NON-BORN–OPPENHEIMER EFFECTS BETWEEN ELECTRONS AND PROTONS

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EXECUTIVE SUMMARY:

The quantum mechanical behavior of nuclei plays an important role in a wide range of chemical and biological processes. The inclusion of nuclear quantum effects and non-Born–Oppenheimer effects between nuclei and electrons in computer simulations is challenging. Our group has developed the nuclear–electronic orbital (NEO) method for treating electrons and select nuclei quantum mechanically on the same level using an orbital-based formalism. We used Blue Waters to perform NEO calculations on systems in which all electrons and one proton are treated quantum mechanically. In addition, we have developed a methodology to study the non-adiabatic dynamics of photo-induced proton-coupled electron transfer (PCET) reactions, using grid-based methods to calculate the nuclear wavefunction for the transferring proton, and have applied this methodology to a hydrogen-bonded phenol–amine complex in solution.

INTRODUCTION

The inclusion of nuclear quantum effects such as zero-point energy and tunneling in electronic structure calculations is important in a variety of chemical systems, particularly those involving hydrogen transfer or hydrogen-bonding interactions. Moreover, nonadiabatic effects, also called non-Born–Oppenheimer effects, between electrons and certain nuclei are significant for many of these systems. In this case, the electrons cannot be assumed to respond instantaneously to the nuclear motions, and the concept of the nuclei moving on a single electronic potential energy surface is no longer valid. This type of non-adiabaticity has been shown to play a critical role in proton-coupled electron transfer (PCET) reactions, which are essential for a wide range of chemical and biological processes, including photosynthesis, respiration, enzyme reactions, and energy devices such as solar cells. The development of non-Born–Oppenheimer methods to enable accurate and efficient calculations of PCET reactions will impact many scientific endeavors, from drug design to the design of more effective catalysts for solar energy devices.

METHODS & RESULTS

In the nuclear–electronic orbital (NEO) approach, typically all electrons and one or a few protons are treated quantum mechanically, and a mixed nuclear–electronic time-independent Schrödinger equation is solved. We have recently proposed an ansatz with the primary goal of improving computational tractability to enable the study of larger systems of chemical interest within the NEO framework. In this approach, denoted NEO-RXCHF, only select electronic orbitals are explicitly correlated to the nuclear orbitals, and certain exchange terms are approximated. Additionally, we have proposed a restricted basis set for the electronic orbitals that are explicitly correlated to the nuclear orbitals. The restricted basis set is a subset of the full electronic atomic orbital basis set, and its use results in a large decrease in the number of multi-particle integrals that must be computed and stored during a NEO-RXCHF calculation.

We performed NEO-RXCHF calculations on Blue Waters on HCN and FHF$^-$ and compared the nuclear density of the proton to benchmarking grid-based calculations. The test calculations indicate that the NEO-RXCHF method provides accurate descriptions of the protons that are treated quantum mechanically. The use of a restricted basis set for the explicitly correlated electronic orbitals results in a speed-up of more than an order of magnitude with nearly no loss in accuracy compared to calculations performed without a restricted basis set. Current efforts are focused on extending the NEO-RXCHF method to multi-configurational systems and the implementation of a new integral code that will further speed up future NEO-RXCHF calculations.

The methodology for investigating the mechanism of condensed-phase photo-induced PCET reactions involves on-the-fly non-adiabatic dynamics on electron–proton vibronic surfaces using surface hopping in a hybrid quantum mechanical/molecular mechanical (QM/MM) framework. A semi-empirical implementation of the floating occupation molecular orbital complete active space configuration interaction method is used to obtain the electronic states of the solute, while the Fourier grid Hamiltonian grid-based method is used to calculate the vibrational states of the transferring proton. The adiabatic vibronic states are obtained by diagonalization of the vibronic Hamiltonian matrix in the basis of these electronic and vibrational states. The solvent is modeled explicitly using a QM/MM approach.

We performed test calculations with a quantum mechanical proton on a hydrogen-bonded phenol–amine complex in 1,2-dichloroethane solution. Our previous studies of this system treated the proton classically. Preliminary results support the characterization of an excited electronic state on which proton transfer is highly favored, in agreement with experimental results and results from simulations with a classical proton (fig. 1). Current efforts are directed toward obtaining experimentally testable predictions, such as hydrogen/deuterium kinetic isotope effects.

WHY BLUE WATERS

The NEO-RXCHF method requires the calculation and storage of trillions of integrals. Our in-house NEO code has been parallelized using a hybrid MPI/OpenMP protocol but still requires a large number of processors and a substantial amount of memory. The use of a large number of processors on Blue Waters is critical to speeding up the computational bottleneck of the calculation of the multi-particle integrals; even more important is the large amount of memory available on Blue Waters because, in contrast to other computer systems, a large number of nodes can be used simultaneously.

For studying photo-induced PCET with a quantum mechanical treatment of the transferring proton, the computational bottleneck is the calculation of the energies, forces, and non-adiabatic couplings between the electronic states at the proton grid points (usually 24) for each molecular dynamics time step, as well as the calculation of the non-adiabatic couplings between the vibronic states. We have used MPI to distribute these calculations over the cores of a single node on Blue Waters. The surface-hopping algorithm requires propagation of a large number of trajectories, which is made possible by the simultaneous use of a large number of nodes on Blue Waters. Moreover, the large amount of memory per node and disk space on Blue Waters have made it possible to run these memory-intensive trajectories and store them for subsequent analysis.

PUBLICATIONS

Sirjoosingh, A., M. V. Pak, K. R. Brorsen, and S. H. Hammes-Schiffer, Quantum Treatment of Protons with Reduced Explicitly Correlated Hartree-Fock Approach. *J. Chem. Phys.*, 142 (2015), 214107, doi:10.1063/1.4921303.

Brorsen, K. R., A. Sirjoosingh, M. V. Pak, and S. H Hammes-Schiffer, Nuclear–Electronic Orbital Explicitly Correlated Hatree-Fock Approach: Restricted Basis Sets and Open-Shell Systems. *J. Chem. Phys.*, 142 (2015), 214108, doi:10.1063/1.4921304.
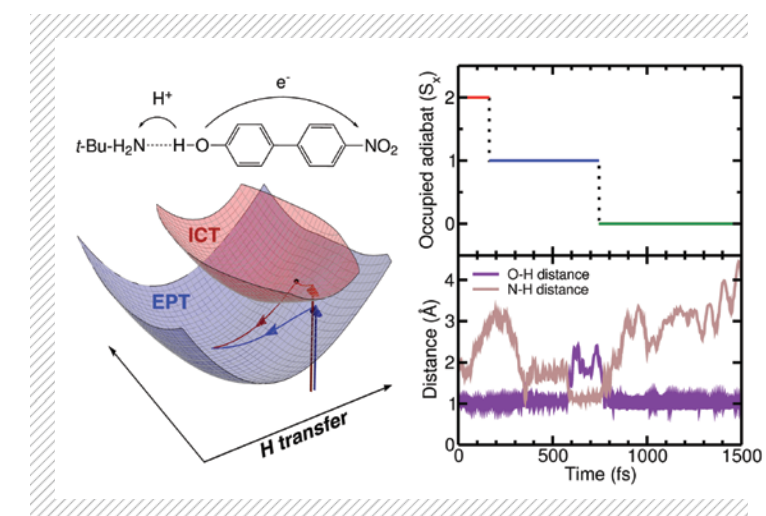

FIGURE 1: *Top left:* The hydrogen-bonded complex between p-nitrophenylphenol and t-butylamine was experimentally studied in 1,2-dichloroethane solution.

Bottom left: The two excited electronic states probed by photoexcitation of this complex.

Right: A representative surface-hopping trajectory in which the transferring proton is treated classically, initiated on S$_x$.