Theoretical Study of the BrO + ClO Cross Reaction

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Abstract: Pathways stemming from the reaction of BrO and ClO radicals are of great interest due to their integral role in stratospheric ozone depletion. An abundance of free halogen radicals, which readily convert ozone to diatomic oxygen, are produced through three pathways:

$$\begin{aligned} \mathrm{BrO} + \mathrm{ClO} &\longrightarrow \mathrm{BrCl} + \mathrm{O_2} \\ &\longrightarrow \mathrm{ClOO} + \mathrm{Br} \\ &\longrightarrow \mathrm{OClO} + \mathrm{Br} \end{aligned}$$

Detailed mechanisms of the above reactions have hitherto been insufficiently characterized in the literature. In this work, optimized geometries and harmonic vibrational frequencies for key stationary points on the potential energy surface have been obtained with high level coupled cluster theory. In the future, these findings will be used to reduce the current uncertainty in regard to the rate constants and branching ratios through theoretical kinetic treatments.

Conformational Analysis of 1,2-disubstituted-2,3-epoxy Cyclopentanol Diastereomers

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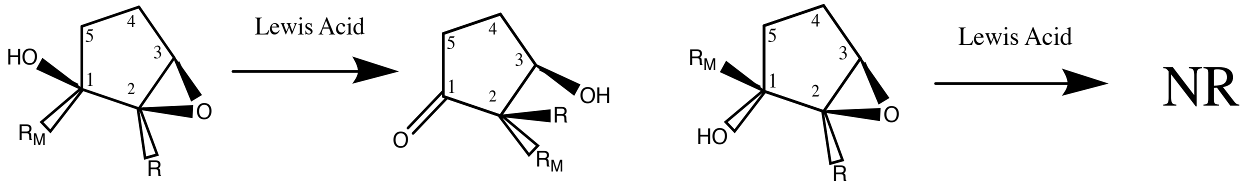
This study examines the intramolecular hydrogen bonding that influences the semipinacol rearrangement of 1,2-disubstitued-2,3-epoxy cyclopentanol to form 2,2-disubstituted-1,3-ketol, which requires the epoxy group to be *cis* to the neighboring alcohol group as shown in Figure 1. A conformational analysis of 17 different 1,2-disubstituted-2,3-epoxy cyclopentanol compounds was performed. Full geometry optimizations were carried out for each diastereomer with the M06-2X method and the cc-pVTZ correlation consistent triple-ζ basis set. Additionally, rotomers of the *cis* conformers that do and do not form a hydrogen bond between the alcohol and epoxy groups were examined. Harmonic vibrational frequency computations on all 51 optimized structures (17 *trans*, 17 *cis* with H-bond, 17 *cis* without H-bond) indicate that each one is a minimum with no imaginary frequencies. Analysis of simple dimethyl fluoro, chloro, and methoxy analogues of these epoxy cyclopentanols reveals that (*i*) the M06-2X/cc-pVTZ energetics are within 0.1 kcal mol^{-1} of CCSD(T)/cc-pVTZ values, (*ii*) the *trans* configurations intrinsically have lower electronic energies than their *cis* counterparts and (*iii*) the intramolecular hydrogen bond typically inverts this order, giving the *cis* conformations lower energies than the corresponding *trans* structures. These trends regarding *cis*/*trans* relative energies did not change when reevaluated with continuum solvation models (PCM and SMD) of dichloromethane.



cis-1,2-disubstituted-2,3-epoxy cyclopentanol

trans-1,2-disubstituted-2,3-epoxy cyclopentanol

Figure 1. Reaction scheme for the semipinacol rearrangement of *cis*-1,2-disubstituted-2,3-epoxy cyclopentanol to form 2,2-disubstituted-1,3-ketol.

A simple rule to predict bound multiexciton states in covalently-linked singlet fission dimers

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Abstract: Since singlet fission is one of the processes that can increase solar cell efficiencies, researchers from various fields have been studying the mechanism of this process. Recent studies of this 2 step process shows the importance of the rate of the second step on the overall rate in singlet fission dimers. This in turn depends on the stability of the microstates of a crucial multi exciton intermediate, the $^1(TT)$ state. In covalently bonded dimers, the through bond coupling also becomes important which was absent in singlet fission active crystals. Here, we provide a simple rule to predict the feasibility of a faster rate for the 2nd step based on the connectivity of the chromophores to the bridging chemical unit. We predict the stability of the $^1(TT)$ microstates using a simple spin lattice argument where the chromophore units are considered like diradicals. In order to test our hypothesis, we have performed ab initio calculations on a systematic series of covalently linked singlet fission dimers. Numerical examples are given, and the limitations of the proposed theory are explored.

Geometric Effects on the Stacking of Nucleobases Analogues

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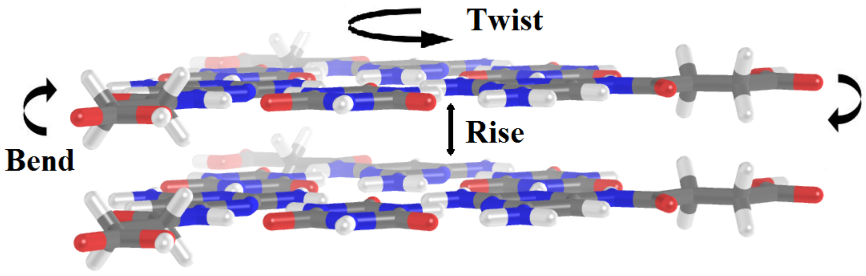
Abstract: A fundamental problem in the origin of life research is that canonical, monomeric nucleic acid bases do not pair in water. Therefore, the question arises as to why they were selected for the pairing mechanism in information transfer. Since prebiotic reaction models produce a multitude of highly similar molecules, one hypothesis proposes that the canonical bases were preceded by other proto-nucleobases that could self-assemble spontaneously [1]. In support of this hypothesis, a system of cyanuric acid and triaminopyrimidine (TAP) modified with an exocyclic organic tail was shown to form long, noncovalent hexad assemblies in water [2]. The stacking of this system is studied here using Symmetry Adapted Perturbation Theory with the jun-cc-pVDZ basis set for hexad geometries optimized at the B97-D3/aug-cc-pVDZ level of theory. Analysis of the effects of the twisting and bending angles as well as the rise distance for various hexad plate systems shows that the system adopts a rigid, helical structure. The effect of the organic tail in TAP on the energy profiles is also reported.



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Oxygen unveils the versatile personality of beryllium: The case of $BeO_{n=1,2,4}$

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Abstract:

The chemical bonding of BeO, cyclic BeO_2, and BeO_4 is explored by constructing potential energy profiles. We employ multi-reference approaches to obtain the energy as a function of the Be-O, Be-O_2, and O_2Be-O_2 distances for ground and excited electronic states. Our calculations reveal for the first time that BeO is triple-bonded formed by a dative bond from Be(^1S;$2s^2$) to O(^1D) and two dative π-bonds to the opposite direction. The ground state of cyclic BeO_2 is shown to be ionic followed by excited states of covalent character. The lowest energy BeO_4 structure comes from an excited state of BeO_2 suggesting an *in-situ* Be($2p^2$) species. These three molecules disclose the various binding modes with which Be forms coordination complexes.

An Analysis of Non-Covalent Interactions in the Addition of Organoboron Reagents to Fluoroketones Using Symmetry-Adapted Perturbation Theory

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Abstract:

Enhancing the enantioselectivity of organocatalytic reactions would greatly improve the efficiency of pharmaceutical processes, for example, the synthesis of anti-parasitic and anti-inflammatory medications. Recently, it has been observed that fluorinated ketones exhibit enantioselective additions to organoboron reagents, and it has been hypothesized that this is due to the additional fluorine-induced electrostatic interactions that stabilize transition states for the desired enantiomers [1]. This work seeks to assess the validity of this claim through the use of the functional-group and atomic partitions of symmetry-adapted perturbation theory (F-SAPT and A-SAPT, respectively). These methods are employed to quantify possible enantiodetermining interactions, both stabilizing and destabilizing, in the possible transition states for the addition of allyl units to fluorinated ketones.

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A Quantum Astrochemical Perspective on the *c*-C_3H Radical with Application to the Interstellar Medium

The interstellar medium (ISM) has been an area of focus for astrochemists and quantum chemists for many years, with particular interest in the presence of interstellar molecules and the resulting chemical processes. The c-C3H radical has been detected in the ISM near the dark molecular cloud TMC-1. With the application of ab initio computational methods using coupled-cluster theory at the singles, doubles, and perturbative triples [CCSD(T)] level, highly accurate quartic force fields (QFFs) are constructed to define the electronic wavefunction for the inter nuclear Hamiltonian. The QFF is used to predict the equilibrium geometry and produce vibrational frequencies, rotational constants, and other spectroscopic data. Moreover, the data produced can be used for corroboration of experiment or previous theory as well as potential detection in the ISM.

Core Excitations in Halogen Molecules and Halogenated Methane using Core-Valence Separated Equation of Motion Coupled Cluster.

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Abstract: Ultrafast X-Ray spectroscopy has become an affordable tool to study core-level electronic transitions in molecules[1,2], and thereby yield valuable information about the charge, oxidation state, hybridization of specific elements, and so on; transient absorption experiments can also provide a tool to study the dymanics of vibrational wavepackets and even the nuclear motion of electrons in molecules[3]. In an effort to develop theoretical methods capable of interpreting such experimental results, we showcase the ability of coupled cluster methods to accurately compute the core-excitations associated with the K-edge of several molecules containing halogens. EOMCC, with a CVS[4] approach, is used to compute the K-edge absorption spectra of various halogenated methane and compared to recent experimental results. Excellent agreement is obtained. Alternatively, the same method is used to compute potential curves for the core-ionized and core-excited states of halogen molecules and related to transient absorption experiments[5].

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Effect of Electrode Surface Structure on Electron Transport in Molecular Junctions

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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 [1]. 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.

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Interaction-Induced Dipole Moments of Carbon Dioxide in Gas-Phase Environments

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Abstract: Modeling the atmospheres of planets can give information about the surface temperatures and paleoclimates of these planets, which can give insights into how the planets and their atmospheres developed. Accurate models of CO_2-rich planetary atmospheres, such as the Martian atmosphere, require us to account for collision-induced absorptions. These absorptions appear in the 0-250 cm^{-1} region of the infrared spectra, and are caused by interaction-induced (I-I) dipole moments in pairs of CO_2 molecules. Studying these I-I dipole moments can aid in creating more accurate atmospheric models. To investigate these I-I dipole moments, we first must calculate the electrical properties, such as the polarizability and hyperpolarizability, of a single CO_2 molecule. The GAMESS ab initio software package was used with a finite-field approach to calculate the energy of CO_2. These results were then used along with an equation formulated by A. D. Buckingham [1] to estimate the polarizabilities and the hyperpolarizabilities of CO_2. Currently, we are exploring the bond-length dependence of the polarizability in order to improve our understanding of I-I dipole moments in CO_2 dimers. An accurate understanding of the bond-length dependence of the CO_2 polarizability will also allow us to provide a framework for understanding the molecule's Raman spectrum.

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Understanding Stereoselectivity of a BINOL-Catalyzed Conjugate Addition

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Abstract: Stereocenters adjacent to heterocycles are prevalent in natural products and pharmaceuticals. However, their synthesis is challenging due to the sensitivity of heterocycles to reaction conditions. A BINOL-catalyzed enantioselective conjugate addition of vinyl boronic acids to heterocycle-appended enones was developed by May and co-workers to increase the scope of synthetically accessible α-chiral heterocycles. [1] The selectivity and rate of the reaction are both strongly dependent on the 3,3' substituent of the BINOL. We have investigated the selectivity of these catalysts using dispersion-corrected DFT methods. Contrary to the common assumption that only the energy difference in barrier heights between (*R*) and (*S*) pathways must be considered, we found that the enantioselectivity is primarily based on the ability of the catalyzed reaction to out-compete the racemic background reaction. This background reaction was itself shown to be accelerated by the additive $Mg(Ot\text{-}Bu)_2$, which was added to promote protonolyzation of the product enolate, further emphasizing the importance of considering the complete reaction picture. Based on our computational results we have found that the rate and selectivity can be correlated with simple descriptors of the transition state, and have designed a new catalyst that is predicted to be both highly active and selective.

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First-Principles Modeling and Interpretation of Ionization-Triggered Charge Migration in Molecules

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Abstract:

Modeling attosecond coherent charge migration in molecules is important for understanding initial steps of photochemistry and light harvesting processes. Ionization triggered hole migration can be difficult to characterize and interpret as the dynamics can be convoluted with excited states. Here, we introduce a real-time time-dependent density functional theory (RT-TDDFT) approach for modeling such dynamics from first principles. Here, orbital occupations and electron localization functions are used to provide insight into how a core-hole can yield valence motion using TDDFT, provided a well-defined initial condition. Calculated results for nitrosobenzene have been compared to those obtained by ADC(4) methods for consistency [1].

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Enhancements of the Psi4 Electronic Structure Package for Research, Education, and Development

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Abstract: Psi4 is an open-source and freely available electronic structure package written in C++ for speed and Python for ease of interaction. It includes most common methods including density functional theory, many-body-perturbation theory, coupled-cluster theory, complete active space SCF, and configuration interaction. Enhancements to the top-level driver enable automatic basis-set extrapolations for optimizations, easily-specified composite methods, and n-body counterpoise-correction wrappers. Through transparent interfacing with external libraries, Psi4 gains capabilities in dispersion correction, PCM solvation, density-matrix renormalization group, effective fragment potentials (EFP), and relativistic corrections. After extensive infrastructure changes made over the past year, Psi4 is easier to obtain, extend, and interface. While retaining the ability to run as an executable with the simple text Psithon syntax, Psi4 gains a new mechanism of importing as a module into python `python -c "import psi4"` and thus ease of calling quantum chemistry operations from a Python script or Jupyter notebook. How to interact with Psi4 for research, education, and development will be discussed.

Automatic active space selection for the excitation energy calculations with driven similarity renormalization group method

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Abstract: The multi-reference driven similarity renormalization group truncated to second order (DSRG-MPRT2) [1] is extended to evaluate electronic excitation energies with model spaces based on a valence CIS or CISD wave function [2]. The results show that CIS/CISD-DSRG-MRPT2 methods are economical and predict excitation energies for closed-shell species with an accuracy comparable to that of other well-established methods. However, selection of the active space to be used with these methods is arbitrary and tedious. To improve this aspect, we implemented two automated methods to construct active spaces. Both approaches use a general projection operator onto a set of targeted valence atomic orbitals. Important orbitals are identified by computing the overlap matrix of the MOs projected onto the target space. In the first approach—based on the valence active space (AVAS) method [3]—we separately rotate occupied and virtual MOs to maximize the overlap with the projection operator. A simpler method is also considered, in which canonical occupied and virtual orbitals are sorted according to the diagonal elements of the overlap matrix projected onto the target space. These two methods arrange the order of orbitals in a convenient way suitable for active space computations. To test these two schemes, we calculated CIS/CISD-DSRG-MRPT2 excitation energies of small conjugated hydrocarbons molecules.

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Calibrating Dipole Moments of Potential Organic Contaminants

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Abstract: In January 2014, approximately 10,000 gallons of a coal-washing mixture was spilled into West Virginia's Elk River. The major component of the spill was crude 4-methylcyclohexane-methanol (4-MCHM). However, there were several other phenyl ethers and cyclohexane derivatives present in the spill as well. The Safety Data Sheets for these compounds were found to be largely incomplete, which is not uncommon for industrial grade chemicals. Without partitioning data, proper containment and clean-up of the spill was made much more difficult. In situations where properties are not available for compounds, responders have access to property estimation software to fill in the gaps as needed. One such program is Estimation Programs Interface (EPI) Suite, which is provided by the U.S. Environmental Protection Agency. EPI Suite uses simplified molecular input line entry specification (SMILES) to obtain toxicology data from the two-dimensional structure of a compound. A major flaw in EPI Suite and similar programs is that it is not possible to distinguish between the various isomers of a compound, and different isomers can have different properties. It is the goal of our lab to calibrate computed permanent dipole moments of potential contaminants similar to those found in the Elk River chemical spill. The training set is comprised of 62 phenyl ether and cyclohexane derivative compounds with well-established experimental dipole moments. The methods we are using are B3LYP, B3LYP with empirical dispersion corrections (GD3BJ) and second order Møller-Plesset Perturbation theory (MP2) with the 6-31G(d') and aug-cc-pVDZ basis sets. Molecular dipole moments can be indirectly or directly compared to structure-activity relationships used in toxicology and environmental fate modelling.

Massively-parallel simulation of reduced-scaling ground and excited state coupled-cluster methods

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Abstract: To greatly increase the reach of conventional many-body techniques like coupled-cluster (CC) we must employ numerical approximations that reduce the prohibitive high-order computational complexity as well as deploy our reduced-scaling CC algorithms on the largest machines available. With these complementary ideas in mind we implemented a simulation framework for reduced-scaling CC methods based on the massively-parallel implementation of ground- and excited-state CC methods in the re-engineered Massively Parallel Quantum Chemistry (MPQC) package [1]. Although the current implementation retains the high complexity of the conventional CC methods, this allows rapid exploration of reduced-scaling ansatz and provides a production-quality solver component for reduced-scaling massively parallel coupled-cluster currently under development.

Both the ground and excited state approaches can utilize arbitrary compressions of the cluster amplitudes, including those based on pair-natural orbitals (PNOs) [2,3]. The idea behind PNOs is quite simple: for each pair of electrons in a system, only a few orbital products contribute substantially to the pair-correlation wave function and pair energy, with the number of PNOs per pair essentially independent of the system size. Furthermore, the PNOs determined using an approximate first-order guess provide a useful subspace for solving the coupled-cluster equations. Using the PNOs as the template, we devise similar compressions to the right- and left-hand vectors in EOM-CCSD. The robust convergence of the simulated reduced-scaling CCSD(T) and EOM-CCSD energies will be demonstrated with respect to the single rank-truncation parameter for systems of unprecedented size.

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

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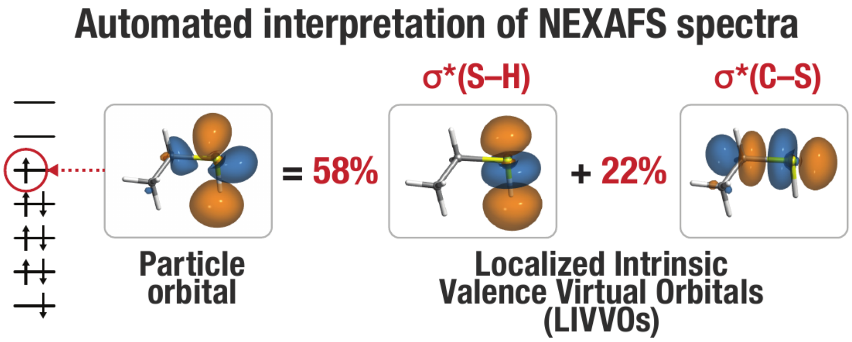
Abstract: Accurate assignments of the unoccupied molecular orbitals involved in electronic excited states are crucial to the interpretation of experimental spectra. Here we present an automated approach to the assignment of excited states by introducing a unique orbital basis known as localized intrinsic 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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Beyond the double harmonic approximation; Improving absorption intensities for HNO

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Abstract: This work aims to calculate accurate absorption intensities for HNO using modern correlation-consistent basis sets and going beyond the limitations imposed by the commonly-used double harmonic approximation. These accurate absorption intensities will be used to interpret experiments carried out at the University of Wyoming, in which HNO is produced photochemically in a solid hydrogen matrix doped with NO molecules [1]. The absorption intensities of HNO were most recently studied over two decades ago [2] in an investigation which implemented a double harmonic treatment based on molecular orbital calculations which employed, by today's standards, very small basis sets. Our previous work has already established that the assumptions included in the double harmonic approximation fail to provide accurate energies and dipole moments for HNO. This is in part due to the unusually long and weak HN bond in HNO, which leads to substantial anharmonic behavior. Our improved energies and dipole moments were calculated by going beyond the double harmonic approximation and using expanded polynomials as functions of uncoupled normal modes, as well as using larger basis sets. Our current work is seeking to include the coupling of normal modes in order to further improve energies and dipole moments, allowing us to compute more accurate absorption intensities.

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Electron Propagator: Application to superhalogens

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Abstract: Superhalogens are clusters with high Electron Affinities (>3.6 eV) and they can exist without the presence of halogen atoms. These properties make superhalogens useful as electrolytes, reactants or doping materials. Electron Propagator Theory (EPT) is an effective tool to predict vertical electron detachment energies of anions(VEDEs)[1]. Previously, Li *et al*[2] compared EPT and ΔCCSD(T) results, obtaining discrepancies larger than 1 eV. Unfortunately, their UHF reference states for CCSD(T) calculations ignored the possibility of Koopmans defects and resulted in invalid comparisons. In this work[3], CCSD(T) and EPT are compared using their corresponding final-state spin densities and Dyson Orbitals. Valid comparisons yield discrepancies of 0.1 eV or less and demonstrate the reliability of the EPT methods for calculating VEDEs of larger systems.

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DFT study of the effect of substituents on the optical spectra and ^{195}Pt NMR shift of Pt complexes

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Abstract:

Density functional theory (DFT) computations have been used to investigate optical and electronic properties of Pt complexes. Computed absorption and emission spectra were compared with experimentally obtained results. Frontier orbitals were studied to understand the contributions of various electronic states involved in the radiative transitions. ^{195}Pt NMR shifts were also computed and compared with experimental results. A comparison between computed and experimental results has been shown. The same model was used to calculate UV-VIS spectra and ^{195}Pt NMR shifts of hypothetical substituted Pt complexes. The results of these calculations show the effects of substitution on the absorption and emission spectra, and the 195Pt NMR shifts of Pt complexes.

Ligand donicity trends in ^{195}Pt NMR chemical shifts with non-relativistic density functional approaches

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It has been shown that non-relativistic density functional approximations can predict ^{195}Pt NMR chemical shifts in a wide range of complexes.[1-2] These chemical shifts, δPt, are a useful measure of electron density about the metal center and can be used to quantify the electron donating ability of coordinated ligands. Trends in the donicity of electron density are analyzed for sets of ligands in various conformations (e.g cis vs. trans) in Pt-containing complexes. Both PBE1PBE and B3LYP density functionals are implemented for both geometry characterizations and NMR computations. The sensitivity of δPt with respect to ligand conformation is also analyzed.

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The structures, energetics and vibrational signatures of small hydrogen bonded dimers involving H_2S

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Abstract: This study focuses on the geometrical, energetic, and vibrational characteristics of two simple dimers in which H_2S either donates or accepts a hydrogen bond: $(H_2S)_2$ and H_2O/H_2S. Full geometry optimizations and harmonic vibrational frequency computations of all clusters and their respective monomers are performed using MP2 and CCSD(T) along with a correlation consistent family of basis sets augmented with diffuse functions on heavy (non-hydrogen) atoms and an additional set of tight-d functions on sulfur (denoted ha$(X + d)$Z, where X=D,T,Q,5). MP2 geometries and harmonic vibrational frequencies were also computed employing the Boys-Bernardi counterpoise procedure (CP). With the ha(5+d)Z basis set, the CP procedure changes the frequencies by less than 5 cm^{-1} and the electronic binding energy by less than 0.05 kcal mol^{-1}. The MP2/ha(5+d)Z electronic binding energy of the $(H_2S)_2$ dimer is -1.89 kcal mol^{-1}. For the mixed H_2S/H_2O dimer, the corresponding MP2 binding energy is -2.81 kcal mol^{-1} when H_2S donates the hydrogen bond and -3.02 kcal mol^{-1} when H_2S accepts the hydrogen bond. CCSD(T) computations with the ha(Q+d)Z basis set indicate that MP2 consistently overbinds in all three cases by approximately 0.2 kcal mol^{-1}. As with other hydrogen bonded complexes, the vibrational frequency associated with the stretching motion of the hydrogen bond donor occurs at lower energy than the corresponding stretching frequency of an isolated fragment. For the $(H_2S)_2$ and H_2S/H_2O dimers, these vibrational frequency shifts have been evaluated within the harmonic approximation as well as with second-order vibrational perturbation theory at the MP2/ha$(X + d)$Z and CCSD(T)/ha$(X + d)$Z levels of theory, where X=D,T,Q.

Towards Multireference Symmetry-Adapted Perturbation Theory

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Abstract: The most widespread method of calculating weak intermolecular interaction energies is the supermolecular approach where one picks up a suitable electronic structure theory based on one of the HF, DFT, MP2, CCSD(T) etc. methods to calculate the energies of the two monomers and the dimer individually [1]. Subtraction of the sum of the two monomer energies from the dimer energy gives the interaction energy. An alternative way to calculate this energy is to treat the interaction as a perturbation on the system of two non-interacting monomers. Symmetry-adapted perturbation theory (SAPT) [1], [2] is such a perturbational approach capable of analyzing the physically interpretable components of interaction such as electrostatics, exchange, induction, and dispersion [3].

Previous works on SAPT were based on an assumption that both interacting monomers can be represented by single-determinant wavefunctions. Whenever this assumption fails, a multireference framework such as the complete active space self-consistent field (CASSCF) approach is necessary to represent the unperturbed monomers. Use of a multireference zeroth-order wavefunction enhances the complexity of the SAPT derivation and implementation substantially. In particular, a different approach is necessary to obtain the first-order perturbed wavefunction required for the induction and dispersion SAPT corrections. In our SAPT(CASSCF) formalism, the induction and dispersion amplitudes are obtained using CASSCF linear response theory [4]. We adopt the density-matrix formalism [5] to derive the exchange corrections within multireference SAPT. In the second order, the resulting expressions involve one, two, and three electron all-active density matrices [6]. In this poster, we provide some initial results for the SAPT(CASSCF) electrostatic, first-order exchange, induction, and dispersion energies for model systems. We also outline the derivation of the (very long) formulas for the second-order exchange induction and exchange dispersion energies. .

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Structural Stability in L12 Co-Al-W

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Abstract: The effects of higher-order alloying on the $L1_2$ (γ') Co-Al-W ternary phase were evaluated via density functional theory. In particular, 3.125 at% Mo, Ti, Ta, Hf, Fe, and V were investigated as possible stabilizers in place of W. From density of states analysis, Ti, Ta, and Hf are seen to stabilize γ' by shifting the energy of the pseudogap towards the Fermi level. Fe appears to fully destabilize the γ' phase, while Mo and V show mixed behavior. In conjunction with charge density analysis, it is clear that alloys which increase the structural stability of the base ternary do so via populating the Co-Al bond instead of the adjacent Co-W bond. Therefore, alloying should proceed with elements which may reinforce the weak Co-Al bond relative to the Co-W bond, which should help increase the resistance of γ' to phase decomposition or mechanical failure. In addition, alloys which correspond to decreased structural stability from a density of states perspective evidently do so via redistribution of charge density to Co-W bonds, resulting in less directionality for the nearest neighbor Co electron cloud.

Quantifying the Halogen Bond in Iodo- and Iodoethynyl Benzene Derivatives and Pyridyl-Capped π-Conjugated Molecular Building Blocks

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Abstract: Halogen bonding has recently garnered a great deal of interest due to its ability to aid in the production of highly-ordered structural co-crystals with enhanced optoelectronic properties. Here, we invesitgate the interaction between a series of iodobenezene (BI) and iodoethnyl benzene (BAI) halogen bond donors with varying substituents (F_2, $(CF_3)_2$, $(NO_2)_2$, and F_5) and furan/thiophene-based acceptors equipped with pyridyl groups (PyrTF and $PyrT_2$). Full geometry optimizations and harmonic vibrational frequency computations are performed on each halogen bonded complex with the M06-2X density functional and a double-ζ correlation consistent basis set augmented with diffuse functions on all atoms and a pseudopotential on iodine (aug-cc-pVDZ for H, C, N, O, S and aug-cc-pVDZ-PP for I; denoted aVDZ). Electronic binding energies indicate that the interaction strength of both the BI and BAI series with either PyrTF or $PyrT_2$ acceptor increase with the electron withdrawing ability of the donor substituents (F_2 <$(CF_3)_2$ <$(NO_2)_2$ <F_5) over a range from -5.65 to -7.99 kcal mol^{-1}. In contrast to numerous trends reported in other studies, the results presented here clearly demonstrate there is no direct correlation between the magnitudes of the binding energies and the corresponding shifts in C-I stretching frequencies that accompany halogen bond formation. To gain insight into this descrepancy, the magnitude of charge transfer for each complex is measured using an NBO and grid-based Bader charge analysis on the M06-2X/aVDZ geometries.

Radicals Derived from Acetaldehyde and Vinyl Alcohol

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Abstract: The products of incomplete butanol combustion include the tautomers vinyl alcohol and acetaldehyde. Along with radicals related to these compounds by removal of hydrogen or hydroxy radicals, vinyl alcohol and acetaldehyde are studied here using *ab initio* methods. The computational methods employed include coupled cluster theory with singles, doubles, triples, and perturbative quadruple excitations [CCSDT(Q)], along with basis sets as large as cc-pV5Z. Relative energies are further refined by including corrections for relativistic effects, the frozen core approximation, the Born-Oppenheimer approximation, anharmonicities, and zero-point vibrational energies. We report for the first time anharmonic frequencies computed for the 1-hydroxyvinyl and 2-hydroxvinyl radicals. In line with observation, we predict the *syn* conformer of vinyl alcohol to be lower in energy than the *anti* conformer by 1.0 kcal mol^{-1}. The alcoholic hydrogen of *syn*-vinyl alcohol is found to be the easiest to remove of those studied, requiring a net input of 83.9 kcal mol^{-1}.

AARON: An Automated Reaction Optimizer for New-catalysts

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Abstract: The traditional experimental screening of potential new asymmetric catalysts can miss potentially powerful catalyst designs and can also fail to identify potentially important catalyst-substrate interactions. Computational quantum chemistry provides a strategy to screen potential catalysts for a given asymmetric reaction by predicting relative free energies of the stereocontrolling transition states. However, this process requires the optimization of sometimes 100s of transition state structures for each catalyst or substrate, which could be a daunting task to complete by hand. Our computational toolkit (AARON) allows us to automatically explore new catalyst designs. The original version of AARON (Automated Alkylation Reaction Optimizer for N-oxides) has been used successfully to design new bipyridine *N*,*N*′-dioxide catalysts for asymmetric propargylations.[1-2] AARON has recently been developed into a more complete, general, and powerful version (AARON 0.92: An Automated Reaction Optimizer for New-catalysts). The capabilities of this new version of AARON will be introduced, along with examples of applications of AARON to the asymmetric dearomatization of β-naphthols and an Rh-catalyzed asymmetric hydrogenation.[3]

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Can Coupled Cluster Theory Describe Polyradical Character?

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Abstract: Polycyclic aromatic hydrocarbon (PAH) systems have been the focus of many investigations in recent years. These materials are nano scale analogs to graphene, which has been shown to posses many properties that make it useful for applications in organic electronic devices. While many PAHs have closed-shell ground states, many examples exist of PAH which have open-shell and radical character in the ground state. In this work two classes of PAHs have been investigated to characterize polyradical features of their ground state electronic structure. The triangular non-Kekulé structures phenalenyl, triangulene, and a π-extended triangulene system with high spin ground states, and zethrene, p-quinodimethane-linked bisphenalenyl, and the Clar goblet, which have singlet-polyradical character in the ground state. Unrestricted Hartree-Fock (UHF), Coupled Cluster with singles and doubles (CCSD), and equation-of-motion CCSD (EOM-CCSD) computations have been carried out on these systems. The natural orbital occupation numbers (NOONs) have been computed to quantify the open shell character of their electronic structure in the ground, and lowest excited states. Given the expense associated with high-level CCSD calculations, the agreement between NOONs and singlet-triplet splitting with different orbital freezing schemes has been investigated. A comparison has been made to results of previous studies [1] where multi-reference methods have been used in order to probe the limitations of single-reference coupled cluster methods for chemical systems of this type.

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Ionization Potential Improved Density Functional Theory for Inner-shell Excitation Energies of the First-Row Transition Metals

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Abstract: The ionization potential improved density functional theory in the QTP family, which enforces the Kohn-Sham eigenvalues of the occupied orbitals equal to the exact ionization potentials, could accurately reproduce many physical and chemical properties and reduce the self-interaction error [1,2]. One property that is challenging in theoretical chemistry is to calculate the inner-shell excitation energies using the time-dependent density functional theory, especially the transition metal systems. And one of the functionals in the QTP family could compute the inner-shell excitation energies of the main group elements with very high accuracy [3]. However, the errors of the calculated results are still somewhat significant when it is applied to the transition metals systems, especially for the excitations from the 1s orbitals. This presentation will introduce a new functional in this family that could improve the accuracy of the inner-shell excitation energies of the first-row transition metal systems. It is designed as a range-separated hybrid functional with optimized parameters. By using the new method, the errors of the inner-shell excitation energies (include the excitations from the 1s orbitals) of the first-row transition metals are considerably reduced compared with the traditional density functional methods. And the corresponding X-ray absorption spectra can be simulated almost directly without shifting.

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Preliminary Evaluation of A New Density Functional for Correlation of All Strengths

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Abstract: The computation of the nondynamic/strong correlation has been a major challenge in density functional theory (DFT) in many application areas. Our group recently proposed the KP16/B13 (Kong-Proynov'16/Becke'13)[1] functional, which has been shown to handle the nondynamic/strong correlation energy. The functional contains only three parameters and was optimized for the fractional spin error and thermodynamic data of a small set of atoms and molecules. In this work, we evaluate the performance of KP16/B13 for a variety of properties including bond energy, ionization potential, electron affinity, atomization energy, reaction barrier, singlet-triplet splitting and isomerization energy of various chemical systems as well as compare KP16/B13 with other existing functionals. Benchmark data is taken from the University of Minnesota 2015 database[2]. Preliminary results show that our model performs well for hydrogen transfer reactions and is competitive when applied to other properties. The KP16/B13 model can be improved through further parameter optimizations.

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Hydrogen Bonding in the Mixed HF/HCl Dimer: Is It Better to Give or Receive?

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Abstract: The ClH$\cdots$FH and FH$\cdots$ClH configurations of the mixed HF/HCl dimer have been optimized using MP2 and CCSD(T) with a series of correlation consistent basis sets augmented with diffuse functions on non-hydrogen atoms, and an extra set of tight d functions on Cl (cc-pVXZ for H, aug-cc-pVXZ for F, and aug-cc-pV(X+d)Z for Cl, where X = D, T, and Q; denoted ha(X+d)Z). Harmonic vibrational frequencies confirmed that both configurations correspond to minima (i.e., $n_i = 0$) on the MP2 and CCSD(T) potential energy surfaces. Additionally, anharmonic vibrational frequencies were computed using both methods with second-order vibrational perturbation theory (VPT2). At the CCSD(T)/ha(Q+d)Z level of theory, the harmonic donor frequency shifts upon complexation (commonly refered to as red shifts) were -40 and -110 cm^{-1} for the ClH$\cdots$FH and FH$\cdots$ClH configurations, respectively, compared to the corresponding anharmonic values of -68 and -132 cm^{-1}. The relative CCSD(T)/ha(Q+d)Z electronic energies showed the FH$\cdots$ClH structure had the lower energy by 0.19 kcal mol^{-1}. However, the inclusion of either the harmonic or anharmonic zero-point vibrational energy effectively made both configurations isoenergetic, with the ClH$\cdots$FH configuration being lower in energy by only 0.03 kcal mol^{-1}.

The role of the first excited state of atomic oxygen (^1D) in the formation of "hypervalent" iodine-oxygen compounds and the oxidation mechanism of alkenes by such species

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This work aims at the comprehension of the oxidation mechanism of alkenes by "hypervalent" iodine reagents, such as iodosobenzene. This is a commonly used reaction to produce epoxy products. The reaction is modeled by simple molecules to avoid complexities arising from the size of the system. To this end we examine the reaction of HIO, which represents the oxidation reagents, with ethylene, which represents the alkenes. At first we performed multi-reference calculations to study of the $HI + O \rightarrow HIO$ and $H_2C{=}CH_2 + O \rightarrow H_2C(O)CH_2$ reactions. Contrary to the long standing belief of the double bond between iodine and oxygen, our analysis shows that iodine donates a pair of electrons to the first excited state of oxygen (^1D). Similarly, ethylene oxide is formed by a similar interaction: the π-bond of ethylene donates an electron pair to $O(^1D)$ and at the same time $O(^1D)$ back-donates an electron pair to the anti-bonding π-orbital. This mechanism results to a dual bond between ethylene and oxygen. Finally, our coupled cluster calculations for $HIO + H_2C{=}CH_2$ reaction confirmed the transfer of an $O(^1D)$ from HIO to $H_2C{=}CH_2$.

Deducing the Optimal Damping Function for the D3 Dispersion Correction to Density Functional Theory

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Abstract: The D3 atom-pairwise dispersion correction by Grimme [1] is a straightforward and effective way to include dispersion in a density functional calculation of interaction energy. While the atom-atom asymptotic constants of the D3 approach provide a very good description of long-range intermolecular interactions, their accompanying short-range damping expression leaves quite a bit of room for improvement. A recent study showed that refitting of original D3 damping parameters can greatly improve the accuracy of the DFT-D3 methods, however, the performance degradation at short range cannot fully be ameliorated by refitting alone [2]. The D3 damping function serves two purposes: including charge-overlap effects beyond the multipole approximation and preventing double counting of correlation at short range. The damping functions currently employed in the popular DFT+D approaches are not flexible enough to reproduce both charge-overlap and switch-off effects and are the limiting factor for the accuracy of DFT-D3. With the aim of enhancing performance at short intermolecular distances, we search for a new form of damping function, assumed to be a fairly arbitrary increasing function with limits of 0 at short range and 1 at long range. We model damping factors as linear combinations of shifted and scaled error functions. The damping parameters are optimized on the 'third generation' composite database consisting of a training set with 1526 data points and a validation set with 6773 data points [2].

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Frozen virtual natural orbitals for coupled cluster properties

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Abstract: The frozen virtual natural orbitals (FVNO) approach, a very useful reduced-scaling technique for calculating ground-state correlation energies, has been extended to calculate higher-order properties at the CCSD and EOM-CCSD levels of theory. Compared to the correlation energies, properties like polarizabilities and optical rotation were found to be much more sensitive to the truncation of the virtual space in the natural orbital basis, with the errors increasing linearly with respect to the number of frozen virtual natural orbitals. The performance of the FVNO approach for such properties, however, can be improved by employing a correction using relatively less accurate methods like CC2. Quite surprisingly, the canonical scheme, where truncation is based on orbital energies, produced relatively lower errors for most of the properties due to inherent cancellation of errors, and a new criterion was devised to help find the size of the optimal domain for truncation of virtual molecular orbitals in the canonical basis. Interestingly, the observations noted above are reversed in the case of finite difference calculations of static properties, illustrating the significance of orbital relaxation which is absent in the coupled cluster based linear response theories.[1]

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Molecular Structures and Energetics of Small Palladium Clusters

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Abstract

There is a substantial interest in the study of small atomic clusters due to the role that they can play in understanding the physical and chemical properties of the bulk as well as their inherent properties, for example for catalysis. Density functional theory and correlated molecular orbital theory at the coupled cluster CCSD(T) level have been used to predict the structures and energetic properties of small $(Pd)_n$ ($n \leq 10$) clusters. The geometries were optimized with the B3LYP, PW91, and M06 exchange correlation functionals with the cc-pVDZ-PP basis sets. The clusters with different spin states and different geometries are calculated to determine the ground state isomer. The normalized clustering energies as well as the atomization energies are calculated. Single point calculations at the CCSD(T) level extrapolated to the complete basis set level at the optimized geometries at the DFT level are performed to obtain more accurate clustering energies. The results for the Pd clusters are compared with our previous work on silver clusters. The work was supported by the DOE Office of Science, Basic Energy Sciences.

Predicting Absorption and Emission Maxima of Tunable Azaborine-containing PAHs

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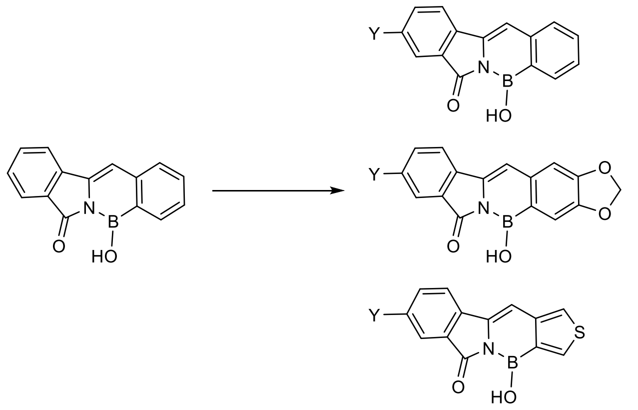
Abstract: Polycyclic aromatic hydrocarbons (PAHs) are now used in a variety of applications due to the tunability of their emission wavelength and intensity. Recently, Schrock and coworkers reported[1] a series of azaborine-containing PAHs with tunable absorption and emission maxima based on the extent of the conjugated π-system. The current computational study employs TD-B3LYP, TD-ωB97xD, TD-cam-QTP-00, CIS(D)//B3LYP, and CIS(D)//CIS to investigate the changes in the absorption and emission maxima from substituting one of these reported compounds with electron–donating and –withdrawing groups. A comparison of the various methods and the experimental values will be presented.



Y = Br, NH_2, NO_2

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Energetics and Vibrational Signatures of Nucleobase Argyrophilic Interactions

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This study investigates the interactions of both purine (adenine and guanine) and pyrimidine (cytosine, thymine, and uracil) nucleobases with a pair of silver atoms (Ag_2). Full geometry optimizations were performed on several structures of each nucleobase/Ag_2 complex and the corresponding isolated monomers using the M06-2X density functional method with a correlation consistent triple-ζ basis set augmented with diffuse functions on all atoms and a relativistic pseudopotential on Ag (aug-cc-pVTZ for H, C, N, and O and aug-cc-pVTZ-PP for Ag; denoted aVTZ). Harmonic vibrational frequencies were computed in order to confirm that each structure corresponds to a minimum on the M06-2X/aVTZ potential energy surface. Relative electronic energies for interactions between Ag_2 and each nucleobase were compared to elucidate energetic differences between isomers. Further analysis of the changes in vibrational frequencies, infrared intensities, and Raman activities reveals how different Ag_2 binding sites might be identified spectroscopically. These results provide molecular-level insight into the interactions between nucleobases and silver which may lead to better understanding and interpretation of surface-enhanced Raman spectroscopy (SERS) experiments on nucleobases and related systems.

Predicting the Properties of High Oxidation State AnF_x Complexes

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There is intense interest in compounds with metals in formal high oxidation states, especially the properties of fluorides for molten salt reactors. These AnF_x complexes are being studied to provide further insights into periodic trends as well as for the design of new separation systems for next generation nuclear fuels. Computational chemistry electronic structure approaches are being used to predict the structures and the vibrational frequencies of neutral, anionic, and cationic actinide fluorides AnF_x where An = Th - Cf to determine the maximum formal oxidation state of the actinide. The different oxidation states of these actinide fluorides together with varying high spin states of each complex were studied using DFT (density functional theory) with the B3LYP exchange-correlation functional. The TZVP basis set was used for F and cc-pvdz-pp basis sets were used for Th, Pa and U and the Stuttgart basis sets with effective core potentials were used for the actinides of Np – Cf. An NBO analysis was performed on each of the complexes and various energetics were calculated for each complex including the electron affinity, ionization energy, bond dissociation energy, fluoride affinity, and fluorocation affinity to provide information on redox properties and Lewis acidities. This work was supported by the US Department of Energy, Office of Science, Basic Energy Sciences.

Analysis of correlated systems using the atomic population of effectively unpaired electrons

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Nondynamic Electron Correlation refers to any molecular system whose ground state energy cannot accurately be defined by the single-determinant Hartree-Fock (HF) or perturbative corrections (e.g. MP2, CCSD) using the HF reference. In quantum calculations, it is important to determine whether the system being studied exhibits significant nondynamic correlation, also known as multireference character. Knowing the degree of multireference character in a system allows one to choose a more appropriate level of theory to apply. So far, popular methods for analyzing nondynamic correlation have been CCSD(T)-based models, which is too costly for all but small systems. Recently, our group proposed an alternative method [1] based on Density Functional Theory (DFT). It produces the atomic population of effectively unpaired electrons (APEUE) that shows the degree of multireference character for each atom. We applied the method to analyze the APEUE of systems with similar composition, but different structures (e.g. ethenone and oxirene, among others). The molecules are part of the W4-11 thermodynamic benchmark dataset [2], of which each system displays varying degrees of nondynamic correlation. Our analysis is computationally efficient and is consistent with CCSD(T)-based methods that have much higher computational costs. The KP16/B13 (Kong-Proynov '16 / Becke '13) functional [3], a new DFT method that can treat nondynamic/strong correlation, was also benchmarked using the W4-11 dataset.

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The Missing Agostomer in the Fluxionality of Cyclohexenylmanganese Tricarbonyl

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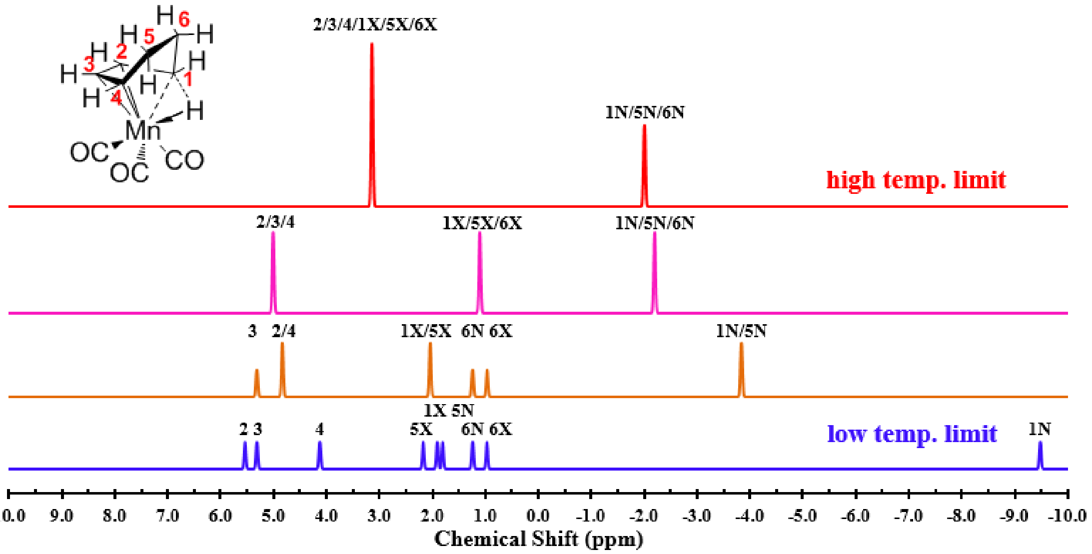
ABSTRACT

The dynamic processes in the fluxionality of cyclohexenylmanganese tricarbonyl [$(C_6H_9)Mn(CO)_3$] complex, which has an Mn-H-C 3-center 2-electron agostic interaction, have been analyzed with density functional theory (DFT). Five fluxional processes in contrast to the previously three reported processes were identified: (1) CO's ligand equivalence, (2) 1, 2-metal migration via C_s diene hydride species, (3) 1, 3-endo fast exchange, (4) 1, 2-agostic isomerization, and (5) hydride transfer process. This investigation identified an important agostic interaction in the fluxionality of $(C_6H_9)Mn(CO)_3$. The 1, 2-agostic isomerization leads to a previously uncharacterized "closed" C_s agostomer with an Mn-H bond length of 2.04 Å, an Mn-H-C bond angle at 104.3°, and ^{1}H NMR chemical shift of the proton in the Mn-H-C unit at -4.7 ppm. Excellent agreement is observed ($R^2 = 0.9949$) when comparing the computed and experimental ^{1}H NMR chemical shifts. Good agreement is observed between the computed free energies of activation and experimentally derived values. The variable temperature ^{1}H NMR spectra were also simulated.



Driven Similarity Renormalization Group: Third-Order 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 second order [4]. The resulting second-order MR perturbation theory (MRPT2) has similar accuracy to other MRPT2 methods including CASPT2 and NEVPT2. In this work, we introduce a third-order multireference perturbation theory based on the driven similarity renormalization group approach (DSRG-MRPT3) [5]. The DSRG-MRPT3 method has several appealing features: a) it is intruder-free, b) it is size-consistent, c) it leads to a noniterative algorithm with N^6 scaling, and d) it includes reference relaxation effects. The DSRG-MRPT3 is implemented using the open-source tensor library AMBIT [6] in the open-source code FORTE [7], which provides shared memory parallelization of tensor contractions. Density fitting and Cholesky decomposition are employed to avoid the direct storage of the electron repulsion integrals. The accuracy of DSRG-MRPT3 is tested on potential energy curves of F_2, H_2O_2, C_2H_6, and N_2 along the F—F, O—O, C—C, and N—N bond dissociation coordinates, respectively. The nonparallelism errors of DSRG-MRPT3 are found significantly better than those obtained by DSRG-MRPT2. We also compute the adiabatic singlet-triplet gap of 9,10-anthracyne. The estimate 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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Raman and Infrared Spectra of Platinum-Based Drugs: Cisplatin, Carboplatin, Oxaliplatin, Nedaplatin, and Heptaplatin

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Platinum-based drugs are some of the most widely used agents in treating various types of cancer. However, there are potential adverse effects such as liver damage and increasing resistance, sometimes in the midst of treatments. In an effort to combat these issues there is a continuous push to design new and improved platinum based drugs. However, only a few such derivatives are known, such as cisplatin, carboplatin, oxaliplatin, nedaplatin, and heptaplatin. In an effort to potentially design better, more effective drugs with less intense side effects, a greater understanding of molecular properties, and how those properties are altered upon drug-DNA binding, Raman and Infrared spectroscopy were explored experimentally and computationally for the aforementioned platinum drugs Various basis sets were used with Density Functional Theory (B3LYP and B97D3) and semiemprical dispersion corrections to discover which methods yielded the closest results to the experimental results. Comparing experimental and computational Raman spectra, we find that aug-cc-pVDZ B97D3 yields the most reliable results.

Electrostatics Induced Reversal of Stereoinduction in Asymmetric Epoxide Desymmetrizations

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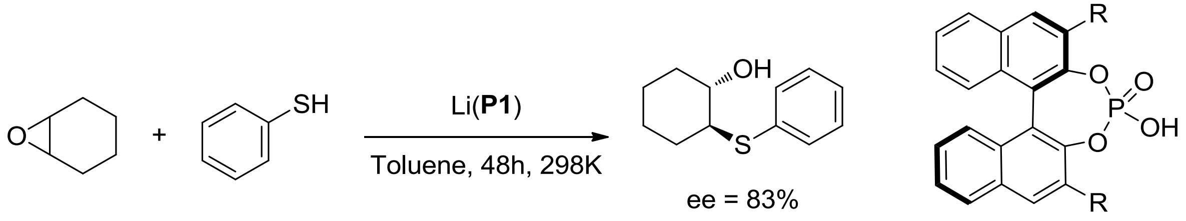
Abstract: Asymmetric epoxide desymmetrization is a key synthetic strategy in obtaining chiral 1,2-functionalized *β*-hydroxy compounds, which are found in a variety of active biological molecules and are of utmost importance in medicinal chemistry. Axially chiral binaphthol derived phosphoric acids (CPA) have been reported to catalyze these desymmetrizations with high enantiomeric excess (*ee*).[1-2] It was recently observed that the sense of stereoinduction was reversed in the desymmetrization catalyzed by alkali metal salts of CPA,[3] compared to the reaction catalyzed by the same CPAs. Density functional theory was used to gain insights into this phenomenon. The metal ion of the CPA salt activates the epoxide by coordinating with the oxygen, thereby facilitating the nucleophilic attack. Analyzing the transition state (TS) structures for the thiolysis of epoxides suggested that steric and dispersion interactions favor formation of one enantiomer while distortion effects favor the other. Upon further analysis, it was observed that the metal ion perturbs the electrostatics around the epoxide, thereby preferentially stabilizing the TS leading to one enantiomer. These data provide further support that electrostatic interactions are the driving force in asymmetric epoxide desymmetrization reactions catalyzed by CPA.[2]



P1: R = $(i\text{-Pr})_3C_6H_2$

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Vibrational Control of Electron-Transfer Kinetics: A unified theoretical framework and a critical experimental test

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Abstract: We present a theoretical framework to describe how transient infra-red (IR) excitation perturbs electron transfer (ET) rates in donor-bridge-acceptor systems. We also present the development of non-equilibrium molecular dynamics (NEqMD), a powerful approach to study IR-excitation induced geometry perturbation and coupling modulation effects. Recent experiments find that IR excitation can change ET rates and can even change the relative dominance of ET and competing reactions. We formulate a comprehensive theoretical framework to describe IR-perturbed ET kinetics, including non-equilibrium initial state populations and IR-perturbed bridge-mediated couplings. We find that these effects can produce either rate slowing or acceleration. The model is used to understand the experimentally observed rate slowing in a donor-bridge-acceptor structure, and to predict the influence of IR excitation on the recombination rate. The predictions were validated experimentally.

Analytic Gradients for V2RDM-CASSCF methods

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Abstract: The CASSCF approach enables an accurate description of the electronic structure of many-electron systems where non-dynamical correlation effects are important. Variational two-electron reduced-density-matrix (v2RDM) methods provide a route to polynomial-scaling implementations of CASSCF, enabling the description of active-spaces larger than those that can be considered using configuration interaction-(CI-) based CASSCF. In this work, we present an implementation of analytic energy gradients for (v2RDM)-driven CASSCF. Expressions for analytic gradients are simplified by the fact that the Lagrangian for the active-space energy is stationary with respect to variations in the active-space reduced-density matrices. We assess the performance of v2RDM-CASSCF relative to CI-based CASSCF in the geometry optimization of 20 molecules. For these molecules, bond lengths from geometry optimization with v2RDM-driven CASSCF are in good agreement with those from CI-driven CASSCF. When enforcing two-particle *N*-representability conditions, v2RDM-CASSCF-optimized bond lengths display a mean unsigned error of 0.006 Å and a maximum unsigned error of 0.0265 Å, relative to those obtained with CI-CASSCF. When enforcing partial three-particle *N*-representability conditions, the mean and maximum errors are reduced to 0.0006 Å and 0.0054 Å, respectively.

Calculated bond dissociation energies of simple peptides for use in analyzing collision induced dissociation processes

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Abstract: For the mass spectrometric analysis of proteins, collision induced dissociation (CID) is often used as a means of primary ion fragmentation. To understand the observed mass spectrometric results of this fragmentation process, computational methods are employed to predict energies related to possible fragmentation pathways and products. Previous predictions of the gas phase acidities of amino acids and peptides at the correlated G3(MP2) molecular orbital theory level in our group agree with the experimental values to within about ±2 kcal/mol and with higher level CCSD(T) calculations extrapolated to the complete basis set limit with additional corrections. These predictions can be compared to experimental mass spectra to enrich our understanding of the processes that occur during CID, in addition to revealing information about the neutral species produced during CID to which the mass spectrometer is blind. Specific results include: (1) The y_1^- anion $NH_2CHRCO_2^-$ is the most intense product ion for dipeptides and their amides; (2) Loss of H_2O is observed for alanine, diglycine, and dialanine amide precursor anions; (3) Loss of CO_2 is observed for dimers, but not monomers or amides; (4) Among amide species, $N\equiv C\text{-}O^-$ was universally observed and the enthalpies for generation of this anion are less than ± 5 kcal/mol; (5) The hydrogen at the C-terminus of the mono- and dipeptide amide molecules facilitated the observable loss of H_2O in the experimental spectra as loss of H_2O was not observed for non-amide species; and (6) Many predicted low energy pathways are not observed in the CID mass spectra. This work was supported by the National Science Foundation.

Delocalized Term Specification on F-SAPT

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Abstract: SAPT (Symmetry-Adapted Perturbation Theory) is a well-known and broadly used tool for analyzing the non-covalent interactions between non-bonded molecules. To create a more chemically relevant picture of the forces around interacting functional groups F-SAPT[1] was developed. While interaction energy between local regions on molecules is of chemical interest and may have broadly reaching implications, there are lingering issues to a truly localized partitioning of energy terms. I will be showing some of the delocalized terms that we have found implementing our own in house version of F-SAPT.

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Geometric energy derivatives at the CCSDT(Q)/CBS limit: The equilibrium geometry and molecular force field of S_0 H_2CO

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Abstract: The spin-adapted non-orthogonal coupled cluster framework [1] has drastically reduced the time it takes to complete coupled cluster singles, doubles, iterative triples (CCSDT), noniterative quadruples (CCSDT(Q)), and iterative quadruples (CCSDTQ) computations. These higher-order coupled cluster methods are now trivial additions in composite approaches such as focal-point analysis (FPA). FPA is a dual-extrapolation procedure in which the composite energy systematically approaches the full configuration interaction (FCI) complete basis set (CBS) limit [2]. In this work, S_0 formaldehyde's equilibrium geometry is determined by way of molecular gradients developed at the CCSDT(Q)/CBS and CCSDTQ/CBS limits with basis sets up to cc-pV6Z using the focal-point approach. A fourth-order expansion about the CCSDT(Q)/CBS structure is made, at the same level of theory, to predict the spectroscopic constants and fundamental vibrational frequencies using second-order vibrational perturbation theory (VPT2) and a discrete variable representation (DVR) variational approach. The generation of this CCSDT(Q)/CBS quartic force field represents a significant advance in the ability of *ab initio* quantum chemistry to predict compact, highly-accurate potential energy surfaces.

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Adiabatic Switching Applied to the Vibrations and Mode-specific Tunneling of syn-CH_3CHOO and Implications for ``Zero-Point Energy Leak'' in Quasi-classical Trajectory Calculations

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Abstract: Quasi-classical trajectory calculations are distinguished from molecular dynamics calculations primarily by the difference in the phase-space used for sampling initial conditions. In the former, this phase space incorporates zero-point energy (ZPE), whereas the latter uses the classical phase space, typically at a given temperature. There are advantages and disadvantages to these approaches. Clearly, the quasi-classical one aims to mimic quantum mechanics, where zero-point energy is a major and essential difference with classical mechanics. But, "ZPE leak", a well-known issue with quasi-classical calculations, has largely prevented the use of the quasi-classical method for larger systems and also is often mentioned as an issue even for smaller systems, where it is routinely used. By not incorporating ZPE, molecular dynamics calculations avoid this issue; however, at the cost of neglecting this important difference with quantum mechanics. In this article we examine ZPE leak from the point of view of rigorous semi-classical quantization; actually the lack thereof. We examine this issue here specifically for syn-CH3CHOO, where the ZPE is roughly twice as large as the barrier for isomerization to the more stable isomer vinyl hydroperoxide. Semi-classical quantization is done for this 18 degrees-of-freedom molecule using adiabatic switching in Cartesian coordinates, using the methodology recently described by us [1]. Good agreement for vibrational energies is found compared to accurate quantum calculations. Finally, some aspects of possible mode-specific isomerization to vinyl hydroperoxide is examined using the adiabatically switched trajectories. We describe a method to incorporate adiabatically switched semi-classical trajectories into the Q_{im} projection theory of mode-specific tunneling [2]. The method is applied to investigate mode-specific isomerization of syn-CH_3CHOO in the deep tunneling regime. A full-dimensional potential energy surface is used in these calculations.

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Broadband absorption spectra from time-dependent coupled-cluster theory

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Abstract: We present some of our contributions to the advancement of explicitly time- dependent coupled-cluster theory towards the efficient computation of linear absorption spectra of molecular systems. Our newly developed explicitly time-dependent equation-of-motion coupled-cluster (TD-EOM-CC) formalism based on the propagation of the CC dipole function possesses great potential for the efficient computation of linear absorption spectra over arbitrarily wide energy windows. This approach introduces no approximations and requires only half of the computational effort of TD-CC methods based on the propagation of the wave function. The TD-EOM-CC formalism is particularly useful when dealing with molecular systems with high density-of-states, or if the spectral region of interest spans a large energy range (> 10 eV). We perform illustrative calculations of the UV-Vis, NEXAFS, and electronic circular dichroism (ECD) spectra of several molecular species relevant to the study of atmospheric chemistry and astrochemistry. Furthermore, we exploit extrapolation techniques based on Pade approximants, these techniques are shown to significantly reduce the computational effort required to simulate NEXAFS spectra.

Conventional strain energies of the oxaphosphetanes and the oxadiphosphetanes

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Abstract: Few studies have been conducted on heterocyclic systems containing phosphorus. This is most likely due to the existence of various forms of phosphorus and because molecular structure data and their interconversions are not completely understood. In this study, the conventional strain energies of 1,2-oxaphosphetane, 1,3- oxaphosphetane, 1,2,3-oxadiphosphetane, and 1,2,4-oxadiphosphetane are determined within the isodesmic, homodesmotic, and hyperhomodesmotic models. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies and zero-point vibrational energies are computed for all pertinent molecular systems using SCF theory, second-order perturbation theory, and density functional theory (DFT). The DFT functionals employed are Becke's three-parameter hybrid functional using the LYP correlation functional and the M06- 2X high nonlocality hybrid functional from Truhlar and Zhao. The basis sets employed are Dunning and coworkers' correlation consistent basis sets: cc-pVDZ, cc-pVTZ, and cc-pVQZ. In addition, cc-pV(D+d)Z, cc-pV(T+d)Z, and ccpV(Q+d)Z basis sets are also investigated to determine the effect of the extra d function for phosphorus on the overall results. Coupled-cluster theory calculations were also performed at MP2/cc-pVTZ and MP2/cc-pVQZ optimum geometries including single and double excitations (CCSD) and CCSD with the inclusion of noniterative, linear triple excitations [CCSD(T)]. The computed conventional strain energies are compared to those of small cyclic hydrocarbons and to other heterocyclic systems. We gratefully acknowledge support from the NSF (EPS-0903787) and from the Mississippi College Catalysts, the alumni support group of the Department of Chemistry & Biochemistry.

Vibrational Frequencies and Spectroscopic Constants of Stable Noble Gas Molecules: $NeCCH^+$, $ArNH^+$, $ArCCH^+$, and $ArCN^+$

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Abstract: The search for possible, natural, noble gas molecules has led to quantum chemical, spectroscopic analysis of $NeCCH^+$, $ArNH^+$, $ArCCH^+$, and $ArCN^+$. Each of these systems has been previously shown to be a stable minimum on its respective potential energy surface. However, no spectroscopic data are available for laboratory detection or interstellar observation of these species, and the interstellar medium may be the most likely place in nature where these noble gas cations are found. The bent shape of $NeCCH^+$ is confirmed here with a fairly large dipole moment and a bright C−H stretching frequency at 3101.9 cm^{-1}. Even if this molecule is somewhat unstable, it is likely observable now that the spectral ranges of where to look have been established. $ArCCH^+$ is much more stable but has dim double harmonic intensities for the vibrational fundamentals and a dipole moment below 0.5 D making its rotational transitions likely buried in the astronomical weeds. Even so, $ArCCH^+$ cannot be excluded as a possibility in laboratory experiments of hydrocarbons in argon-rich environments. $ArCN^+$, on the other hand, has a dipole moment of greater than 3.5 D, an observable C−N stretching fundamental at 2189.6 cm^{-1} (4.567 microns), and a viable formation pathway through HCN, a highly-abundant interstellar molecule. Consequently, these molecules containing noble gas atoms are spectroscopically classified at high-level for the first time and may be present in observable regions of outer space.

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EOM-CCSD calculations with the natural transition orbitals

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Abstract: In this poster, we present the possibility of the equation-of-motion coupled cluster method single and double excitations (EOM-CCSD) [1] with the reduced space. For the compact description of excited states, we use the natural transition orbital (NTO) scheme [2], which is generated from the simple random phase approximation (RPA). The performance is tested for the valence and Rydberg excitations. Other excited state calculations such as equation-of-motion second order many-body perturbation theory (EOM-MBPT(2)) will be discussed briefly as well.

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On the Chirality of Antimalarial Drug Candidates

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Abstract: A dichloromethane extract of *Trichospira verticillata* from the Natural Products Discovery Institute was discovered to have good antiplasmodial activity. After purification, four new germacranolide-type sesquiterpene lactones named trichospirolides A-D (**1** - **4**) were isolated from *Trichospira verticillata.* The structures of the new compounds were elucidated by analysis of their 1D and 2D NMR spectra and MS data. The relative and absolute configurations were assigned based on a comparison of calculated and experimental ECD and UV spectra, specific rotations, and internuclear distances for all possible diastereomers for each compound. Herein, we report the stereochemical assignment of these four compounds.

Enhanced Ionization of Peptides using Cr(III): Developing the Basis for Proteomics Studies

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Abstract: The goal of the Human Proteome Project is to elucidate all of the proteins in the human body. One common, cost effective and reliable approach is the use of tandem mass spectrometry as it is a highly reproducible analytical technique. It has been shown that the addition of Cr(III) to peptide solutions being electrosprayed has great promise for expanding the range of acidic and basic peptides that can be studied by positive ion mass spectrometry and also for increasing the sensitivity and accuracy of the analysis. Computational chemistry is being used to study the interactions of Cr(III) with neutral and anionic (parent –H anions). By calculating the enthalpy of the reaction of the peptide anions and the neutral species, we are improving our understanding of how chromium cations interact with these species, providing structural and energetic information not available from mass spectrometry experiments. The calculations are done using density functional theory with the B3LYP exchange-correlation functional. We are also studying the diprotonated species as part of our study to see how Cr(III) in solution can enhance such protonation states. We have already discovered differences that are dependent on the structure of the side chain. This work is supported by the National Science Foundation.

Towards Efficient Canonical Product Decomposition in TiledArray Framework

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Abstract: Several forms of tensor decomposition[1] have recently emerged as a route towards reduced scaling electronic structure. The CANDECOMP/PARAFAC (CP) decomposition is a classic format that represents a tensor as a sum of component rank one tensors. As a step towards developing an efficient distributed-memory parallel computation of CP form of a tensor we implemented the alternating least squares (ALS) algorithm[2,3], a classic approach to computing CP that is relatively low computational cost; only recently has its convergence been analysed rigorously[4,5]. We used ALS to compute CP decomposition of several types of tensors that commonly arise in the electronic structure theory. Finally, we discuss possible strategies for implementing ALS efficiently using TiledArray, a high-performance generic tensor framework for distributed memory parallel machines[6].

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Heterocyclic Isomers of Forbidden and Non-forbidden Pathways

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Ab initio methods were employed to locate both disrotatory and conrotatory pathways for the isomerization of the tricylic structure shown below (Figure 1). Geometry optimizations and frequencies were computed using the complete active space self-consistent field (CASSCF) method on the reactant, transition states, and products. The active space consisted of 10 electrons in 10 orbitals spanning C1-C4. Single point energies were computed at the multi-reference MP2 (MRMP2) level. The transition states were confirmed by completing intrinsic reaction coordinate (IRC) computations. Four transition states were located for the hetero atoms oxygen and sulfur and eight for nitrogen and phosphorous. The isomerization occurs through breaking two bonds in the tricylco moiety structure, C1-C4 and C2-C3 or C1-C3 and C2-C4. The order these two bonds break leads to different transition states.

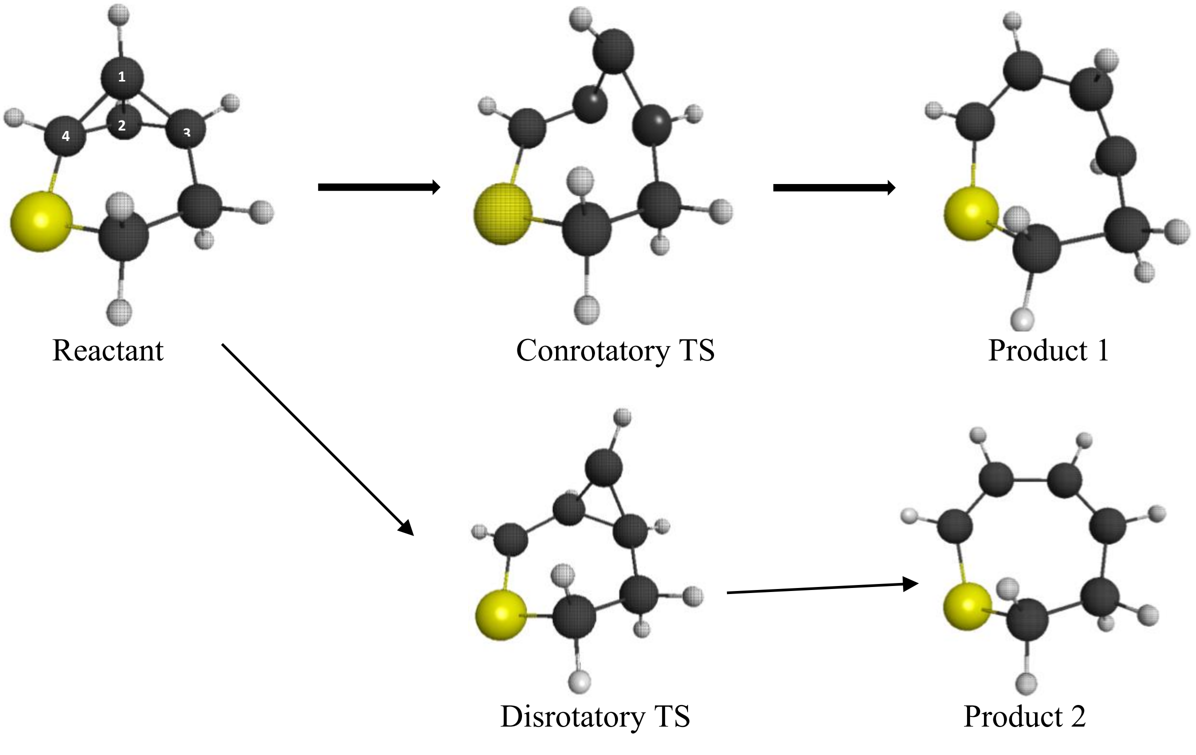

Figure 1. This figure shows the initial reactant with the attached hetero atom and its products after following two possible pathways, disrotatory and conrotatory.

Tunneling Splitting and Vibrational Spectrum of Cyclic Formic Acid Dimer Based on Full-dimensional Potential Energy and Dipole Moment Surfaces

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Abstract: We report a full-dimensional, permutationally invariant [1] potential energy surface (PES) and dipole moment surface (DMS) for the cyclic formic acid dimer. This PES is a least-squares fit to 13475 CCSD(T)-F12a energies. The energy-weighted, root-mean-square fitting error is 11 cm^{-1} and the barrier for the double-proton transfer on the PES is 2848 cm^{-1}, in good agreement with the directly-calculated *ab initio* value of 2853 cm^{-1}. The dipole moment surface is a fit to dipole expectation values of the 13475 configurations computed at MP2 level of theory. The tunneling splitting is computed using a reduced-dimensional Hamiltonian with relaxed potentials. The highest-level, four-mode coupled calculation gives a tunneling splitting of 0.037 cm^{-1}, which is roughly twice the experimental value. The tunneling splittings of $(\text{DCOOH})_2$ and $(\text{DCOOD})_2$ from one to three mode calculations are, as expected, smaller than that for $(\text{HCOOH})_2$ and consistent with experiment. The PES and DMS are used to calculate the energies and intensities of vibrational transitions of the formic acid dimer, based on vibrational self-consistent field and configuration interaction method, and the vibrational spectrum is obtained

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Using power of exact conditions to develop density functionals

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Abstract: A correlated orbital theory (COT) has an effective one-particle operator which include electron correlation. Kohn-Sham density functional theory (KS-DFT), can be considered as a COT[1]. One of the conditions that COT should satisfy is that orbital eigenvalues approximate the exact principal ionization potentials for occupied orbital in a molecule. Under GKS-DFT formalism, the IP condition is a consequence of adiabatic TDDFT and beyond being an accurate approach for excitation energies[2]. When an electron is excited into the continuum, all the KS ground state orbital energies should be good approximations to IP's. To satisfy the COT condition, $-IP_m = \epsilon_m = \langle\varphi_m|f + \Sigma_{cc}|\varphi_m\rangle \approx \langle\varphi_m|H + J + \mathrm{V}_{xc}|\varphi_m\rangle$ demands that V_{xc} be an accurate approximation to the non-local, $-K + \Sigma_{cc}$.

Guided by this principle minimally parameterized QTP functionals were constructed[3,4]. These QTP functional showed less self-interaction error, correct bond dissociating curves, correct long-range behavior for charge transfer complex, and competitive thermochemical accuracy when compare to similar functionals[5]. QTP00 functional showed excellent results for core excitations and QTP01functional also showed the accurate prediction of valence and Rydberg excitation. QTP02 functional is based on ωB97 formalism and an improvement upon QTP00 and QTP01. Here H, J, K, E, and V_{xc} stands for one-electron Hamiltonian, Coulomb integral, exchange integral, self-energy, and exchange Coulomb potential respectively.

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Investigation of Enhanced Vibrational Signatures of High Energy Density Materials

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This investigation studies the interactions between various high energy density materials (HEDMs) and a pair of silver atoms (Ag_2), as well as the corresponding perturbations in their infrared (IR) and Raman spectra. Full geometry optimizations of Ag_2 bound to various argyrophillic sites of these compounds are being carried out along with the corresponding harmonic vibrational frequency computations using the M06-2X density functional and a correlation consistent triple-ζ basis set augmented with diffuse functions on all atoms and with a relativistic pseudopotential for Ag (i.e., aug-cc-pVTZ for H, C, N, and O and aug-cc-pVTZ-PP for Ag). For the simplest of these compounds, FOX-7, three energetically competitive binding motifs (within 3.0 kcal mol^{-1} of each other) have been identified with key differences in their vibrational spectra. These results have been compared to those for an isolated FOX-7 molecule to examine changes in the vibrational frequencies, IR intensities, and Raman activities upon complexation. This procedure is currently being extended to RDX, HMX, and TATP. These results will provide molecular-level insight into the interactions between HEDMs and silver which may lead to better understanding and interpretation of highly sensitive surface enhanced Raman spectroscopy (SERS) experiments on HEDMs.

Optimizing Sparsity Screening for Density Fitting on Manycore Architectures

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Abstract: The four-center, two-electron integral tensor of quantum chemistry is a major bottleneck due to its storage cost of $\mathcal{O}(n^4)$. Moreover, both Coulomb ($J_{\mu\nu} = (\mu\nu|\sigma\lambda)D_{\sigma\lambda}$) and exchange ($K_{\mu\nu} = (\mu\sigma|\nu\lambda)D_{\sigma\lambda}$) tensors are built as $\mathcal{O}(n^4)$. To alleviate these costs, density fitting reduces the four-center integrals to a three-center form. The resulting three-index integrals require $\mathcal{O}(n^3)$ storage and the Coulomb ($J_{\mu\nu} = Q_{\mu\nu}Q_{\sigma\lambda}D_{\sigma\lambda}$) and exchange ($K_{\mu\nu} = Q_{\mu\sigma}Q_{\nu\lambda}D_{\sigma\lambda}$) tensors can be built in $\mathcal{O}(n^3)$ and $\mathcal{O}(n^4)$, respectively. If sparsity is utilized, the cost of Coulomb and exchange builds can be reduced to $\Omega(n)$ for sufficiently sparse systems. Therefore, effective sparsity screening algorithms are imperitive for scalable methods. Unfortunately, current sparsity screening algorithms for density fitting are not tailored for use on manycore architectures. The algorithm used in the Psi4 electronic structure package takes advantage of permutataional symmetry and stores screened integrals in a form similar to compressed sparse row format. However, this requires the copying of three dimensional quantities when the integrals must be unpacked for dense matrix multiplications. This requires substantial memory bandwidth, hinders vectorization, and ultimately renders the algorithm unviable when scaling to many cores. We propose a new sparsity screening algorithm which overcomes the hindrances of the current algorithm. We choose to neglect the permutational symmetry of the three-center integrals and instead store the screened integrals in a 'pruned' sparsity form. The resulting method is not only viable on manycore architectures, but also allows for superior vectorization on modern SIMD architectures.

Extensions of the adaptive configuration interaction method for computing challenging excited states

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Abstract: We detail and compare various algorithms to compute excited electronic states using our recently developed adaptive configuration interaction method (ACI)[1]. In principle, ACI is capable of describing all types of excited states (multi electron, charge transfer, etc.) equally well. We develop both state-specific and state-averaged algorithms to compute excited states whose accuracy can be tuned by a user-specified parameter, σ. The state-specific algorithms allow for direct control of the error of each state, though each state must be computed sequentially and ensuring orthogonality among individually optimized states can become complicated. Alternatively, the state averaged schemes are more efficient in that they compute all states simultaneously, but some degree of state-wise tunability is lost. We compare each algorithm using methylene excited states, the lithium fluoride avoided crossing, and all-trans polyene benchmark data, requiring up to a CAS(24,24) active space.

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Di-copper Catalysis in 1,3-dipolar Cycloadditions: A Reaction Valley Study

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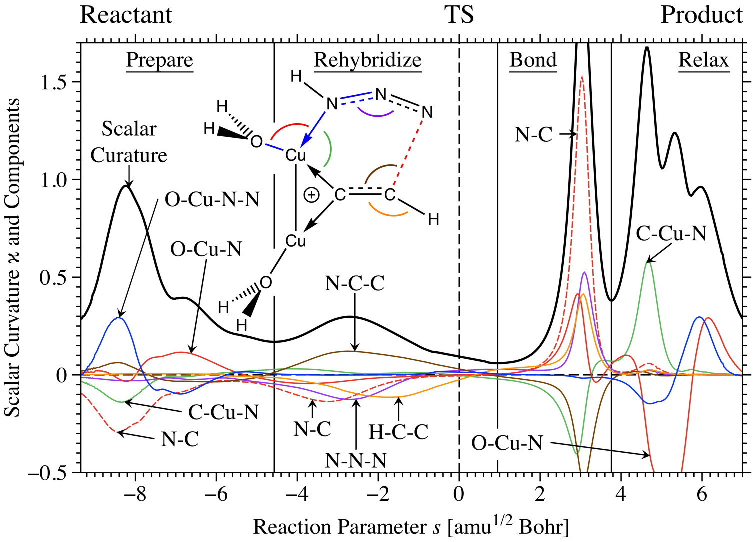
Abstract: Catalysis is one of the major chemical challenges of our time. Transition metal catalysis specifically has the potential to facilitate the synthesis of desirable chemicals. This work is a mechanistic investigation of homogeneous catalysis using the Unified Reaction Valley Approach.[1-4] Rather than investigating just the energetics of a catalyzed reaction, the potential energy surface is explored in the vicinity of the reaction path following it from its start to its end. In this way, the reaction valley is studied for the purpose of unraveling the coupling between vibrational and translational motions of the reaction complex, which is decisive for the mechanistic outcome.

A dual level approach was used, based on Coupled Cluster theory for the energetics and a lower level method for the description of the reaction valley. Eight Cu-catalyzed 1,3-dipolar cycloadditions to acetylene are analyzed. Decomposition of the reaction path curvature into internal coordinate components allows identification of chemical events, such as rehybridization and bond formation, as they occur along the reaction path. A di-Cu catalyst converts a one step mechanism to a two step mechanism, where each step has a significantly lower barrier than the uncatalyzed reaction. Electronic reasons for the effectiveness of the Cu catalyst in the cycloaddition reactions will be discussed.

Figure: For the Cu-catalyzed 1,3-dipolar azide-alkyne cycloaddition ($\Delta E^a = 13.9$, $\Delta_R E = 10.7$ kcal/mol, CCSD(T)), the scalar curvature (bold black line) of the reaction path is given as a function of the mass-weighted arc length *s* of the path. The transition state is at *s*= 0. The colored lines show the changes in the curvature components associated with the internal coordinates of the complex.



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Capturing Plasmon-Molecule Dynamics in Dye Monolayers on Metal Nanoparticles using Classical Electrodynamics with Quantum Embedding

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Abstract: A multi-scale hybrid quantum/classical approach using classical electrodynamics and a collection of discrete three-level quantum systems is used to simulate the coupled dynamics and spectra of a malachite green monolayer adsorbed to the surface of a spherical gold nanoparticle (NP). This method utilizes finite difference time domain (FDTD) to describe the plasmonic response of the NP within the main FDTD frame-work and a three-level quantum description for the molecule via a Maxwell/Liouville framework. To avoid spurious self-excitation, each quantum molecule has its own auxiliary FDTD subregion embedded within the main FDTD grid. The molecular parameters are determined by fitting the experimental extinction spectra to Lorentzians, yielding the energies, transition dipole moments, and the dephasing lifetimes. This approach is suited to modeling thousands of molecules on the surface of a plasmonic NP. There is good agreement with experimental extinction measurements, predicting the plasmon and molecule depletions. Additionally, this model captures the polariton peaks overlapped with a Fano-type resonance profile observed in the experimental extinction measurements. This technique can be generalized to any nanostructure/multi-chromophore system, where the molecules can be treated with essentially any quantum method.

How do ether and amine bridges affect the conjugation in monomacrocyclic dendrimers?

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Abstract:

Conjugated dendrimers have been studied for their use in preparing photoreactive materials and for their light harvesting properties. One of the main goals of the Mississippi College Organic Research Group (MC-ORG) is to design and prepare flat, two-dimensional dendrimers. It has been found that when twisting occurs about the single bonds of the dendrons, there is a decrease in energy transfer and therefore loss of conjugation and reduced light harvesting properties. The MC-ORG has been synthesizing "flat" dendrimers that cannot lose this conjugation due to the ethynyl units being locked in place by ether connections. These ether connections are made during an intermediate step when a monomacrocyclic dendrimer is formed. The MC-ORG has successfully created a monomacrocyclic dendrimer with a three carbon ether connection. The goal of this research is to determine whether a one, two, or four carbon connection would also form this ether connection without twisting of the ethynyl units. This ether connection is in the position *meta* to the ethynyl groups. Another goal will be to determine if one, two, three, and/or four carbon connections can be placed *ortho* to the ethynyl groups. It will also be determined if amine bridges would also lock the ethynyl bridges in place and form flat dendrimers. This amine connection is studied with different carbon lengths in the bridge and also in the positions both *ortho* and *meta* to the ethynyl groups. To investigate these questions, optimum structures are computed at the SCF and DFT levels of theory. The functionals employed are B3LYP, M06-2X, and ωB97XD. All calculations use correlation consistent basis sets. Finally time-dependent DFT calculations are used to investigate the UV-Vis spectra in order to determine if these various ether and amine connections will improve conjugation within the structure. We gratefully acknowledge support from the NSF (EPS-0903787) and from the Mississippi College Catalysts, the alumni support group of the Department of Chemistry & Biochemistry.

High Accuracy Computation of Major *n*-Butanol Combustion Pathways

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Abstract:

The continued use of non-renewable fossil fuels is a cause for concern regarding their long-term feasibility. Small molecules are often blended into fuels to tailor their physical properties and to enhance fuel efficiency. Such additives are chosen not just for their effects on the physical properties of fuel, but also for their renewability. Recent advances in biobutanol production processes have increased the viability of butanol as a fuel additive.[1-2] Biobutanol offers many advantages as a fuel additive, including the possibility of its eventual use as a standalone fuel.[1,3] The present study uses high-accuracy extrapolated *ab initio* methods to examine the H-atom combustion pathways of *n*-butanol, focusing on the toxic byproducts formaldehyde and acetaldehyde, in hopes of elucidating the energetics of these important reactions.

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Energetics of Group 13 and 15 Cyanides and Cyanide Adducts

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Abstract

The cyanometallates show valuable fundamental properties and applications in the fields of hybrid polymers, magnetic materials, and 3D metal organic frameworks. Some crystalline cyanometallates are known to possess nonlinear optical properties. In general, the synthesis of cyanometallates commonly involves the reaction of simple metal salts such as chlorides or bromides with ionic cyanide salts such as KCN or $[(n\text{-Bu})_4N][CN]$ in aqueous solutions. Experimentally, different novel ways of preparing these cyanides and their corresponding py or bipy adducts were explored. Electronic structure calculations were performed at the density functional theory (DFT) and correlated molecular orbital theory (MP2) to determine the structures of these compounds from a number of possible conformers and to assign the vibrational spectra of the synthesized cyanides and cyanides adducts. The energetics of the cyanide additions reactions and adduct formation in both gas phase and solution were predcited. We studied group 13 cyanides and cyanides adducts with M = Ga, In, Tl and Group 15 for M = As and Sb. This work was supported by the Department of Energy, Basic Energy Sciences, EFRC (UNCAGE-ME) and Catalysis Centers Programs.

The Interstellar Formation and Spectra of the Noble Gas, Proton-Bound $HeHHe^+$, $HeHNe^+$, & $HeHAr^+$ Complexes

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Abstract: The sheer interstellar abundance of helium makes any bound molecules or complexes containing it of potential interest for astrophysical observation. This work utilizes high-level and trusted quantum chemical techniques to predict the rotational, vibrational, and rovibrational traits of $HeHHe^+$, $HeHNe^+$, and $HeHAr^+$. The first two are shown to be strongly bound, while $HeHAr^+$ is shown to be more of a vander Waals complex of argonium with a helium atom. In any case, the formation of $HeHHe^+$ through reactions of HeH^+ with $HeH3^+$ is exothermic. $HeHHe^+$ exhibits the uintessentially bright proton-shuttle motion present in all proton-bound complexes in the 7.4 micron range making it a possible target for telescopic observation at the mid-IR/far-IR crossover point and a possible tracer for the as-of-yet unobserved helium hydride cation. Furthermore, a similar mode in $HeHNe^+$ can be observed to the blue of this close to 6.9 microns. The brightest mode of $HeHAr^+$ is dimmed due the reduced interaction of the helium atom with the central proton, but this fundamental frequency can be found slightly to the red of the Ar–H stretch in the astrophysically detected argonium cation.

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A Transition State Trapped? QM-model Examination of Biphenyl Torsional Rotation within an Engineered Thr-tRNA Synthetase

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Abstract: Recently, a modified threonyl-tRNA synthetase was structurally designed to stabilize the planar conformation of the biphenyl side chain of a non-canonical p-biphenylalanine residue [1]. This stabilization of the planar conformation is significant as the equilibrium geometry of gas phase free biphenyl has a twisted dihedral angle ~45 degrees and has transition states at both coplanar and perpendicular ring conformations. The energetics of biphenyl bond rotation within the environment of the engineered threonyl-tRNA synthetase protein remains unclear. Using a method developed by our lab to systematically create QM-only cluster models based upon local amino acid interactions, we performed geometry optimizations, frequency calculations, and transition state searches at the B3LYP-GD3BJ/6-31G(d′) level of theory with implicit solvation on models of the synthetase cores to obtain biphenyl rotational energy diagrams. Our results for several of the modified cores indicate the van der Waals forces of the surrounding residues effectively generate energy landscapes that constrain the biphenyl to new minima on the potential energy surface. Transition states for the planar conformation of biphenyl were not found for the cluster model of the experimentally determined coplanar biphenylalanine. This suggests the transition state known for the coplanar conformation of free biphenyl is completely eliminated on the energy landscape of our threonyl-tRNA synthetase models.

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Prediction and Characterization of Alkaline-Earth (M = Be, Mg, Ca, Sr, and Ba) Metallacyclopentadienes and Relevant Derivatives

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Abstract: Alkaline-earth metallacyclopentadienes are an active area of research in synthetic chemistry, notable for their roles as precursors of key cyclopentadiene derivatives.[1-2] However, experimental characterization is limited due to their challenging synthesis and subsequent isolation. Herein, we report systematic theoretical studies of MC_4H_4 (M = Be, Mg, Ca, Sr, Ba) rings and experimentally relevant complexes. Benchmarking against CCSD(T) and experiment shows reasonable performance for the B3LYP, BP86, and M06-2X density functionals in predicting the equilibrium geometries, thermochemistry, and vibrational spectra of these species. NICS indices[3-4] and extra cyclic resonance energies (ECRE)[5-6] confirm that the compounds in question possess antiaromatic character. For both the bare MC_4H_4 rings and larger complexes, the Be-containing compounds were found to be the most strongly bound species. Such viability is explained via ring strain, electron densities, natural bond orders, and orbital analyses. Given that the second least viable Mg complex has been reported in recent experiments,[2] synthesis and characterization of the other group IIA analogs are anticipated.

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Predicting the Gas Phase Acidities and pK$_a$'s of early actinides

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Abstract

Nuclear energy is a promising alternative to combustion of fossil fuels that does not contribute to global warming. There is a need to separate actinides from each other and from other fission products for the design of new reactors that can reuse spent fuel as well as for environmental cleanup. Modern electronic structure theory in combination with the experimental data can be used to predict the acidity of the actinide ions in aqueous solution. We are predicting the gas phase acidities and pK$_a$'s of aqueous An = Th – Pu in different oxidation states from +III to +VI. The acidities of the actinides in the +IV oxidation state with one solvation shell around the actinide cation were predicted initially and compared to experiment. The results showed that a second solvation shell is necessary to correctly predict the acidity of these actinide cations. The calculations were done by using density functional theory including relativistic effects with effective core potentials. The COSMO self-consistent reaction field intrinsic solvation model was used to predict free energies in aqueous solution including pK$_a$'s. The work was supported by the DOE Office of Science, Basic Energy Sciences.

Adsorption of CO_2 on Models of Metal-Organic Frameworks

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Abstract: Metal-organic frameworks (MOFs) are made of organic molecules coordinated to metal centers to form a periodic crystalline structure with high porosity and, potentially, open metal sites. This class of structures has seen increased interest in the literature for the interchangeability of their components and their various potential applications, one of which is the selective adsorption of gas molecules. The selective capture of anthropogenic CO_2 from large scale energy production is a particularly interesting application for these systems. High accuracy *ab initio* calculations can provide a detailed understanding of the particular interactions that can influence the selectivity of these systems for a given gas, but the bulk nature of the MOFs makes such calculations intractable. For this reason, the current study uses four model structures of MOFs interacting with CO_2 to mimic the large scale systems. Mn, Co, and Zn metal centers are considered in each structure to yield a total of 12 systems. The potentially multi-reference nature of the systems is taken into consideration and complete active space self consistent field (CASSCF) and post-CASSCF correlation methods are used to benchmark the interaction energies of the MOF models with CO_2. Symmetry-adapted perturbation theory (SAPT) energy decompositions provide further insight into the components of these interactions. Additionally, a number of density functionals are compared to the benchmark results to determine which variants are best able to reproduce the accuracy of the higher-level methods.

Dipole-bound States of Zwitterions

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Abstract:

Molecules form two basic classes of anions. On the one hand, the excess electron can occupy a valence orbital, and the resulting anions are referred to as valence states. These anions can be very stable (by several eV), say, the CN^- anion, but they can also be metastable (also by several eV), say, the benzene anion. On the other hand, the excess electron can be attached via long-range interactions, and occupy a far more diffuse non-valence orbital. Depending on the nature of the leading long-range term these anions are referred to as dipole-bound, quadrupole-bound, polarization-bound, or correlation-bound. The electron binding energies (EBE) of these non-valence anions are typically small, that is, in the range of 1 to about 100 meV.

In the past, many EBEs of dipole-bound states have been measured (for a collection see [1]) and an empirical analysis of the available and some additional data [2] suggests that the EBE follows a steep power law of the dipole moment. However, it is not so clear whether this trend will hold for larger dipole moments, because the data set is heavily skewed towards molecules with relatively low to intermediate polarity-something that would most probably be true of any randomly selected set of molecules.

Therefore, we decided to study the EBEs of several highly polar molecules computationally. Conventional molecules with high dipoles are formamide (4.6 Debye) and hexafluro-cyclohexane (5.7 Debye). A molecule that is far more polar owing to its Zwitterion character is an isomer of C_5H_2 (8.8 Debye), and the most polar molecule in our study is glycine betaine, which is a true Zwitterion and has a dipole moment of more than 11 Debye.

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Ab initio potential energy surface for flexible CO_2-H_2O and VSCF/VCI vibrational analysis for the dimer and the hydrated clathrate, $CO_2@(H_2O)_{20}$, using the local monomer model

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Abstract: We report an *ab initio*, full-dimensional, potential energy surface (PES) for CO_2-H_2O, in which two-body interaction energies are fit using a basis of permutationally invariant polynomials and combined with accurate potentials for the non-interacting monomers. This approach, which we have termed "plug and play" is extended here to improve the precision of the 2-body fit in the long range. This is done by combining two separate fits. One is a fit to 47,593 2-body energies in the region of strong interaction and approaching the long-range and the second one is a fit to 6,244 2-body energies in the long-range. The two fits have a region of overlap which permits a smooth switch from one to the other. All energies are obtained at the CCSD(T)-F12b/aug-cc-pVTZ level of theory. Properties of the full PES, *i.e.*, stationary points harmonic frequencies of the global minimum, etc. are shown to be in excellent agreement with direct CCSD(T)-F12b/aug-cc-pVTZ results. Diffusion Monte Carlo calculations of the dimer zero-point energy are performed and dissociation energy, D_0, of 785.0 cm^{-1} is obtained using that ZPE, D_e and the rigorous ZPEs of the monomers. VSCF/VCI MULTIMODE calculations of fundamentals are reported and are in good agreement with available experimental results. Finally, the dimer PES together with an existing water *ab initio* water potential are used to develop a potential for the CO_2 hydrate clathrate $CO_2(H_2O)_{20}$ (5^{12} water cage). A full normal mode analysis of this hydrate clathrate is reported as are the local-monomer VSCF/VCI intramolecular fundamentals of CO_2.

Efficient and Automated Computation of Molecular Geometries at the Coupled-Cluster Complete Basis Set Limit with Focal-Point Methods

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Abstract: In order to consistently examine reaction energies or other properties at the CCSD(T)/CBS limit, geometries should be evaluated at the same level of theory. However, the computational cost can be quite high for obtaining CCSD(T)/CBS benchmark values. The focal-point approach can accelerate convergence to the CBS limit by capitalizing on the use of small basis sets to capture higher-order electron correlation effects. Studies of focal-point optimizations are currently limited because the composite gradients are needed during the geometry optimization procedure, and therefore, require support by the quantum chemistry program itself. With the use of implemented focal-point gradients in PSI4, geometries of closed-shell systems of the W4-11 database (Chem. Phys. Lett. **2011**, *510*, 165) were optimized at the MP2/CBS(XZ,YZ) + $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$/NZ level of theory (denoted as CCSD(T)/[XYZ; δ:NZ]; XYN = TQD, TQT, Q5T). Similar computations were performed using the heavy-aug-cc-pVXZ basis sets, i.e. CCSD(T)/[haXYZ; δ:haNZ]; XYN = TQD, TQT, Q5T. Bond lengths and angles of the resulting geometries were compared to those of reference geometries optimized at CCSD(T)/ha6Z (J. Chem. Phys. **2016**, *145*, 104101). All methods (on average) overestimate bond lengths and underestimate bond angles. Overall, CCSD(T)/[haTQZ; δ:haTZ] provides benchmark quality geometries for the best cost of the methods that were evaluated, albeit with some exceptions involving second row elements.

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The Prototypical Transition Metal Carbenes: $(CO)_5Cr{=}CH_2$, $(CO)_4Fe{=}CH_2$, and $(CO)_3Ni{=}CH_2$

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Abstract: Transition metal carbene complexes have received interest in the field of organometallic chemistry due to their potential for use as catalysts in carbon-carbon bond forming reactions. Here, we present a density functional study of the most prototypical of such carbenes, these methylene-substituted transition metal carbonyls. These complexes have not been synthesized experimentally. Five functionals (B3LYP, BP86, M06-L, ωB97X, and ωB97X-D) were utilized along with a cc-pVTZ basis to obtain structures and dissociation energies. In addition, bonding analysis was performed to gain insight into the nature of the metal-carbene double bond.

Benchmark Comparison of Docking Protocols for Discovery of Receptor-Targeted Drugs

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Abstract: G protein coupled receptors (GPCR) are of interest in anticancer drug development due to their involvement in cell survival processes. Molecular docking studies are an effective tool to generate information about ligand-receptor interactions as a part of early stage drug discovery. Lysophosphatidic acid receptor 2 (LPA_2) is a receptor associated with cell survival processes. Ligands that interact with and block the activity of the LPA_2 receptor, known as antagonists, are therefore of interest as pre-clinical candidates for cancer therapy. We utilized a set of known LPA_2 antagonists with experimentally determined potencies as a benchmark data set in order to select appropriate parameters for docking studies to be applied in future studies aimed to prioritize untested antagonist candidates for experimental screening. Docking parameters explored include the forcefield and scoring method. Several compounds in the set have the potential to tautomerize or ionize under the assay conditions, so docking studies on multiple forms were applied to predict the bioactive forms. One compound additionally had unknown stereochemical configurations, requiring that multiple stereoisomers be docked to identify the isomer most consistent with the experimental potency. Through our docking studies, we determined the parameters that give docking results comparable to experimental data. This is our first step in progressing towards developing a prioritized list of antagonist candidates for potential drug development.

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Actinide +3 and +4 Aqueous Hydrolysis Reactions: Initial Steps in Actinide Aggregation

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Abstract: The properties of nanocolloids of the actinides give rise to promising applications in the design of new fuels for advanced nuclear reactors. The tri- and tetra-valent actinides exhibit extensive hydrolysis and condensation behavior due to their high charge density and acidity. Proton transfer reactions play an important role in colloidal particle formation, especially the initial steps. Electronic structure calculations were used to predict the properties of metal +4 cations embedded in water as well as the structures generated by loss of protons. We are predicting the thermodynamic properties of water/hydroxide clusters of Cf and Bk in the +3 and +4 formal oxidation states. This provides insights into the solvation structure including the size of the first solvation shell and the acidity, the pK_a. The calculations were done by using density functional theory including relativistic effects with effective core potentials. The behavior of these monomers in aqueous solution is studied using COSMO as a solvation method to enable the calculation of aqueous pK_a's. The work was supported by the DOE Office of Science, Basic Energy Sciences.

Full-dimensional, *ab initio* many-body potential energy and dipole moment surfaces for hydrated proton

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Abstract: We report full-dimensional, *ab initio* many-body potential energy surface (PES) and dipole moment surface (DMS) of hydrated proton. The PES is truncated at the three-body level using *ab initio* hydronium, Zundel and water potential energy surfaces. A new hydronium-water-water (h-w-w) 3-body interaction is also included in the PES based on around 50000 CCSD(T)-F12/aVDZ energies. The DMS is constructed from one- and two-body dipole moments using Zundel, water and newly fitted hydronium dipole moment surfaces. Both geometry optimization and harmonic frequency analysis of ${H_7O_3}^+$ and ${H_9O_4}^+$ are done using PES and high level *ab initio* method. The PES is shown to be very accurate in describe the vibrational motions of these typical protonated water clusters. Applying weighting method to assign hydronium core, the PES can also be used for representing the potential of Zundel-like structures including bare ${H_5O_2}^+$, ${H(H_2O)_6}^+$ and ${H(H_2O)_8}^+$, as well as the proton transfer process. We also present vibrational spectra of ${H_7O_3}^+$, ${H_9O_4}^+$[1] and their fully deuterated molecules. These spectra have very good agreement with experiments and our calculation can provide detailed explanations for the "mysterious" infrared spectrum[2][3].

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Benchmarking of Spin-Orbit Coupling via Four-Component Relativistic Methods

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Abstract: Among current electronic structure methods, fully relativistic four-component (4c) methods based on the Dirac Hamiltonian treat spin-orbit coupling with the most rigorous approach, as spin treatment arises naturally from the formulation and does not need to be included in an *ad hoc* manner. Spin-orbit splittings can provide an insightful benchmark criteria for the assessment of 4c methods available. However, there has not been extensive studies on this due to the computationally demanding nature of relativistic methods. Using the newly implemented fully relativistic methods in BAGEL, spin-orbit splittings of period 2-5 p-block elements were calculated using 4c-CASSCF, 4c-CASPT2, and 4c-MR-CISD+Q methods with uncontracted Dunning basis sets. Comparison with experiment reveal that while 4c methods give quantitatively correct results they do not consistently yield spectroscopic accuracy for p-block elements.

Recent developments in the projector configuration interaction method

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Abstract: The projector configuration interaction (PCI) method has been reported as a robust and deterministic method for application to strongly correlated electrons [1]. We report recent developments that focus on improving the accuracy and convergence rate of the PCI. First, we designed an algorithm to compute more accurate energy and wave function without increasing computational cost by implementing a Hermitian version of the PCI method. Second, to overcome the linear convergence limit of polynomial projection method, we combined the PCI with Davidson–Liu eigenvector solver to accelerate convergence. With these improvements, the PCI shows less than half of the non-parallelism error in the previous non-Hermitian algorithm and three times faster convergence to the ground state than the conventional polynomial projection scheme in benchmarking the N_2 dissociation potential energy curve.

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Exploring n-body Effects in the Many-Body Expansion

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Abstract: Computational chemistry is a valuable tool, but expanding its capabilities to include larger systems as are desirable in biological, solid state, and solution study applications is difficult due to the computational complexity. Often, quantum mechanical accuracy is sacrificed by utilizing smaller basis sets, reduced levels of theory, or even molecular mechanics. In hopes of maintaining high level quantum mechanical theory, fragment based schemes have been introduced where calculations on large systems are replaced by a larger number of calculations on smaller systems.

Here, the many-body expansion (MBE) with a Valiron-Mayer function counterpoise (VMFC) correction is studied using pentamer geometries in order to build on previous works where the maximal truncation order was less than 5 in order to seek a definitive answer for the truncation order of the MBE. Diverse chemical systems were studied ranging from completely nonpolar (methane), to moderately polar (formamide), to highly polar (hydrogen fluoride). Of course, water structures are present as well, and the total number of systems fully studied with DFT, MP2, and CCSD(T) is 15. These 15 systems were studied using complete basis set (CBS) extrapolated frozen natural orbital (FNO) CCSD(T) theory, MP2/a(Q5)Z+ΔCCSD(T)/a(XY)Z, where Y is aug-cc-pVQZ for over half of the systems, with the rest of the systems having a maximal coupled cluster basis of aTZ or aDZ. DFT calculations were carried out with five functionals for all geometries in order to compare the accuracy to the VMFC results. These pentamer geometries were created by removing a subset of 5 molecules from crystal structures — additionally, water, HF, CO_2, and Ar cluster global minimum geometries were assessed in order to test the VMFC scheme with optimal geometries.