

Quantum Chemistry without Wavefunctions

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Abstract: Complete active space self-consistent field (CASSCF) methods are enormously important in quantum chemistry, as they allow for the description of states dominated by more than one electronic configuration. In CASSCF, the electronic structure of the active space is often represented by a configuration interaction (CI) expansion of the active-space wave function. Unfortunately, the exponential complexity of the full CI wave function severely limits the size of the active space that can practically be considered. For a large-active-space CASSCF algorithm, one must abandon CI in favor of an approach with more desirable scaling properties, such as the density matrix renormalization group (DMRG) or variational two-electron reduced-density method (v2RDM) methods. Using state-of-the-art semidefinite programming techniques and density-fitting approximations, we have developed a v2RDM-driven CASSCF procedure that can treat active spaces with 50 electrons in 50 orbitals and the simultaneous optimization of nearly 2000 orbitals. Analytic gradients are also available for the approach, and v2RDM-CASSCF-optimized bond lengths typically agree with those from configuration-based approaches to within a few hundredths of an angstrom. Lastly, excited electronic states can also be obtained within the v2RDM-CASSCF framework using an extended random phase approximation. However, a proper treatment of excitations from degenerate ground states requires the consideration of pure-state N -representability conditions.

New primitive Gaussians based on per electron energy convergence criteria

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Abstract: Even the simplest electronic structure calculation depend on the proper choice of two parameters, namely level of theory and basis set, and they can be equally important in obtaining meaningful and accurate answers. Notwithstanding the central role of correlation energy in high-accuracy calculations, Pople-style[1] and correlation consistent,[2] arguably the most popular basis sets, are based on theories with well-known deficiencies in the description of the correlation phenomenon. The former is optimized at the SCF level, that is, it does not come from a correlated method, while the latter depends on truncated configuration interaction (CISD) calculations, a non-size extensive method. On the other hand, coupled cluster (CC) not only does not suffer from these drawbacks but also surpasses CI analogs in their capacity of recovering correlation energy.[3] However, CC methods had not been employed in the development of new basis sets until recently, where they were used in conjunction with the atomic natural orbital (ANO) procedure to generate superior contraction coefficients from the primitives found in the correlation consistent bases.[4] These primitive sets are constructed by the addition of Gaussian functions that recover approximately the same amount of correlation energy, and it is assumed that the same number of primitives is suitable to treat all atoms in a given row of the periodic table. Here, we turn to a convergence criterion that is based on the energy improvement per electron, instead of the total energy recovery per additional primitive. The *sp* primitives are calculated from an optimized degree 5 Legendre polynomial for improved convergence,[5] while the polarization functions (*d* and higher angular momentum) come from optimized even-tempered expansions at the MBPT(2) level, which are shown to yield very similar results to CCSD(T) in terms of optimized exponents. The new primitive sets are converged within each angular momentum shell to a predetermined energy threshold per electron in the total CCSD(T) energy upon addition of extra functions for a given angular momentum.

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Tools for the Computational Design of Asymmetric Catalysts

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Abstract: The development of new catalysts for asymmetric organic reactions typically proceeds by the experimental screening of potential new designs. This requires the synthesis and testing of many catalysts that will ultimately prove ineffective. We envision an alternative approach to catalyst development driven by the computational screening of virtual libraries of potential designs. Toward this end, I will describe a Perl module (AaronTools) that provides functions for building, manipulating, and analyzing molecular and supramolecular structures, creating input files and parsing output files from popular electronic structure packages, and interacting with common batch queuing systems. I will also introduce a computational toolkit built using these tools (AARON: An Automated Reaction Optimizer for New catalysts) that automates the optimization of the 100s of transition state and intermediate structures needed to predict stereoselectivities of complex asymmetric organic reactions.^[1-2] Illustrative examples of the application of AARON will be presented,^[3] along with a brief summary of the latest developments.^[4]

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Electron correlation methods for near-degenerate electronic states based on the driven similarity renormalization group

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Abstract: We have recently demonstrated that it is possible to combine conventional Quantum Chemistry many-body approaches with flow renormalization group methods to produce a new family of electronic structure theories. These methods have several advantages: (i) they are numerically-robust and avoid intruder states, (ii) they lead to equations that are relatively simple, and (iii) they are easily generalized to multi-determinantal reference states. An important aspect of our work has been to reformulate the similarity renormalization group (SRG) of Głazek and Wilson and Wegner [1,2] into a practical quantum chemistry approach, the *driven* SRG (DSRG) [3]. Recently, we examined new approximation schemes for the DSRG that are both accurate and economical. This talk will focus on second- and third-order perturbative approximations of the DSRG [4,5] equations and their generalization to treat near-degenerate ground and excited states.

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PSI4NUMPY: An Interactive Quantum Chemistry Programming Environment for Reference Implementation, Rapid Development, and Education

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Abstract: A cornerstone of the development of novel quantum chemistry methods is the translation of paper-and-pencil theory into an efficient computer program. To do this, low-level programming languages are typically employed; however, such implementations tend to be convoluted, as raw speed is the focus rather than either readability or reproducibility. Any attempt at re-implementation must then proceed with the originally published equations as the only reference, whereby critical programming details must be re-discovered through a similarly heroic effort to the original implementation. To address these issues, the PSI4NUMPY project [1] leverages the PSI4 quantum chemistry package and the Numerical Python (NUMPY) library to create an interactive quantum chemistry programming environment for reference implementations, rapid development, and education. This environment allows for quantum chemistry-specific quantities computed with PSI4 and strided tensor manipulations performed with NUMPY to be called directly from within the high-level Python programming language. Therefore, implementations of novel methods may be developed quickly and programmed concisely, while maintaining a relatively low execution time. Provided as a series of short Python scripts, reference implementations for a variety of popular quantum chemistry methods (including Hartree–Fock, Møller–Plesset, coupled cluster, electron propagator, and symmetry-adapted perturbation theories) address the community need for clear, readable programs which disseminate the details of such methods’ implementation. Additionally, interactive tutorials discussing both the theory and implementation of these methods and others offer a unique educational framework for novice and experienced quantum chemists alike.

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The Molecular Sciences Software Institute

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Abstract: The Molecular Sciences Software Institute (MolSSI) is a nexus for science, education, and cooperation serving the worldwide community of computational molecular scientists — a broad field including of biomolecular simulation, quantum chemistry, and materials science. The Institute, which was recently funded by the National Science Foundation as part of the White House’s National Strategic Computing Initiative, will spur significant advances in software infrastructure, education, standards, and best-practices that are needed to enable the molecular science community to open new windows on the next generation of scientific Grand Challenges, ranging from the simulation of intrinsically disordered proteins associated with a range of diseases to the design of new catalysts vital to the global chemical industry and climate change. The MolSSI will enable the computational molecular science community to work together to leverage its diverse capabilities that will reduce or eliminate the gulf that currently delays by years the practical realization of theoretical innovations. Ultimately, the Institute will enable computational scientists to tackle problems that are orders of magnitude larger and more complex than those currently within our grasp. This lecture will provide an overview of the Institute’s structure, goals, and vision.

Interactions of CO₂ with metal organic frameworks and metal oxide nanoclusters

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Abstract: Acid gases, especially CO₂, play an important role in a range of large-scale energy applications. Acid gas conversion can make use of reactive sorbents and catalysts, but these materials must not substantially degrade under operating conditions. Metal oxides, metal organic frameworks, and clays may be used for these purposes, but interactions of acid gases with these complex materials are poorly understood. In order to improve our understanding of such materials, we have been using electronic structure methods to better understand these interactions in terms of ‘physisorption’ and ‘chemisorption’ type processes. The interactions of CO₂ with models of MOF-2 (M₂BDC₄ for M = Co²⁺, Cu²⁺, and Zn²⁺), Group II oxide nanoclusters, Group IV and Group VI transition metal oxide nanoclusters, and actinide oxides have been predicted with density functional theory benchmarked by correlated molecular orbital theory calculations at the CCSD(T) level. The results are being correlated in terms of molecular properties such as Lewis acidities, redox capability, bond energies, and complexation energies. The work is supported by the Department of Energy, Basic Energy Sciences EFRC (UNCAGE-ME) and Geochemistry programs.

Interaction of Atomic Oxygen with Ag(111) and Ag(110) Surfaces: Oxygen Adsorption and Kinetics at Surface versus Subsurface

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Abstract: Transition metals are commonly used to catalyze transformations of small organic compounds, but the mechanisms of these catalytic reactions are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions on silver surfaces, the role of subsurface oxygen (oxygen adsorbed just beneath the surface) in surface reconstruction and oxidative catalysis by silver has yet to be elucidated. Does subsurface oxygen affect catalysis by changing the electronic and geometric properties of silver, or does it emerge to the surface to directly interact with reactants? Does it initiate or promote surface reconstructions of silver? Does the participation of subsurface oxygen change with reaction conditions, such as surface structure, surface temperature, and oxygen coverage? Answers to such questions will promote a deeper mechanistic understanding of heterogeneous catalysis by silver, and help to design more effective industrial catalysts. In the present study, density functional theory (DFT) was used to probe the interactions of atomic oxygen with the surface and subsurface of Ag(111) and Ag(110) surfaces. The goal was to investigate the adsorption and kinetics of surface and subsurface oxygen at different coverages on the metal surfaces, and examine their effects on the structural and catalytic properties of silver. On the Ag(111) surface, it was found that both surface and subsurface adsorption energies decreased with oxygen coverage, but surface adsorption weakened more drastically than subsurface adsorption, resulting in oxygen binding more strongly to the subsurface than to the surface at coverages above 0.5 ML. In contrast, surface adsorption remained stronger than subsurface adsorption at higher coverages on the Ag(110) surface. Calculations also show that kinetic barriers for formation of subsurface oxygen or its emergence into the surface are strongly dependent on coverage, indicating that the direct participation of subsurface oxygen in catalysis might strongly depend on coverage. Overall, our results provide valuable insight into the competition between adsorption and kinetics of oxygen on different facets of the silver surface, the importance of charge transfer in the binding and motion of atomic oxygen on silver, and the role of subsurface oxygen in catalysis by silver.

Two-step model of ultrafast interfacial electron transfer in dye-semiconductor assemblies

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Abstract: Interfacial electron transfer (IET) is one of the steps in light-harvesting process that occurs in various assemblies for solar energy conversion, such as dye-sensitized solar cells or dye-sensitized photoelectrosynthesis cells. This work investigates IET in a model pyridine-TiO₂ assembly, with the goals to assess the validity of the Fermi's golden rule for calculation of the IET rates, understand the importance of conformational sampling in modeling the IET process, and establish an approach to rapid computational screening of dye-sensitizers that undergo fast IET into the semiconductor. Our results suggest that IET is a two-step process, in which the electron is first transferred into the semiconductor surface states, followed by the diffusion of the electron into the nanoparticle bulk states. Furthermore, while Fermi's golden rule and related approaches are appropriate for predicting the initial IET rate (i.e., initial transfer of electron from dye into the semiconductor surface states), they are not reliable for prediction of the overall IET rate. Inclusion of the conformational sampling at room temperature into the model offers a more complete picture of the IET process, leading to a distribution of IET rates with the median rate faster than that of the IET rate obtained for the fully-optimized structure at 0 K. Finally, the two most important criteria for determination of the initial IET rate are the percent of electron density on linker in the excited state as well as the number of the semiconductor acceptor states available at the energy of the excited state. Both of these can be obtained from relatively simple electronic structure calculations either at *ab initio* or semiempirical levels of theory and can be thus used for rapid screening of dyes with desired properties.

Theoretical studies of phosphoryl transfer enzymes

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Abstract: The mechanisms of phosphoryl transfer enzymes have garnered considerable attention. Fluoro-containing metal species have been used as transition-state and ground-state analogues in a variety of phosphoryl transfer enzymes and have shed light on the nature of the requirements in the active site to catalyze phosphoryl transfer. Some of our work on phospholipase D (PLD), tyrosyl-DNA phosphodiesterase I (Tdp1), human histidine triad nucleotide binding protein 1 (hHINT1), fructose-1,6-bisphosphatase (FBP), cyclic adenosine monophosphate dependent protein kinase (cAPK), and β -phosphoglucomutase (β -PGM) will be discussed.

CAM-LDA0: The Reincarnation of the Local Density Approximation

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Abstract: Kohn-Sham Density Functional Theory (KS-DFT) is the most popular electronic structure method applied throughout science and engineering. The exchange-correlation (XC) local density approximation (LDA) was the earliest density functional used to investigate the electronic structure of chemical systems in KS-DFT. Since then, the LDA has been the bedrock of the field of density functional development. In this contribution, we discuss the roles of the non-local exchange and the local-density approximation in the improvement of the quality of the fundamental gap, and in the enhancement excitation-energy estimations. We suggest that the combination of these two concepts is dominant for the calculation of excitation energies of molecules in the optical regime and beyond. As an illustration of the wide range of possibilities created by our work, we report CAM-LDA0: a three-parameter functional, with 1/4 global and 1/2 long-range Hartree-Fock interaction, respectively; a range separation factor of 1/3; and pure LDA exchange and correlation. We show that CAM-LDA0 matches the accuracy of CAM-B3LYP for electronic excitations, with the advantage of reduced computational cost due to the omission of the generalized-gradient corrections. These findings have been recently reported in the *The Journal of Physical Chemistry A* [1].

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Why Computational Chemists Should Not Be Ignored: The Effect of Ether and Amine Bridges in the Conjugation of Monomacrocylic 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 goals of an experimental research group at my institution 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 experimental group has been synthesizing “flat” dendrimers that they think 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 monomacrocylic dendrimer is formed. The experimental group has successfully created a monomacrocylic 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 ω B97XD. 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.

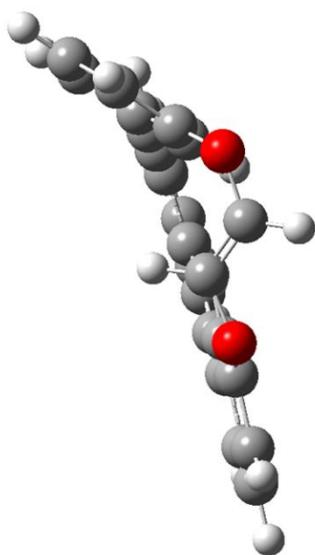


Figure 1: Benzenes with Meta Diethynyl Bridge

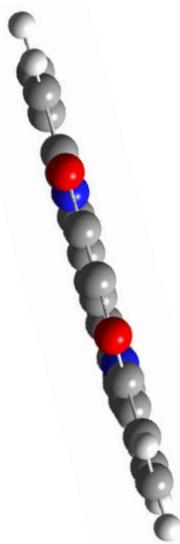


Figure 2: Pyridines with Meta Diethynyl Bridge

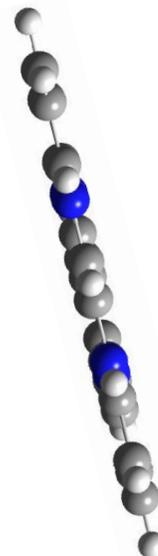


Figure 3: Pyridines with Meta Alkenyl Diamino Bridge

Thermochemistry: Not as Boring as You Might Think

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Abstract:

Developed during the last decade by Ruscic and collaborators at Argonne National Laboratory, Active Thermochemical Tables (ATcT) represents an entirely new and revolutionary way to approach the subject of thermochemistry. Traditional thermochemistry has advanced piecemeal and willy nilly, through individual spectroscopic, kinetic, calorimetric, etc. measurements often supplemented by ‘recommendation of ‘standard (in the non-thermodynamic sense) through the actions of various critical review committees (NIST-JANAF, CODATA, etc.). In contrast, ATcT is a holistic approach that views each molecule as connected in principle to all other species through within constructs called thermochemical networks. In ATcT, thermochemical parameters such as bond energies, ionization potentials, and enthalpies of formation are solved for self-consistently using all available relevant information. Many bond energies once known to, say, a few kcal mol⁻¹ have now been established with a precision that is at least an order of magnitude better than before, which clearly has enormous practical consequences for modelling studies. This talk reviews the surprisingly interesting topic of where do these heats of formation come from? and outlines the basic ideas in ATcT. Due to the high interconnectedness of many chemical species through the thermochemical network paradigm, it transpires that knowing any individual property (say, an ionization potential) can potentially impact properties of any number of different species. Hence, there is virtue to constantly improving our knowledge of fundamental molecular properties that goes well beyond just putting another decimal place on it. ATcT actively seeks accurate measurements and calculations for key quantities, which will be illustrated by a recent study of the photoelectron spectrum of hydrogen peroxide

An economical theory for chemical bonding

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Abstract: The last hundred years chemists have come up with several effects to explain the chemical bonding. A list of the most common ones include hybridization, hypervalency, hyperconjugation, aromaticity, resonance, electronegativity, and different kinds of orbitals such as bonding, anti-bonding, non-bonding, HOMO, LUMO, SOMO, etc. Each of these theories is appropriately designed to describe a specific group of molecular systems, and may cause confusion or rise contradictions when applied to different systems. The ongoing discovery of "exotic" species urges an economic and clear theory which can explain the bonding in terms of the electrostatic forces and spin coupling. We presently show that the two principles "molecules are made of atoms" and "atoms bear excited electronic states" are sufficient to account for every chemical bond. Here we focus on the case of beryllium oxides, transition metal complexes such as $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{N}_2)_6$, and "hypervalent" compounds.

Excited State Transition Energies and Properties in Solution from a Smooth Dielectric Model

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Abstract: A quantum mechanical solvation model is presented for a solute embedded in a polarizable dielectric medium, where the solute cavity is determined from an electronic isodensity surface in a smooth two-parameter model previously implemented in plane-wave-based density functional theory computations. In this work, solvent-solute interactions are incorporated into a Hartree-Fock framework and captured via numerical solution of the nonhomogenous Poisson equation on a real-space grid through an interface between PSI4 and the DL_MG multigrid solver library. The method is applied here to compute excited state transition energies and properties with the equation-of-motion coupled-cluster singles and doubles method (EOM-CCSD). Results are presented for solvated water, as well as formaldehyde, acetone and *trans*-acrolein, which have low-lying $n \rightarrow \pi^*$ transitions and associated blue shifts in aqueous solution. Comparisons are made with other theoretical approaches, including popular implicit solvation models and QM/MM methods, in addition to available experimental data.

Folding Mechanisms of Small Proteins GB1 and LB1

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Abstract: The B1 domains of protein G (GB1) and protein L (LB1) are two small proteins that bind to antibody immunoglobulin G (IgG). GB1 and LB1 are similar in size (about 60 residues), and also have an overall similar structure (β -hairpin-- α -helix-- β -hairpin). However their sequences are very different, possessing only 15% identity in a structure-based alignment [1,2]. Therefore, there are interesting comparisons in their folding mechanisms. Experimental evidence indicates that LB1 folds in a two-state manner; while GB1 folds in a more complex way -- an early stage intermediate may exist in the folding path. The folding mechanisms are still under extensive experimental and computational study. Here, we used a new all-atom structure-based method to investigate the folding mechanisms of GB1 and LB1. In this approach, folded structures of the two proteins were used to construct the restraints and they are stabilized by Lorentzian attractive term instead of conventional harmonic term [3]. We presume that our model will be able to identify two-state and non-two-state proteins, and give more insights on their folding pathways.

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A Direct Measure of Metal-Ligand Bonding Replacing the Tolman Electronic Parameter

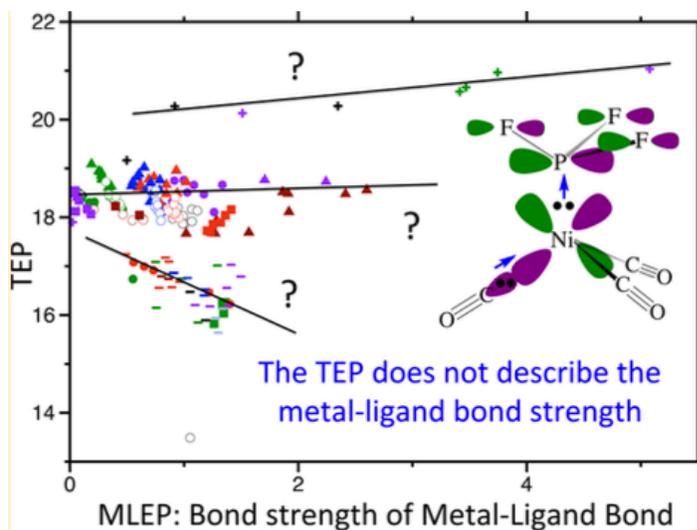
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Abstract: The prediction of the catalytic activity of transition metal complexes is a prerequisite for homogeneous catalysis. The Tolman Electronic Parameter (TEP) was derived to provide this information. It is based on the CO stretching frequencies of metal-tricarbonyl complexes $L-M(CO)_3$ with varying ligands L. It has been used in hundreds of cases as is documented by as many publications.

We show [1] that the TEP is misleading as *i*) it is not based on mode-decoupled CO stretching frequencies and *ii*) a quantitatively correct or at least qualitatively reasonable relationship between the TEP and the metal-ligand bond strength does not exist. This is demonstrated for a set of 181 nickel-tricarbonyl complexes using both experimental and calculated TEP values. Even the use of mode-mode decoupled CO stretching frequencies does not lead to a reasonable description of the metal-ligand bond strength.

A reliable descriptor replacing the TEP is obtained with the help of the metal-ligand local stretching force constant. For the test set of 181 Ni-complexes, a direct metal-ligand electronic parameter (MLEP) in the form of a bond strength order is derived, which reveals that phosphines and related ligands (amines, arsines, stibines, bismuthines) are bonded to Ni both by σ -donation and π -back donation. The strongest Ni-L bonds are identified for carbenes and cationic ligands. The new MLEP quantitatively assesses electronic and steric factors and it can be determined for any metal or transition metal complex, whether it contains CO ligands or not.



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Density Functional Theory Method for Nondynamic/Strong Correlation

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Nondynamic and strong correlation imposes the major challenge to the current density functional theory (DFT), and counts for the majority of the failures of DFT in a variety of areas such as catalysis, organic open-shell molecules and materials. The problem is often characterized as multireference in nature. In this talk, we will present a density functional model based on single-determinant Kohn-Sham density functional theory [1]. It combines Becke'13 method with a new model for kinetic correlation via adiabatic connection based on physical arguments and some exact conditions for both the weak and strong correlations. The result is a single-term functional for correlation of all strength, and is named as KP16/B13 (Kong-Proynov'16/Becke'13). KP16/B13 is the first model of its kind implemented with self-consistent field. The preliminary results show that the model, with only three empirical parameters, recovers the majority of left-right nondynamic/strong correlation upon bond dissociation and performs well for near equilibrium properties such as heats of formation, singlet–triplet energy splittings of diradicals. It also describes well a linear chain of H atoms with many strongly correlated electrons. The new development offers the hope for efficient computation of systems with multireference in nature.

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Resonance Energies and Lifetimes from Extrapolation Methods: Robust Algorithms and a Critical Analysis

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Abstract:

An electronic resonance is an electronic state of an $(N + 1)$ -electron system that lies energetically above the N -electron system, and therefore in the scattering continuum of the N -electron state. Examples are temporary anions such as N_2^- , the Be^- , or the benzene anion, small dianions in the gas phase such as CO_3^{2-} or SO_4^{2-} , core-ionized atoms and molecules decaying via the Auger process, and the Auger-like decay of inner-valence ionized clusters. Resonances are characterized by their so-called resonance position, E_r , that is, the energy above the N -electron state, and by their width, Γ , which plays—cum grano salis—the role of a first-order decay constant. In other words, there is a typical decay time, $\tau = \hbar/\Gamma$, which is inversely proportional to the width.

Characterizing a resonance with standard—or at least more or less standard—quantum chemistry methods is a challenge. If a standard basis set is used, the continuum is so poorly described that any description of the decay is suppressed, because the excess electron is effectively trapped in a basis set box. Using more and more diffuse functions gives a better and better discretization of the continuum, however, then the resonance state mixes with the continuum states, and from a straightforward calculation one obtains at best a rough idea of the resonance position but at worst the lowest energy of the discretized continuum. Almost from the beginning of computational chemistry, various so-called L^2 -methods have been put forward to address this challenge. All L^2 -methods have one thing in common: The original Hamiltonian is parametrized, and E_r and Γ are extracted from a study of the behavior of the eigenvalues of the parametrized Hamiltonian as functions of the parameter. One example are extrapolation methods. Here an artificial stabilizing potential is added to the Hamiltonian, the stabilization is increased until the resonance state is turned into a bound state, and then further increased until enough bound state data have been collected so that these can be extrapolated back to vanishing stabilization. The lifetime of the resonance can be obtained from the same data, but only if the extrapolation is performed by analytic continuation (ACCC). Here we outline progress regarding the ACCC method, and critically examine the dependence of the results on the following: The artificial stabilizing potential used in the data collection step, different ACCC variants, and the energy-range of input data for the extrapolation.

Can We Find Interstellar Nitrogen Hiding in Exotic Molecules?

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Abstract: The nitrogen molecule is one of the most strongly bound systems known. It also makes up a vast majority of the Earth's atmosphere. However, the origin of this molecule in the atmosphere is still largely unknown. Is the nitrogen primordial to the Earth or was it formed through biological or geological processes? One way to find out is through observation of stellar systems similar to the early solar system. The chief issue is that N_2 is not observable through vibrational or rotational means due to a lack of a permanent or induced dipole moment, and electronic observation is difficult to quantify. As a result, molecular tracers must be observed, instead. Dinitrogen bonds are notoriously unstable making laboratory synthesis and observation is difficult for such species. However, quantum chemical techniques are not hampered in such ways making them ideal for spectral prediction and structural analysis. This work will discuss the structure, binding, and relative energetics of the $NNHNN^+$, $NN-HCO^+$, and $CO-HNN^+$ proton-bound complexes where the proton-shuttle motion is exceptionally bright. Additionally, the rovibrational spectra and relative energies of $HNNS$ radicals will be described where previous work has predicted these species to be intermediates in the formation of N_2 and the recently observed SH radical.

Proton-Bound Complexes: A Major Challenge for Vibrational Analysis

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Abstract: I will review a general approach to develop and employ full-dimensional potential and dipole moment surfaces in VSCF/VCI calculations of highly-coupled vibrational motion in proton-bound complexes. Examples include the proton-bound N_2 [1] and CO[2] dimers and proton-bound water clusters, $H_7O_4^+$ and $H_9O_4^+$. [3] A controversy about the latter “Eigen” complex will be addressed, as it points out some limitations of “*ab initio* molecular dynamics” approaches to IR spectroscopy.

References

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Core-Hole Initiated Charge Migration with TDDFT

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Abstract: Attosecond electron dynamics in molecules underpins a range of important processes such as light harvesting, photochemistry, and ultrafast spectroscopy. Modeling these dynamics from first principles is important for predicting and interpreting ultrafast experiments. In the case of large molecules, however, correlated techniques can be prohibitively expensive. Here, time-dependent density functional theory (TDDFT) offers a promising alternative, but limitations in the exchange-correlation functional, especially the adiabatic (local-in-time) approximation limit the accuracy of the results.

In this talk, I will present a study demonstrating the validity of TDDFT for core-hole triggered charge migration in nitrosobenzene. Specifically, by initializing the system with an unambiguous initial state (a nitrogen K-edge core-hole), real-time TDDFT with hybrid functionals captures hole migration across the molecule with accuracy comparable to ADC(4) [1]. These results suggest that given an initial state that is a good reflection of a molecule after interaction with an exciting or ionizing pump field, adiabatic TDDFT adequately captures the dynamics.

References

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