RIGOROUS QUANTUM-CLASSICAL SIMULATION OF ELECTRON TRANSFER IN A BACTERIAL PHOTOSYNTHETIC REACTION CENTER

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RESEARCH SUMMARY

Photosynthesis forms one of the core biological energy cycles responsible for the maintenance of life on Earth and has existed in some form since the earliest days of evolution, persisting today in bacteria, algae, and green plants. The molecular apparatus of photosynthetic energy conversion exhibits many similarities between different prokaryotic families, and even plant photosystems share some common motifs with the reaction centers of purple bacteria [1]. Moreover, the efficiency of these systems in trapping and converting light to other forms of energy is extremely high and has served to inspire human attempts to collect and store solar energy [2]. As a result, an improved understanding of the processes involved in natural photosynthesis has implications for the past, in understanding the origin and development of life on Earth, as well as the potential to inform the future with a focus on clean, renewable energy sources.

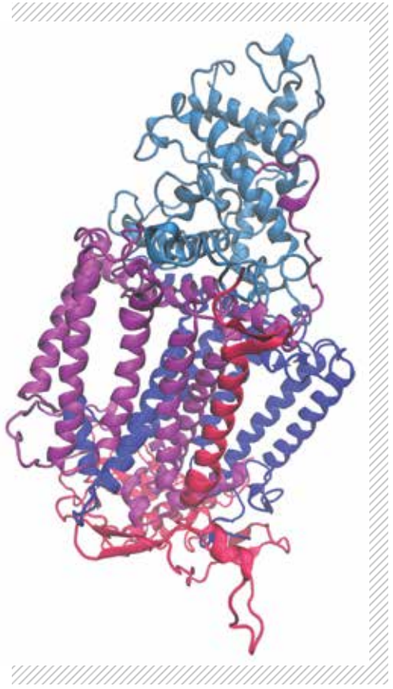

FIGURE 1: A visualization of the protein backbone of the reaction center in *Bcl. viridis*. The L, M, and H chains are shown in dark blue, purple, and red, respectively. The cytochrome unit is shown in light blue at the top.

Theoretical and experimental progress in understanding and characterizing the molecular processes of photosynthesis has the potential for major impact on the development of clean energy technologies. However, aspects of the theoretical side of this work are hampered by the fact that the electron dynamics induced as part of the photon capture event require a quantum mechanical description for accurate treatment. It also requires a fully-quantum description of the surrounding reaction center protein, and solvent molecules would be too computationally expensive to complete. Several approaches have been developed to work around this issue, but the simplest have major shortcomings when applied to chemical problems [3], and others introduce *ad hoc* elements which limit their rigor and accuracy. Recently, progress has been made on a rigorous approach to decoupling the study of a quantum mechanical system from its surrounding classical environment, in the form of the quantum-classical path integral (QCPI) [4,5], and this method is now computationally efficient enough to apply to biological problems.

We are in the process of applying a highly parallel version of our QCPI code, coupled to the LAMMPS molecular dynamics package [6] to simulate the first steps of electron transfer in the photosynthetic reaction center of the purple bacterium *Blastochloris viridis*. Our initial results from the molecular dynamics compare well to previous studies [7,8], but extend them significantly in that the behavior of the entire protein complex is included in the dynamics, and the simulation takes place at fully-atomistic resolution. The output of this work will have promise not only as a source of insight into the molecular mechanisms of biological charge transfer, but also as the first direct test of the linear response approximation in a protein system. It will be a landmark on the path toward truly rigorous simulation methods of large biochemical systems.

WHY BLUE WATERS

The expert staff and extensive computational resource available through Blue Waters was essential in this research program. The staff helped to convert the old parameterization of reaction center cofactors by Treutlein *et al.* [9] into a more modern format. They provided additional assistance with improving these parameters where our more complete dynamical simulations indicated potential problems, increasing our confidence in the results of the quantum-classical calculations.

From a computational standpoint, the high degree of parallelism and the large per-node memory available on Blue Waters is critical in performing our calculations within a reasonable time frame. This is because the QCPI method requires not only a path summation but also an average over many initial conditions. Together, these represent significant computational expense not feasible in a serial approach. However, the QCPI formalism is amenable to a message packing interface (MPI)+MPI decomposition which dramatically reduces running time and exhibits very favorable parallel scaling, making the approach feasible for atomistic simulation of realistic systems provided many cores are available. Additionally, the large memory capabilities available on Blue Waters ensure that all of the dynamical information required by each node can be stored locally, saving costly disk access and providing additional computational savings.

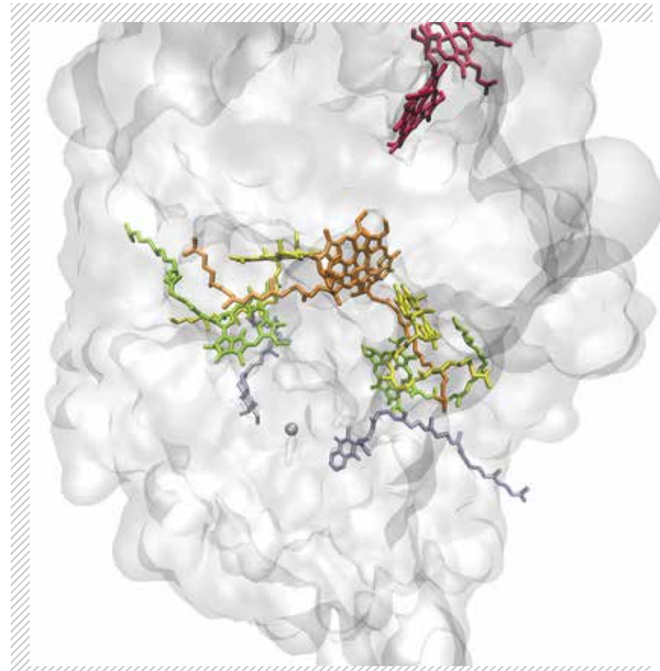

FIGURE 2: A close-up of the cofactors in the L and M chain region where the first stages of electron transfer occur. The most important participants in these early stages are the special pair of bacteriochlorophylls (shown in orange), the accessory bacteriochlorophylls (yellow), and the bacteriopheophytins (green).

Thomas Allen intends to continue pursuing research in a postdoctoral position upon completion of the University of Illinois Urbana-Champaign Chemical Physics Ph.D. program.

"Based on the charge transfer work I have performed using Blue Waters, I have been offered a position with Peter Rossky at Rice University, " he says. "The research program there is focused on the understanding and application of charge transfer models and mixed quantum-classical simulation to problems in materials science, with an emphasis on solar energy conversion. I will be starting at this position in Fall 2016, and I look forward to continuing to pursue the research threads which Blue Waters has made possible for me to study."