the energetics and reaction dynamics of reactions in condensed media. The method applies classical MD to sample instantaneous configurations of solvent molecules or protein residues, and performs QM/MM optimization to gain "environment-perturbed" transition structures/reactants in the snapshots. Free energies were calculated by normal mode analysis and then averaging over different configurations. Transition state normal mode sampling is then conducted to gain an ensemble of transition state geometries and momenta. These are used to initiate QM/MM reaction dynamics trajectories. This method has been applied in water-accelerated Diels-Alder reaction, allylboration of benzaldehyde, and SpnF enzyme-catalyzed Diels-Alder reactions. And it is being applied in 1,3-dipolar cycloaddition, P450-catalyzed oxidation and chorismate mutase-catalyzed Claisen rearrangement. These studies provide insight into how solvent molecules/protein residues dynamically enhance the reaction in a single molecule level, and how post-transition state dynamics determines the selectivity of reactions in solvent or enzyme.



Frankenstein Bootstrap Embedding: A Low-Scaling, Internally Consistent, Hierarchically Improvable Density Matrix Embedding Scheme For Strongly Correlated Systems

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Abstract:

Recently, density matrix-based embedding schemes have shown promise for describing strongly correlated systems with low computational cost. All these methods start with solving a system at a low level of theory, partitioning it into fragments, and then solving the embedding problem for each fragment using a high-level theory. Accurate energetics have been reported for model systems, such as Hubbard model and hydrogen rings. However, an intrinsic ambiguity arises when they are applied to systems without translational symmetry, wherein different partitions lead to different results. In this work, this ambiguity is circumvented by incorporating the idea of method of increment into bootstrap embedding theory, which was developed recently by our group. The resulting method, which is termed Frankenstein Bootstrap Embedding, has three advantages. First, it does not rely on any specific partitions of the system, and is thus internally consistent. Second, it forms a hierarchy of approximations which can systematically improve the accuracy. Third, it has low computational scaling and thus is promising for systems of large size. Numerical results on translationally invariant model systems demonstrate competitive performance compared with bootstrap embedding. Additionally, tests on systems without translational symmetry show potential applicability in more general systems, including molecules.

Spurious Rydberg States in the Particle-Particle Tamm-Dancoff Approximation

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Abstract:
Recently, there has been much interest in the “particle-particle random-phase approximation” (pp-TDA) and its Tamm-Dancoff approximation variant (pp-TDA). These approaches to electronic structure theory form the ground state together with single and double excitations as two-electron attachments to a doubly-ionized reference determinant. Previous work has indicated that this formalism offers comparable accuracy to methods such as configuration interaction singles (CIS) and time-dependent density functional theory (TDDFT) with the added advantage of being able to describe conical intersections between the ground and excited states. However, here, we demonstrate that pp-TDA, especially the pp-TDA-HF variant, suffers from extensive contamination by low-lying Rydberg states that render details of the excitation spectrum ambiguous and the corresponding excited states unphysical. We attempt to identify the deficiencies in pp-TDA by isolating the effects of, first, the Hartree-Fock exchange by varying the Hartree-Fock character in the reference determinant and, second, the double-cation character of the reference determinant by modulating the HOMO occupation in the reference determinant.

Structure of Monomeric and Segmented Huntingtin Protein

Leili Zhang, Hongsuk Kang, Francisco X. Vázquez, Binquan Luan and Ruhong Zhou

Abstract:

Huntington's disease (HD) is a neuronal degenerative disease caused by abnormal length of polyglutamine (polyQ) in huntingtin exon-1 (HTT) proteins. The definitive cause of HD is generally tied up with the aggregation and/or fibril formations from HTT. However, the structural information of the intrinsically disordered HTT in physiological conditions has not been fully uncovered. Several previous studies pointed to different if not controversial secondary structure compositions of HTT in water, as a monomer or upon aggregation. Here, we investigate the structures of the complete HTT exon-1 and segments of HTT exon-1 with temperature REMD and conventional MD simulations. Selective conclusions have been drawn. For example, glutamines (Gln) act like a glue in holding up HTT protein structures, leading to an unusually small scaling factor from polymer physics (0.22). Both beta-sheet contents and alpha-helix contents of HTT increase with the increment of Q-length. The first 17 residues of HTT (HTT-N17) maintains a helical structure on micelles, while adopting mostly random coil structures in the solution with 3 widely used force fields. NMR chemical shift and NOESY calculations confirm that the force fields generally agree well with the experimental measurements. Here, with more and comprehensive information on the HTT structures, we aim to understand the biophysics of HD on a molecular level. We hope the efforts we are making now are able to contribute to the discovery of a cure to the currently incurable HD.

Recent developments in projector configuration interaction method

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Abstract:

Theoretical chemists seek to compute the most accurate wave functions within the same computational time. For configuration interaction (CI) methods, the computational time is proportional to the number of Hamiltonian matrix elements (determinant couplings) computed. To compute more accurate wave functions, selected CI methods try to identify the most important determinants [1] and diagonalize the corresponding Hamiltonian matrix exactly. However, this approach is limited to a CI space containing around 4 million determinants [2], because all couplings between determinants in the CI space are needed. In contrast, the projector configuration interaction (PCI) method aims to compute only the most important couplings [3]. Thus, the PCI method is capable of including more determinants in CI spaces and provide more accurate wave functions with the same computational cost. However, the result accuracy and convergence rate were not optimal in the original version. Recently, we implemented a Hermitian version of the PCI method to compute more accurate energies and wave functions without increasing the computational time. To accelerate convergence, we also overcome the linear convergence limit of the polynomial projection method by implementing the Davidson–Liu eigenvector solver in the PCI method. The PCI with these improvements shows less than half of the non-parallelism error and three times faster convergence than the original version in benchmarking the N2 dissociation potential energy curve.

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Extracting aggregation free energies of mixed clusters from simulations of small systems: application to ionic surfactant micelles

Xiaokun Zhang, Lara Patel, Olivia Beckwith, Robert Schneider, James T. Kindt

Abstract:

The extraction of equilibrium cluster free energies from simulations of cluster formation is one of the key challenges in the computational studies of aggregation and nucleation process. This poster reports our newly established PEACH ("Partition-enabled analysis of cluster histograms") method for extracting equilibrium cluster size distribution and cluster free energy from direct small-N (60 surfactans or fewer) simulations of constant NVT or NpT ensemble. The PEACH method was applied to the simulations of micelle formation of sodium octyl sulfate (SOS) using a coarse-grained forcefield with an implicit water model.

Analysis of the simulations shows that our approach is reliable and yields a good free energy fit across various system sizes and concentrations. Moreover, the predicted cluster distributions for a large-N (560 surfactants) system match well with direct simulations. The method shown in the report reduces a significant amount of computational cost and provides insight into the sampling statistics of cluster formation.

Accurate correction of delocalization error in transition metal catalysis by hybrid functionals and DFT+U

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Abstract:

First-principles electronic structure calculations (e.g. with density functional theory or DFT) provide unique insights into computational materials and catalyst design. However, the approximations made in efficient, semi-local DFT models lead to large energetic and density delocalization errors that prevent predictive accuracy on some of the most compelling materials, e.g., correlated transition metal oxides. We carry out a systematic study to identify commonalities in how diverse approaches for approximate delocalization error correction (i.e., DFT+U and hybrid functionals) perform on representative bulk and slab models of catalytic transition metal oxides. We also compare these observations to our previous work on molecular inorganic complexes[1,2] and extended, complex-like transition metal solids. For these methods, we describe the effect these approaches have on properties relevant for heterogeneous catalysis, including the electron densities, surface formation energies, vacancy formation energies and adsorption energies. The results show periodic-table-dependent, ligand-dependent, and method-dependent behaviors in the solid state that can be rationalized based on chemical bonding but diverge from our previous observations in molecules[1,2]. Our work provides insights into whether addressing delocalization error aids in obtaining accurate energetic properties of transition metal catalysts.

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Many-Pair Expansion: A Density Functional Hierarchy for both Strongly and Weakly Correlated Systems

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Abstract:

Density functional theory (DFT) has been the workhorse for quantum chemical simulations of molecules and materials, but still suffers from several limitations. Common density functionals share self-interaction errors, and are unable to describe strong correlations and dispersion interactions. Here, we present a many-pair expansion (MPE) in DFT that is capable of systematically correcting any deficiencies of an approximate density functional. The electron density of a system is first decomposed into a sum of localized, nodeless two-electron densities, which are used to construct relevant four-, six-, … electron densities. Numerically exact results for these few electron densities can then be employed to improve an approximate density functional via any of several many-body expansions. The resulting hierarchy gives accurate results for several important lattice models- Hubbard model in 1D and 2D[1] and PPP model of conjugated polymers[2]. We also show how this method can be implemented for molecular systems, and demonstrate improvements to reaction energies, barriers and bond breaking for a few small molecules[3]. We conclude MPE thus provides a hierarchy of density functional approximations that is promising for both strongly and weakly correlated systems.

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Modeling vibronic effects in absorption spectra of solvated dyes

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Abstract:

The correct treatment of vibronic effects is vital for the modeling of absorption spectra of solvated dyes, as many prominent spectral features can often be ascribed to vibronic transitions. Vibronic spectra can be straightforwardly computed in the framework of time-dependent density-functional theory (TDDFT) and the Franck-Condon approximation for small dyes in solution by making use of popular implicit solvent models. However, implicit solvent models neglect specific solute-solvent interactions and provide only an approximate treatment of solvent polarisation effects on the electronic excited state. Furthermore, temperature-dependent broadening effects are lost in the implicit solvent approach, meaning that vibronic spectra computed in this way have to be broadened by a homogeneous broadening parameter chosen to match experimental results. We address these shortcomings by combining the vibronic fine structure of an excitation obtained in the Franck-Condon picture with vertical excitations computed for a large number of uncorrelated molecular dynamics (MD) snapshots, where significant parts of the solvent environment are treated fully quantum mechanically. The approach relies on the computation of only a small number of vibronic spectra, while solvent effects on the electronic excitations of the system are fully accounted for at the TDDFT level and temperature-dependent broadenings are treated through the MD sampling. We test the proposed method on nile red and the green fluorescent protein chromophore in polar and non-polar solvents and obtain an excellent agreement with experiment, both regarding the width and the shape of the computed spectra. We also consider a second approach to the prediction of absorption spectra of solvated systems, where the computation of vibronic spectra can be avoided entirely by instead obtaining the autocorrelation function of fluctuations in the TDDFT excitation energy directly from an MD trajectory. We compare and contrast the two approaches with regards to the reliable computation of absorption spectra for small dyes in solution.