

NON-BORN-OPPENHEIMER EFFECTS BETWEEN ELECTRONS AND PROTONS

Allocation: Blue Waters Professor/24.0 Knh
PI: Sharon Hammes-Schiffer¹

¹University of Illinois at Urbana-Champaign

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 have used Blue Waters to perform NEO calculations on systems in which all electrons and one proton are treated quantum mechanically. Also, we have developed a methodology to study the nonadiabatic dynamics of photo induced proton-coupled electron transfer (PCET) reactions. The electronic potential energy surfaces are generated on-the-fly, and grid-based methods are utilized to calculate the nuclear wave function for the transferring proton. We 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to the nuclear motions, and the concept of the nuclei moving on a single electronic potential energy surface is no longer valid.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 nonadiabaticity has been shown to play a critical role in 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 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 orbital(s), and certain exchange terms are approximated. We recently incorporated an improved integral package into the NEO code. The new integral code enables the use of a direct algorithm for the NEO-RXCHF method and provides a multiple order of magnitude speed up while significantly reducing the memory overhead. Current efforts for the NEO-RXCHF method are focused on benchmarking proton basis sets for small molecules with the goal of obtaining accurate proton wavefunctions.

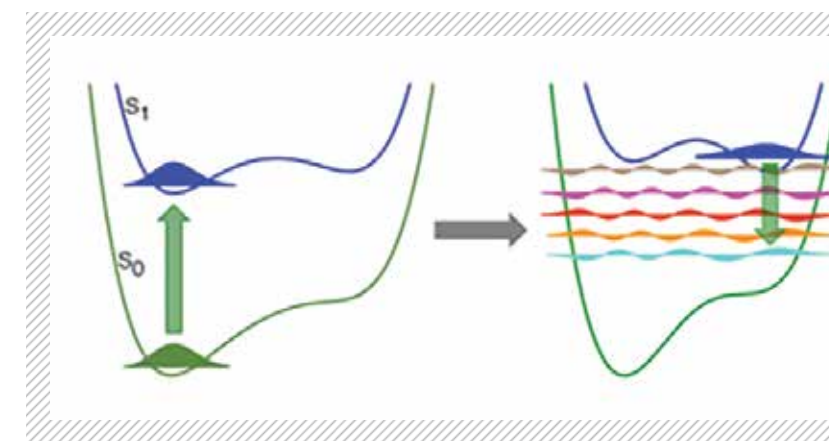
The methodology for investigating the mechanism of condensed phase photoinduced PCET reactions involves on-the-fly nonadiabatic dynamics on electron-proton vibronic surfaces using surface hopping in a hybrid quantum mechanical/molecular mechanical (QM/MM) framework. The solute is treated quantum mechanically, while the solvent is modeled using an empirical force field. We performed calculations of photoinduced PCET

for a hydrogen-bonded phenol-amine complex in 1,2-dichloroethane solution. Our recent calculations treated the proton quantum mechanically, whereas our previous studies of this system treated the proton classically. Our new results highlight the important role of solvent reorganization in facilitating proton transfer to an excited electronic state with significant charge transfer character. Because of the absence of proton tunneling between localized proton vibrational states, replacing hydrogen by deuterium does not change the overall rate of decay to the ground state in this system. Thus, an important conclusion of this work is that the absence of an isotope effect on the overall relaxation rate does not necessarily signify the absence of proton transfer.

WHY BLUE WATERS

The NEO-RXCHF method requires the calculation of **trillions of integrals**. Our in-house NEO code has been parallelized using the message passing interface (MPI) protocol but still requires a large number of processors. Additionally, with the implementation of a direct algorithm for the NEO-RXCHF method, the fast calculation of the integrals is even more important, as the integrals must be calculated many times during the calculation instead of a single time at the start. The speed and scalability of Blue Waters is crucial in enabling large NEO-RXCHF calculations.

For studying photoinduced PCET with a quantum mechanical treatment of the transferring proton, the computational bottleneck is the calculation of the energies, forces, and nonadiabatic couplings between the electronic states at the proton grid points (typically 24) for each molecular dynamics time step. We have used MPI to distribute these calculations over the cores of a single node on Blue Waters. The large number of trajectories required by the surface hopping algorithm are made possible by the simultaneous use of a large number of nodes on Blue Waters. Moreover, the large 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. Assistance from the project staff has been crucial in successful building and testing of the locally modified MOPAC code (a program frequently used in computational chemistry) on Blue Waters.



NEXT GENERATION WORK

We hope to perform NEO-RXCHF calculations with inclusion of electron-electron correlation on larger molecular systems such as DNA base pairs on a next-generation Track-1 system. The current largest NEO-RXCHF calculation has been performed on a three-atom molecule without any electron-electron correlation, so this would represent significant progress for the NEO-RXCHF method. We also hope to study photoinduced PCET occurring on timescales longer than a few picoseconds as well as in large biomolecular systems. With a next-generation Track-1 system, it may also be possible to use an *ab initio* multiconfigurational method instead of a semiempirical multiconfigurational method in a QM/MM framework to simulate condensed phase photoinduced PCET.

PUBLICATIONS AND DATA SETS

Sirjoosingh, A., M. V. Pak, K. R. Brorsen, and S. Hammes-Schiffer, Quantum treatment of protons with reduced explicitly correlated Hartree-Fock approach. *J. Chem. Phys.*, 134 (2015), p. 214107.

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Goyal, P., C. A. Schwerdtfeger, A. V. Soudackov, and S. Hammes-Schiffer, Proton quantization and vibrational relaxation in nonadiabatic dynamics of photoinduced proton-coupled electron transfer in a solvated phenol-amine complex. *J. Phys. Chem. B*, 120 (2016), pp. 2407-2417.

FIGURE 1: For the *p*-nitrophenylphenol-amine hydrogen-bonded complex in 1,2-dichloroethane solution, photoexcitation to an electronic state with significant charge transfer character is followed by solvent reorganization. The resulting change in asymmetry of the proton potential on the excited electronic state leads to proton transfer from the phenol to the amine. Decay to the ground vibronic state is dominated by vibrational relaxation on the ground electronic state.