ESF Short Visit Grant-3889- Final Report
Molecular Simulations in Biosystems and Material Science
Nicholas Polizzi
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I visited Professor Daan Frenkel at the University of Cambridge to study relevant techniques for the simulation of biological electron transfer processes. While at Cambridge, I also visited with Professor Michiel Sprik and his post doctoral fellow, Jun Cheng. In London at University College London, I met with Dr. Jochen Blumberger and his group also in the context of developing simulation techniques relevant to electron transfer in biomolecules. This scientific visit lasted ten days, from August 24th through September 3rd.

The ability to characterize the electron transfer rate depends on accurate calculations of the electronic coupling interaction energy between the electron donor and acceptor. Not only must the calculations of this interaction energy be accurate, but also the fluctuations about its mean value must be appropriately accounted for. Typically these fluctuations have been calculated from configurational "snapshots" of molecular dynamics simulations. The problem with this conventional approach is that the configurations simulated most likely are not transition state configurations, which are the configurations relevant to electronic coupling interaction energy calculations. So how then does one simulate an ensemble of transition state configurations from which accurate distributions of the electronic coupling interaction energy can be attained?

From my meetings with Daan Frenkel, Michiel Sprik and Jochen Blumberger, we have arrived at two different methods to answer this important question. The first, motivated by Dr. Frenkel, is to run a short molecular dynamics trajectory for a given number of time steps, after which a Monte Carlo accept/reject move is performed for the entire trajectory. The acceptance criteria is based on the energy gap between the electron located on the donor and the electron located on the acceptor. By definition, the transition state configuration is defined as that for which the energy gap is zero. By accepting the short trajectories subject to this monte carlo move based on the energy gap approaching zero, one can arrive at a transition state ensemble.

The second method involves running a molecular dynamics simulation under the bias of a Kirkwood parameter. The Kirkwood parameter is a mixing potential; that is, it mixes the potential surface of the donor-localized system with the potential surface of the acceptor-localized system. Essentially, one propagates the nuclear motion of the system on a potential energy surface that is a mixture of the two final states: charge on donor and charge on acceptor. Ideally, choosing the appropriate mixing potential will provide the ensemble of configurations where the energy gap is at or near zero. From these configurations, one can determine the appropriate magnitude and fluctuations of the electronic coupling interaction energy.

Each of the above methods involves calculation of the energy gap, which is nontrivial if both donor and acceptor are present in the same system. For classical models, the energy gap is easily calculated; but quantum chemical calculations are more subtle, as DFT often unphysically delocalizes the electron and can not accurately calculate excited states. Further work includes exploration of the proposed methods for acquiring a transition state ensemble as well as exploring appropriate methods for calculating the energy gap, which may likely involve a quantum mechanical/molecular mechanical approach.

This visit was valuable in that it facilitated new ideas on how to appropriately simulate electron transfer events. The short time period of the trip was not ideal to perform the simulations we discussed, but these will be run by me at Duke University in the near future. I intend to have future collaborations with Daan Frenkel regarding these simulations for attaining electron transfer transition state ensembles. My understanding of the field suggests this work is novel and could lead to a highly cited publication. If indeed a paper does result from this work, the ESF will be appropriately acknowledged for this travel funding. I also intend to collaborate further with Jochen Blumberger, who has extensive experience in simulating the behavior of biomolecules to uncover electron transfer parameters such as free energy changes and reorganization energies.

My experience at Cambridge and UCL was a highly stimulating one. The environments at both universities were very congenial. I would seriously consider a second visit to follow up on these ideas, and I would like to thank the ESF for helping initiate such an ambitious project.