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

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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

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

Key cofactors for initial 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

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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?
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

The QCPI Method

\[
\rho_{\text{red}}(s^\pm_N; N\Delta t) = \int dq_0 \int dp_0 \, P(q_0, p_0) Q(s^\pm_N, q_0, p_0; N\Delta t)
\]

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

The QCPI Method

\[ \rho_{\text{red}}(s_{N}^{\pm}; N\Delta t) = \int dq_{0} \int dp_{0} P(q_{0}, p_{0}) Q(s_{N}^{\pm}, q_{0}, p_{0}; N\Delta t) \]

\[ P(q_{0}, p_{0}) = e^{-\beta H(q_{0}, p_{0})} \]
The QCPI Method

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

\[ P(q_0, p_0) = e^{-\beta H(q_0, p_0)} \]
The QCPI Method

\[ \rho_{\text{red}}(s^\pm_N; N\Delta t) = \int dq_0 \int dp_0 P(q_0, p_0) Q(s^\pm_N, q_0, p_0; N\Delta t) \]

- \( Q(s^\pm_N, q_0, p_0; N\Delta t) \) derives from path sum
- Consists of propagator elements plus phase factor for each path
The QCPI Method

\[ \rho_{\text{red}}(s_{N}^{\pm}; N\Delta t) = \int dq_0 \int dp_0 \, P(q_0, p_0) Q(s_{N}^{\pm}, q_0, p_0; N\Delta t) \]

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

\[ \rho_{\text{red}}(s^\pm_N; N\Delta t) = \int dq_0 \int dp_0 P(q_0, p_0) Q(s^\pm_N, q_0, p_0; N\Delta t) \]

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
- 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
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

Results

We have constructed a harmonic model from simulated energy gap correlation functions.

- Approximate convergence at $\Delta t = 14$ fs, $k_{\text{max}} = 4$
- 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