2015-16

Joseph O. Hirschfelder Lectures in Theoretical Chemistry

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(Photo)electrocatalysis: Theory and Mechanisms of Charge Transfer at Metal Surfaces

Monday, October 19 2:00 p.m. Room 1315 Chemistry

Efficient electrochemical energy conversion is critical to facilitating clean, efficient electricity generation via fuel cells and likewise generating fuels from (photo)electrocatalysis. The essence of electrochemical energy conversion involves charge transfer excitations. Quantum mechanical simulations of electrochemistry tend to employ density functional theory (DFT), but conventional DFT fails to treat these types of excitations correctly due to exchange-correlation functional limitations. Our embedded correlated wavefunction (ECW) theory will be introduced and then the rest of the talk will be devoted to using this theory to understand (photo)electrochemical reactions at metal surfaces. ECW theory treats charge transfer accurately by properly including exact electron exchange and correlation in a region of interest while the extended metal background is described via periodic DFT, encapsulated in a so-called embedding potential. First, we shall show that ECW theory is able to accurately describe the first step of the oxygen reduction reaction that occurs at fuel cell cathodes, while conventional DFT completely fails, with direct comparisons made to gas-surface dynamics experiments. Second, we shall describe how an unusual form of photoelectrocatalysis can also be captured by this theory, namely plasmon-induced hot electron dissociation of molecules on metal nanoparticles, again with comparison made to experiments.

Renewable Fuels and Chemicals from Photoelectrocatalysis

Tuesday, October 20 11:00 a.m. Room 1315 Chemistry

To maintain our quality of life and to enable people in developing countries to live similarly in the centuries ahead, while simultaneously minimizing harm to the environment, chemists must find ways to cleanly and efficiently capture and convert carbon dioxide into fuels and chemicals, as an alternative to fossil fuel feedstocks. Moreover, we need a source of renewable hydrogen gas for the chemical and biofuels industries to replace the current fossil-fuel-derived processes. There are many daunting challenges to developing efficient strategies to produce renewable fuels and chemicals; we must break down the problem and address each part. My research uses first principles quantum mechanics and statistical mechanics simulations to evaluate key properties of materials and molecules necessary for (photo)electrocatalytic water splitting and carbon dioxide reduction. In this lecture, I will give an overview of our work in this area, touching on transition metal oxide photoelectrocatalytic processes but mainly focusing on investigating mechanistic issues associated with how aromatic amines near GaP electrodes photoelectrochemical reduce CO_2.

Quantum Mechanics without Wavefunctions

Wednesday, October 21 2:00 p.m. Room 1315 Chemistry

Evaluating mechanical properties of lightweight metal alloys for fuel-efficient vehicles, investigating liquid lithium films for fusion reactor walls, and studying charge-discharge cycles of next generation Li-ion battery anodes are three projects that may appear to have nothing in common other than that they could be part of a larger energy research portfolio. However, all three exploit a quantum mechanics method - orbital-free density functional theory (OFDFT) - that directly evaluates electron distributions instead of wavefunctions. This technique is orders of magnitude faster than standard Kohn-Sham DFT because it scales quasilinearly with a small prefactor. As such it can be used to study many thousands of atoms with quantum mechanics, or to perform longer time scale *ab initio* molecular dynamics on smaller samples. Consequently, OFDFT is able to explicitly study, e.g., plasticity in metals and liquid metal dynamics. I will give a brief history of our work in this field and then present our recent advances in OFDFT methods and applications that now furnish accurate treatment of semiconductors and transition metals, extending the reach of OFDFT nearly to the full periodic table.