Rigorous Quantum-Classical Simulation of Electron Transfer in a Bacterial Photosynthetic Reaction Center

Thomas Allen (PI: Nancy Makri)

Department of Chemistry
University of Illinois

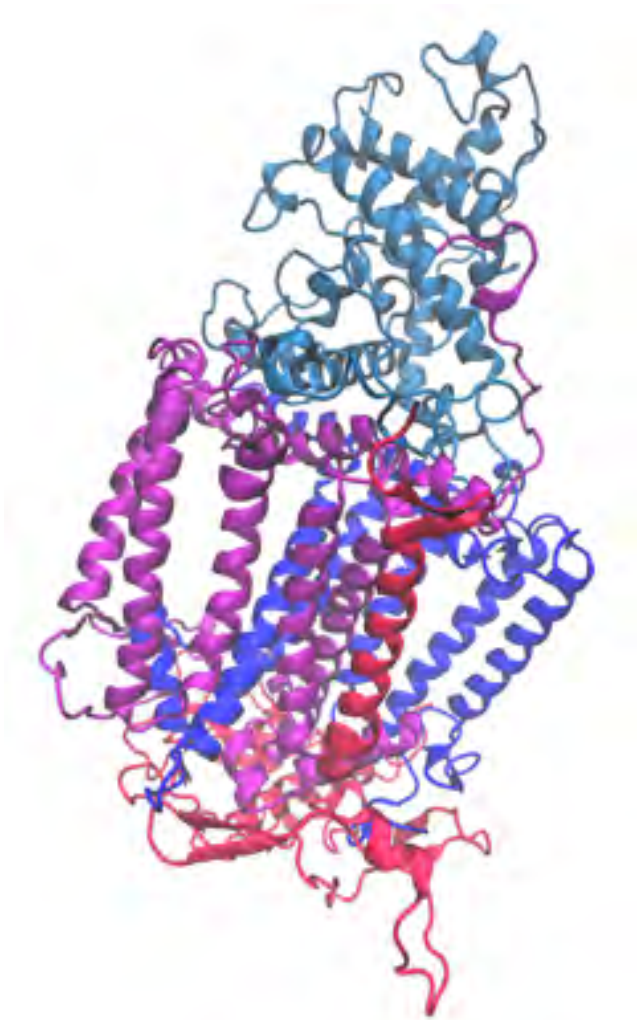
June 13, 2016

Introduction - Overview

- Photosynthesis is a key biological energy cycle
- Emergence of photosynthesis occurred early in history of life
- Structural similarities appear across kingdoms of life
- Human interest in replicating efficiency of energy transfer

Zinth and Wachtveitl, *ChemPhysChem* **6**, 871 (2005). Photo Credit: Amartya Bose.

Introduction - Reaction Center

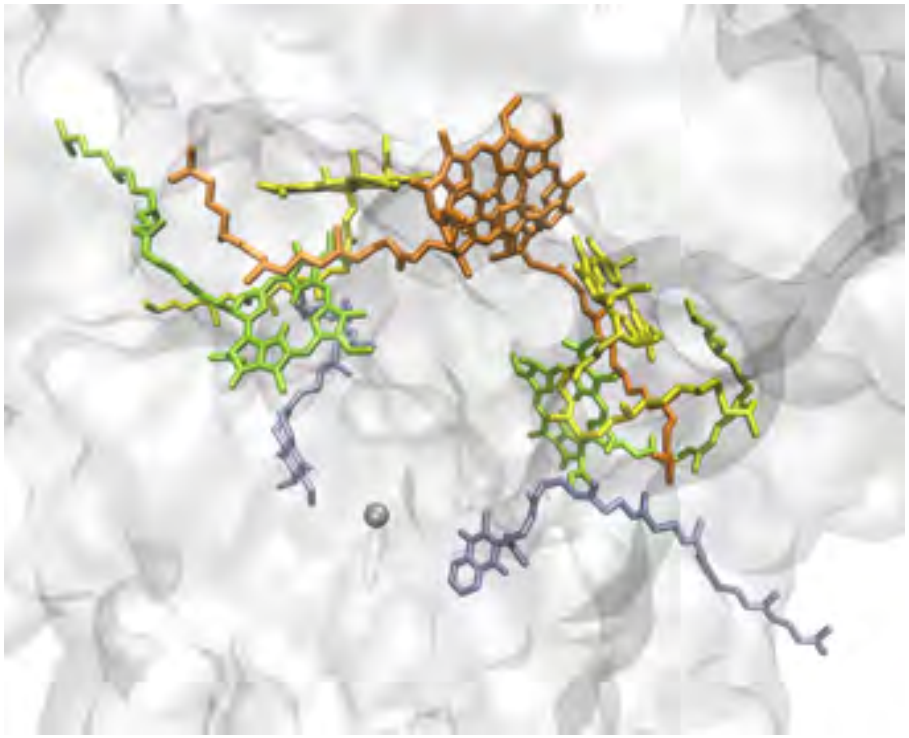


- Peptide backbone consists of four subunits: L, M, H, and C
- L and M domains are embedded in the membrane, where charge separation occurs
- Cofactors bound with C_2 symmetry, only L branch participates

Deisenhofer et al., *J. Mol. Bio.* **246**, 429 (1995).

Introduction - Reaction Center

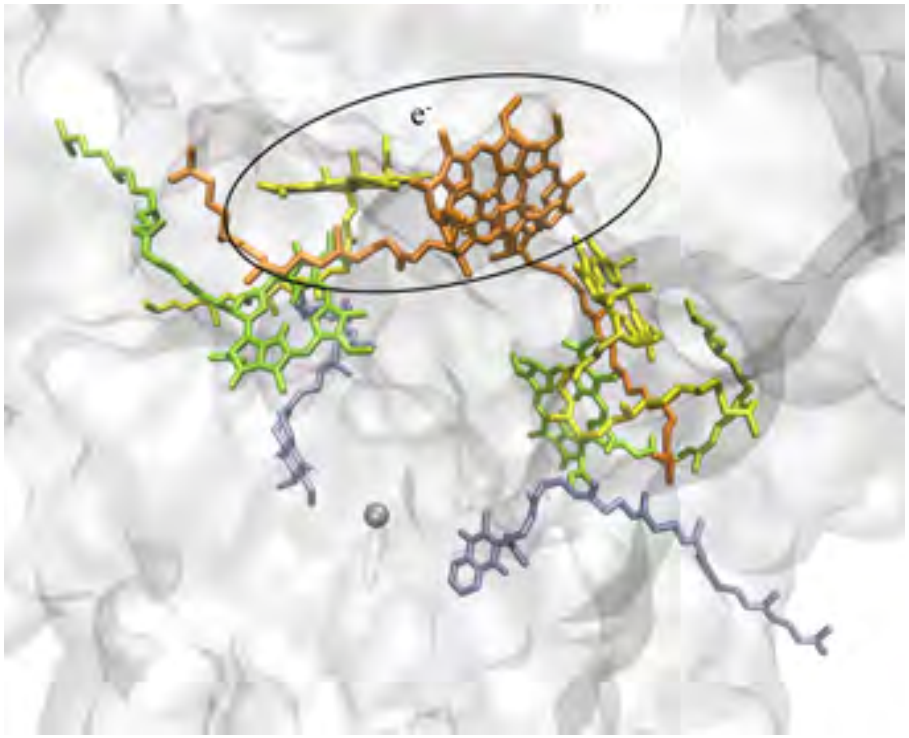
- Key cofactors for inital electron transfer are Bcl and Bph
- Reaction ends with reduction of quinones
- We focus on rapid initial charge separation, $SP^* \rightarrow Bcl$
- Can compare atomistic and simplified simulations
- Implications for linear response



Zinth and Wachtveitl, *ChemPhysChem* **6**, 871 (2005).

Challenges

- Electron transfer is quantum mechanical
- Protein environment consists of many atoms, complex interactions
- Suggests a mixture of quantum and classical simulation
- How can we maintain rigor and accuracy with mixed description?



The QCPI Method

- One approach to rigorous quantum-classical dynamics is through the path integral
- Path-based description is local, avoiding question of how to combine wavefunctions and trajectories
- Paths are also independent, allowing for efficient parallelization
- Structure of the method is ideal for highly parallel architecture

Lambert and Makri, *J. Chem. Phys.* **137**, 22A552 and 22A553 (2012).

The QCPI Method

$$\rho_{red}(s_N^{\pm}; N\Delta t) = \int dq_0 \int dp_0 \, P(q_0, p_0) Q(s_N^{\pm}, q_0, p_0; N\Delta t)$$

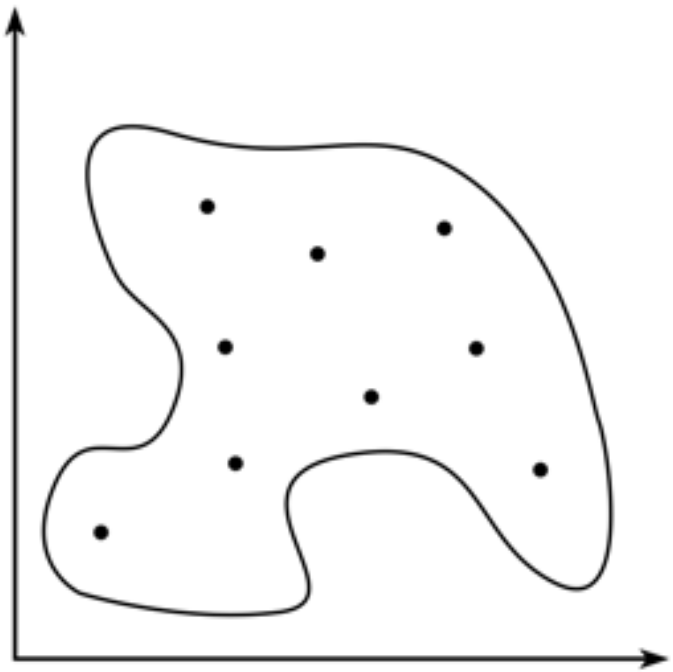
- The Quantum-Classical Path Integral (QCPI) expression allows us to solve for $\rho_{red}(s_N^{\pm}; N\Delta t)$
- The density matrix contains all the information about observable system (transfering electron)
- Result is cast in terms of average over separate path sums
- We consider these terms in context of BW architecture

Lambert and Makri, *J. Chem. Phys.* **137**, 22A552 and 22A553 (2012).

The QCPI Method

$$\rho_{red}(s_N^{\pm}; N\Delta t) = \int dq_0 \int dp_0 \, P(q_0, p_0) Q(s_N^{\pm}, q_0, p_0; N\Delta t)$$

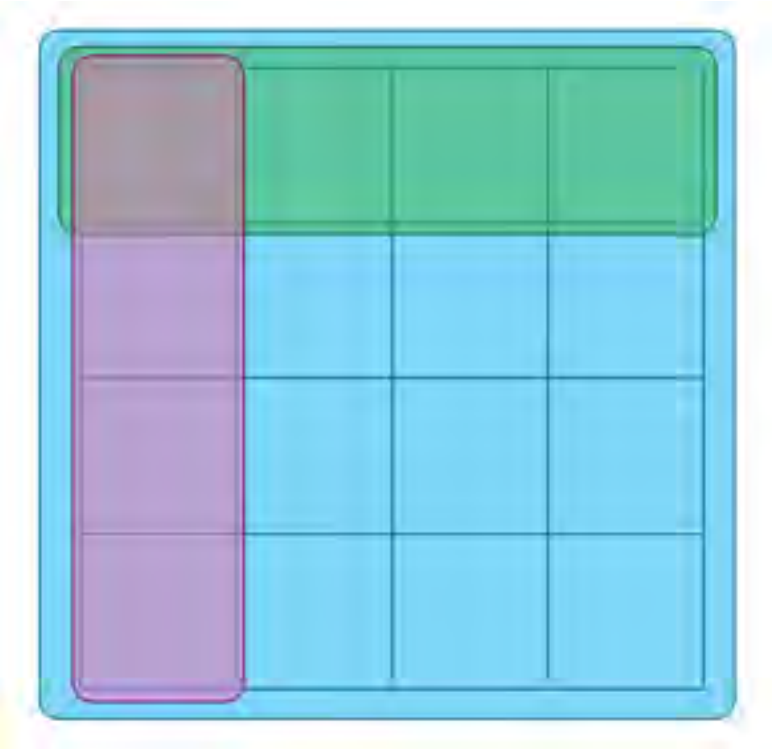
$$P(q_0, p_0) = e^{-\beta H(q_0, p_0)}$$

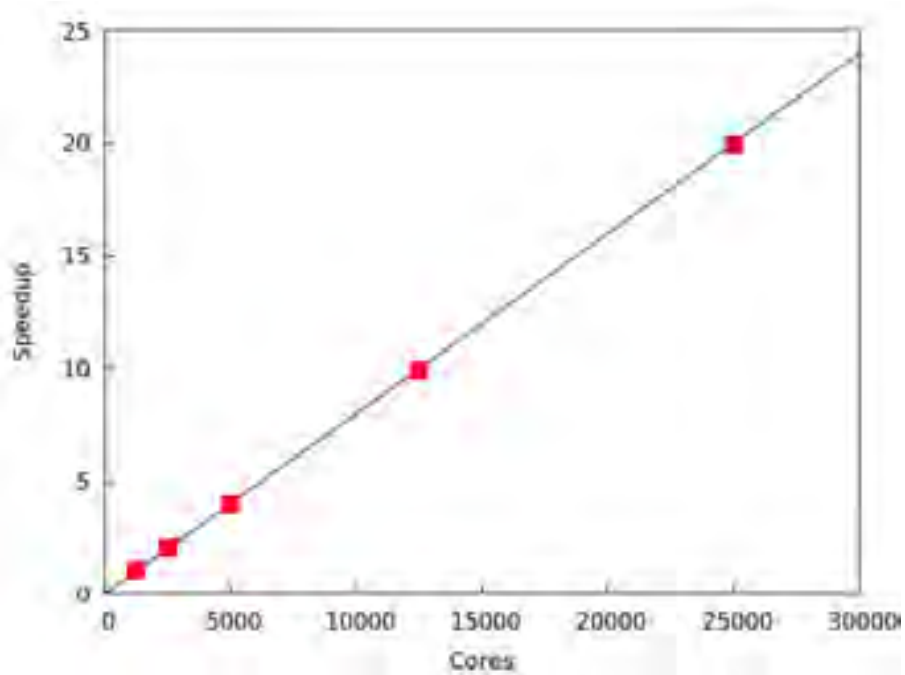


The QCPI Method

$$\rho_{red}(s_N^{\pm}; N\Delta t) = \int dq_0 \int dp_0 \, P(q_0, p_0) Q(s_N^{\pm}, q_0, p_0; N\Delta t)$$

$$P(q_0, p_0) = e^{-\beta H(q_0, p_0)}$$

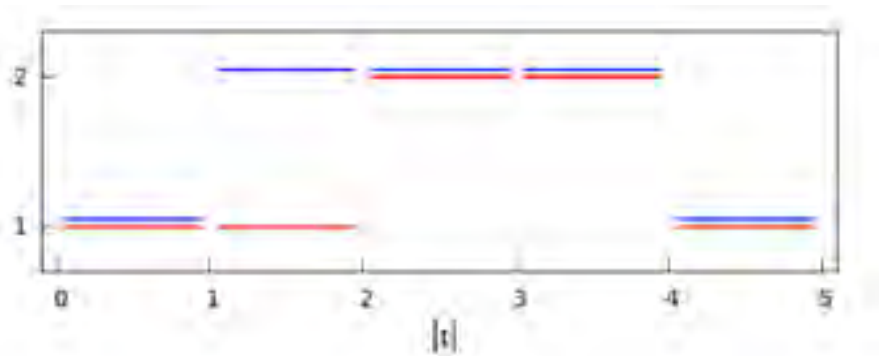


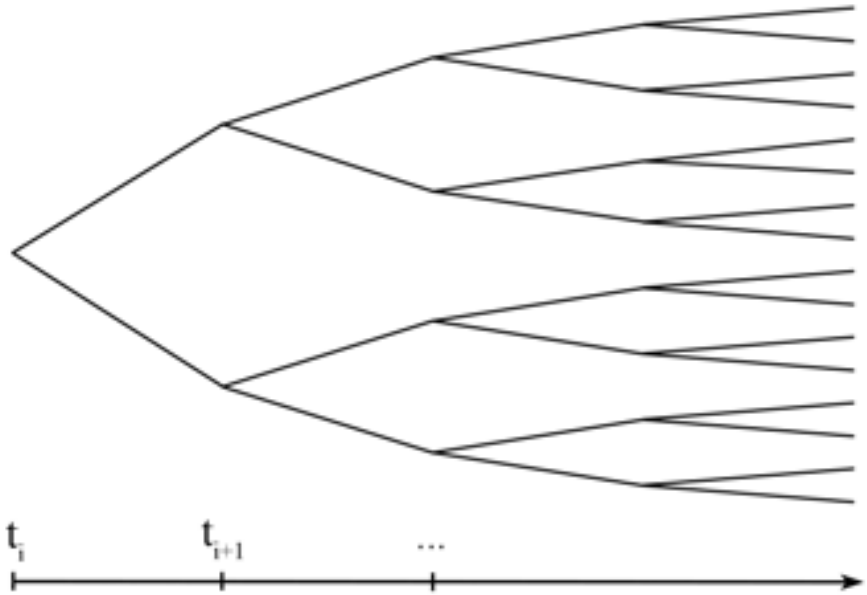


The QCPI Method

$$\rho_{red}(s_N^{\pm}; N\Delta t) = \int dq_0 \int dp_0 \, P(q_0, p_0) Q(s_N^{\pm}, q_0, p_0; N\Delta t)$$

- $Q(s_N^{\pm}, q_0, p_0; N\Delta t)$ derives from path sum
- Consists of propagator elements plus phase factor for each path

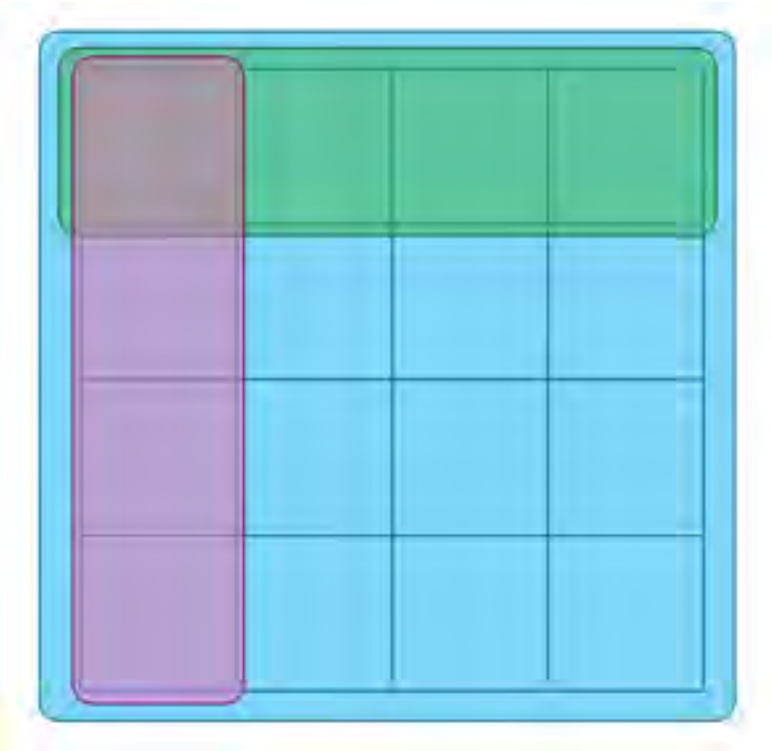


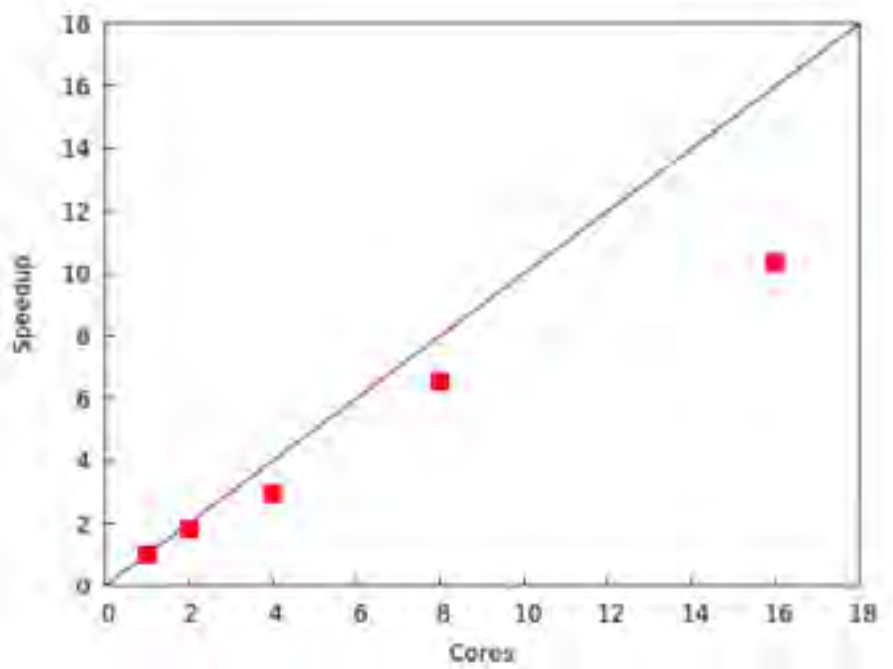


The QCPI Method

$$\rho_{red}(s_N^{\pm}; N\Delta t) = \int dq_0 \int dp_0 \, P(q_0, p_0) Q(s_N^{\pm}, q_0, p_0; N\Delta t)$$

Path propagation can be split over cores as well (MPI+MPI)

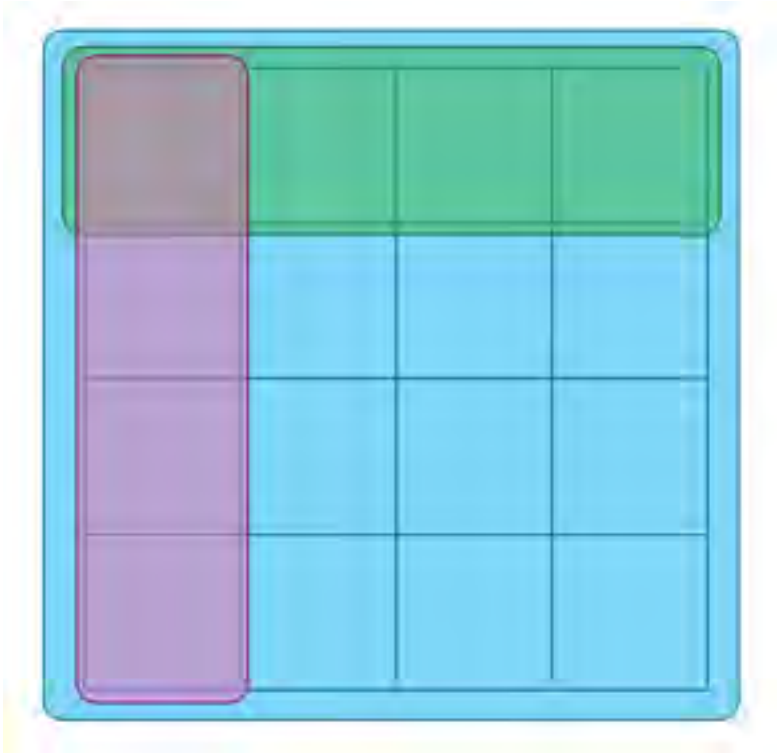




The QCPI Method

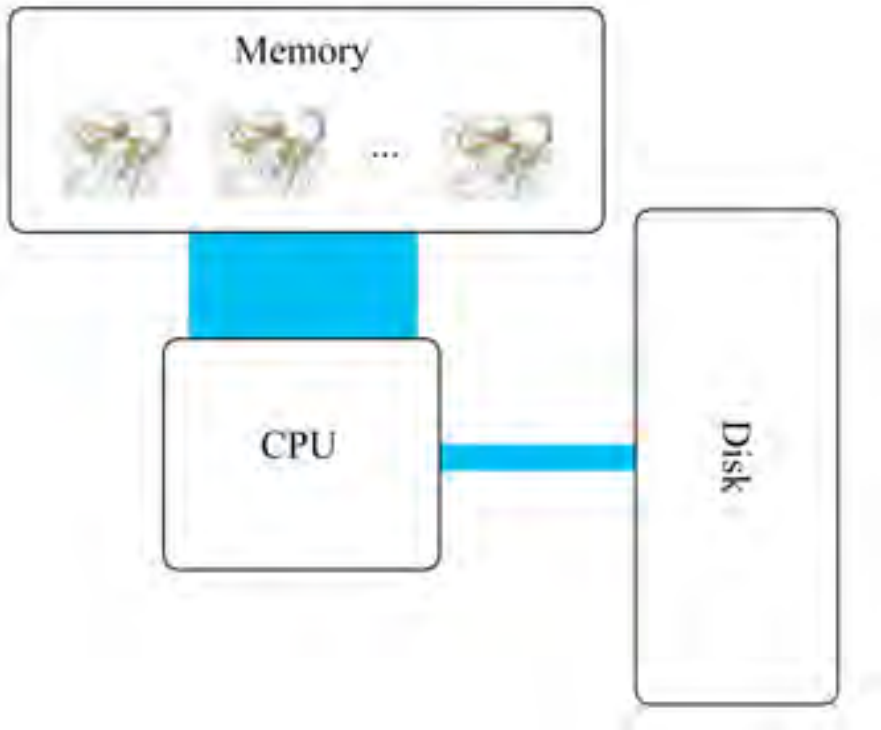
$$\rho_{red}(s_N^{\pm}; N\Delta t) = \int dq_0 \int dp_0 \, P(q_0, p_0) Q(s_N^{\pm}, q_0, p_0; N\Delta t)$$

Final layer of parallelism is in MD package



The QCPI Method

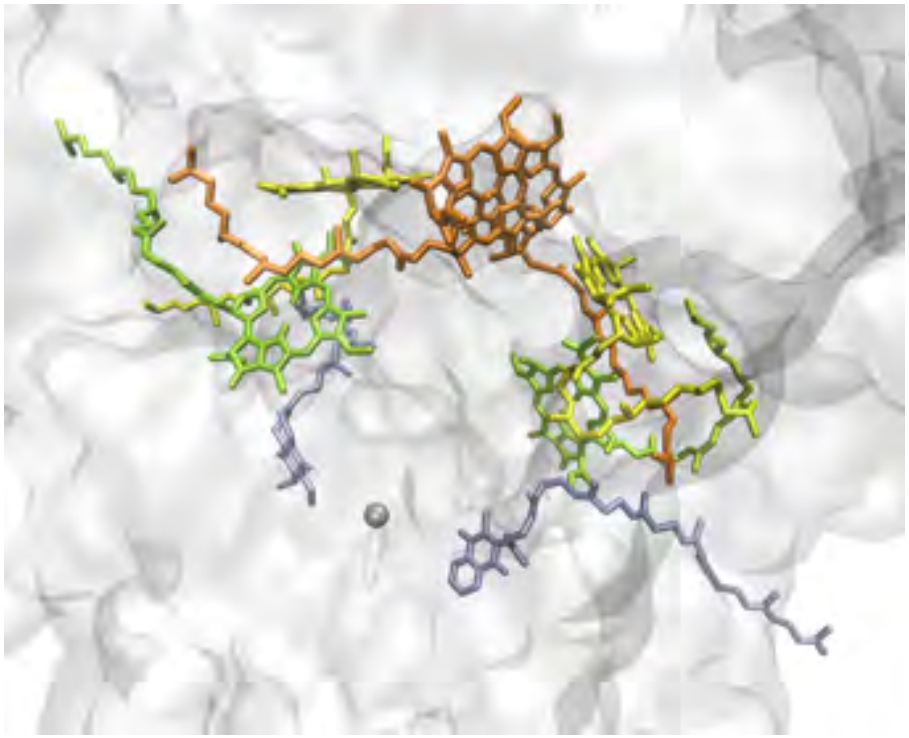
Large per-node memory also increases performance



Combination of QCPI and Blue Waters makes quantum dynamics feasible even for very large MD simulations

Model Building

- Protein backbone can be treated via standard force fields
- Quantum system has two-state representation
- Cofactors must be parameterized for MD simulation
- Victor at NCSA helped sort out and update cofactor parameters



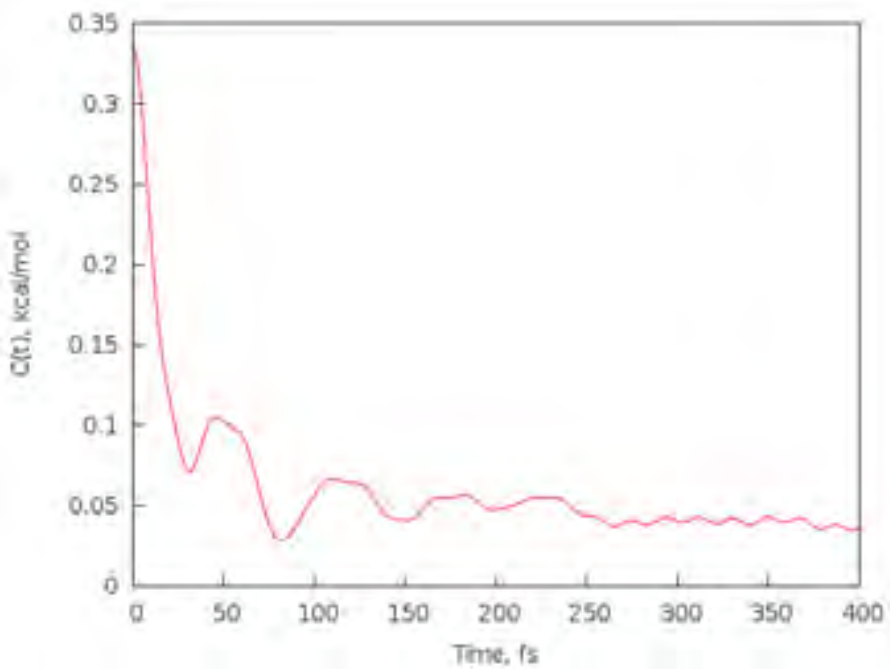
Simulation Details

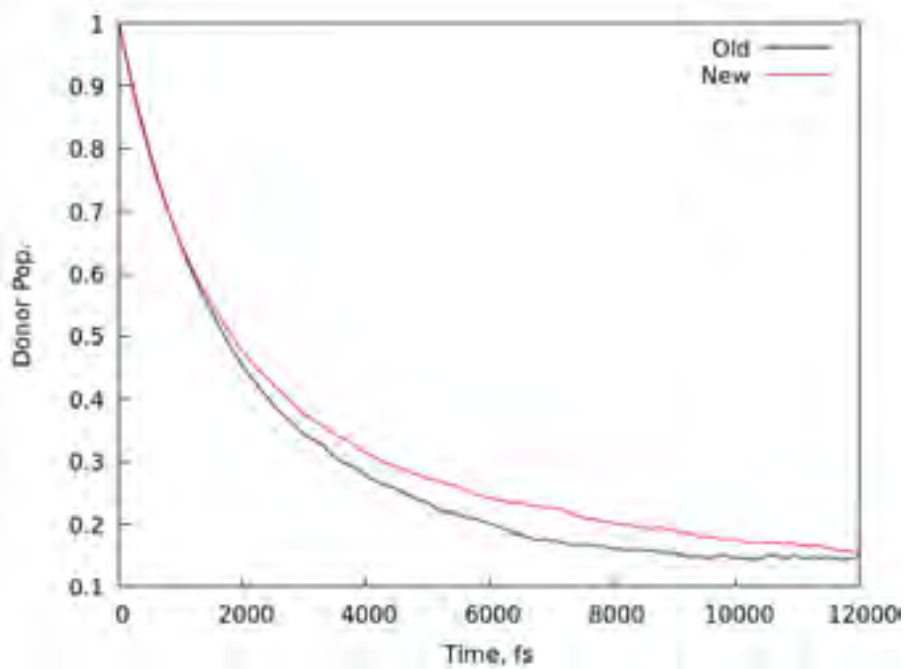
- Protein parameters were taken from CHARMM 36 force field
- Cofactor parameters from work by Treutlein
- Protein was placed in periodic box with border of 15 Å on each side, charges were neutralized with randomly-placed sodium ions
- Only crystallization waters were treated explicitly
- Several sets of forces and integrators were tested; Implicit/PPPM Coulomb, NVT/Langevin

Treutlein et al., in *The Photosynthetic Bacterial Reaction Center*, Springer (1988).

Results

We have constructed a harmonic model from simulated energy gap correlation fuctions





- Approximate convergence at $\Delta t = 14$ fs, $k_{max} = 4$
- Continuing to investigate dielectric scaling

Future Work

- Perform full atomistic QCPI simulation
- Compare to results in harmonic limit to test linear response
- Explore 3-state models to capture complete ultrafast dynamics
- Expand treatment to new systems (rhodopsin, DNA, proton transfer)

Acknowledgements

BLUE WATERS
SUSTAINED PETASCALE COMPUTING

NCSA

NSF