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Electronic Structure Theory for Spin-Forbidden Reaction Dynamics

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14. ABSTRACT
This project included theoretical studies of electronic structure methods development and light-mediated chemistry. Included in the electronic structure component of this work is new work on multireference methods that include electron correlation based on the Complete Active Space method with 2nd order Perturbation Theory treatment of electron correlation –CASPT2. One part of this work was concerned with visualizing complex-valued molecular orbitals which arise when spin-orbit coupling, magnetic fields or complex absorbing boundary conditions are included in the Hamiltonian. Another part was concerned with evaluating gradients of energies, and derivative couplings when a complex valued shift is applied to the perturbation theory evaluation. In the light-mediated chemistry studies, we used electronic structure theory to evaluate reorganization energies and related properties for the interpretation of experiments in the Emily Weiss group in which the “Marcus Inverted” regime for triplet-triplet energy transfer was observed for the first time. Also, we developed the first fully retarded quantum electrodynamics treatment of plasmonic excitation in spherical nanoparticles.

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Abstract (250 words)

This project included theoretical studies of electronic structure methods development and light-mediated chemistry. Included in the electronic structure component of this work is new work on multireference methods that include electron correlation based on the Complete Active Space method with 2nd order Perturbation Theory treatment of electron correlation –CASPT2. One part of this work was concerned with visualizing complex-valued molecular orbitals which arise when spin-orbit coupling, magnetic fields or complex absorbing boundary conditions are included in the Hamiltonian. Another part was concerned with evaluating gradients of energies, and derivative couplings when a complex valued shift is applied to the perturbation theory evaluation. In the light-mediated chemistry studies, we used electronic structure theory to evaluate reorganization energies and related properties for the interpretation of experiments in the Emily Weiss group in which the "Marcus Inverted" regime for triplet-triplet energy transfer was observed for the first time. Also, we developed the first fully retarded quantum electrodynamics treatment of plasmonic excitation in spherical nanoparticles.

Report:

There were a total of 5 papers published based on this research, representing 5 projects concerned with theory development and its applications to leading edge problems in molecular electronic structure and dynamics, and to the interaction of light with semiconductor or metallic nanoparticles. The content of each of these papers is described below.

1. Visualizing Complex-Valued Molecular Orbitals
Al-Saadon, Rachael; Shiozaki, Toru; Knizia, Gerald
JOURNAL OF PHYSICAL CHEMISTRY A 123 3223-3228 (2019)

This paper reports an implementation of a program for visualizing complex-valued molecular orbitals. The orbital phase information is encoded on each of the vertices of triangle meshes using the standard color wheel. Using this program, we visualized the molecular orbitals for systems with spin-orbit couplings, external magnetic fields, and complex absorbing potentials. Our work has not only created visually attractive pictures but also clearly demonstrated that the phases of the complex-valued molecular orbitals carry rich chemical and physical information on the system, which has often been unnoticed or overlooked.

2. Imaginary Shift in CASPT2 Nuclear Gradient and Derivative Coupling Theory
Park, JW; Al-Saadon, R; Strand, NE; Shiozaki, T

JOURNAL OF CHEMICAL THEORY AND COMPUTATION, 15, 4088-4098 (2019)

This paper reports the analytical nuclear gradient theory for complete active space second-order perturbation theory (CASPT2) with imaginary shift, which is commonly used to avoid divergence of the perturbation expression. Our formulation is based on the Lagrangian approach and is an extension of the algorithm for CASPT2 nuclear gradients with real shift. The working equations are derived and implemented into an efficient parallel program. Numerical examples are presented for the ground- and excited-state geometries and conical intersections of a green fluorescent protein model chromophore, p-HBDI-. We also report timing benchmarks with adenine, p-HBDI-, and iron porphyrin. It is demonstrated that the energies and geometries obtained with the imaginary shift improve accuracy at a minor additional cost which is mainly associated with evaluating the effective density matrix elements for the imaginary shift term.

3. Multireference Electron Correlation Methods: Journeys along Potential Energy Surfaces
Park, JW; Al-Saadon, R; MacLeod, MK; Shiozaki, T; Vlaisavljevich, B
CHEMICAL REVIEWS 120, 5878-5909 (2020)

Multireference electron correlation methods describe static and dynamical electron correlation in a balanced way and, therefore, can yield accurate and predictive results even when single-reference methods or multiconfigurational self-consistent field theory fails. One of their most prominent applications in quantum chemistry is the exploration of potential energy surfaces. This includes the optimization of molecular geometries, such as equilibrium geometries and conical intersections and on-the-fly photodynamics simulations, both of which depend heavily on the ability of the method to properly explore the potential energy surface. Because such applications require nuclear gradients and derivative couplings, the availability of analytical nuclear gradients greatly enhances the scope of quantum chemical methods. This review focuses on the developments and advances made in the past two decades. A detailed account of the analytical nuclear gradient and derivative coupling theories is presented. Emphasis is given to the software infrastructure that allows one to make use of these methods. Notable applications of multireference electron correlation methods to chemistry, including geometry optimizations summarized at the end followed by a discussion of future prospects.

4. Observation of “Marcus Inverted” Kinetics for Dexter Energy Transfer from a Quantum Dot to a Molecular Acceptor, John W. Rosenberg, Yue Wu, Subhajyoti Chaudhuri, George C. Schatz, and Emily A. Weiss, J. Am. Chem. Soc, (2020) in press.

This paper describes the observation of both “Marcus normal” and “Marcus inverted” regions in a plot of the rate constant for Dexter-type triplet-triplet energy transfer (TTEnT) from a series of CdSe quantum dots (QDs) to 1-pyrenecarboxylic acid (PCA) *vs*. the driving force for the reaction. An inverted region has not been observed for reactions involving electron exchange between QDs and molecules before. A fit of this plot to the classical Marcus equation yields a reorganization energy of 0.14 eV. Electronic structure calculations indicate that the reorganization is primarily attributable to polarization of the solvent rather than nuclear rearrangement of the PCA molecule.

5. Quantum electrodynamics description of localized surface plasmons at a metal nanosphere, Kuniyuki Miwa and George C. Schatz, *arXiv:2007.04233*, 2020.

A canonical quantization scheme for localized surface plasmons (LSPs) in a metal nanosphere is presented based on a microscopic model composed of electromagnetic fields, oscillators that describe plasmons, and a reservoir that describes excitations other than plasmons. The eigenmodes of this fully quantum electrodynamic theory show a spectrum that includes radiative depolarization and broadening, including redshifting from the quasi-static LSP modes, with increasing particle size. These spectral profiles correctly match those obtained with exact classical electrodynamics (Mie theory). The present scheme provides the electric fields per plasmon in both near- and far-field regions whereby its utility in the fields of quantum plasmonics and nano-optics is demonstrated.