

Quantum-Classical Path Integral Simulation of Electron Transfer Reactions in Solution

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BLUE WATERS

Quantum Mechanics is subtle and hard!

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t)$$

- On the atomic scale: quantum interference, coherence, tunneling, entanglement...
- On the macroscopic scale: incoherent, classical behavior.
- The required computational effort appears to grow exponentially with the number of degrees of freedom.

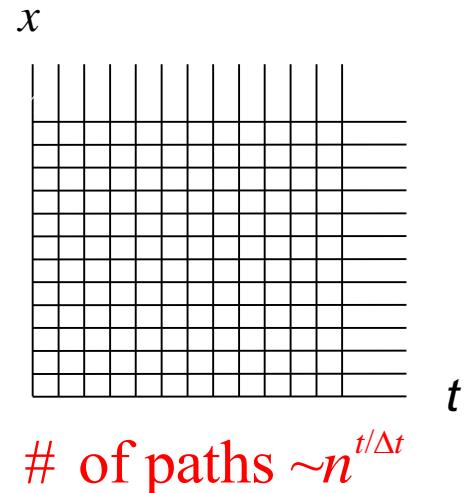
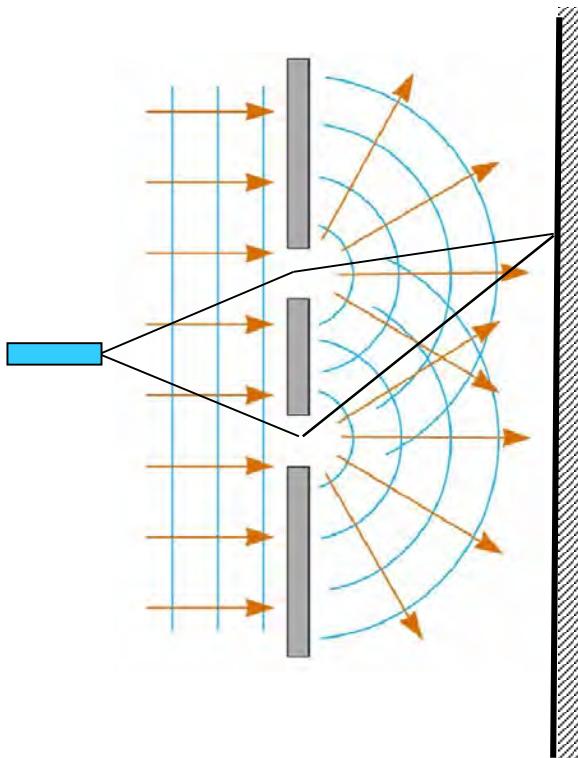
The Quantum Leap Challenge

- Need novel simulation tools suitable to complex many-body quantum mechanical processes.
- Understanding the complexity of many-body quantum mechanics can aid in the development of first-principles simulation algorithms that make no approximations.

An attractive alternative: Feynman's path integral

$$\langle x'' | e^{-iHt/\hbar} | x' \rangle = \sum_{\text{all paths } k} \exp(i\Phi_k/\hbar)$$

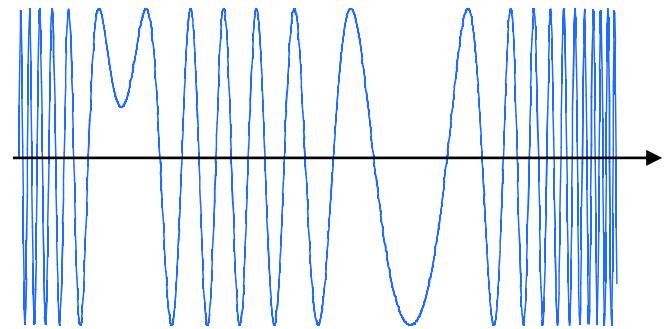
quantum superposition



The total quantum amplitude is the sum of the amplitudes along *all* possible paths.

All paths have the same weight!

Real part of integrand
(M grid points)



Number of grid points $n \sim M^d$ – astronomical number of terms!

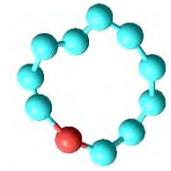
Dynamics vs. Thermal Equilibrium

The quantum Boltzmann operator can be thought of as the propagator in imaginary time:

$$e^{-i\hat{H}t/\hbar} \leftrightarrow e^{-\beta\hat{H}}$$

Equilibrium properties: “Path Integral Monte Carlo” 😊

Efficient methodology, no need for approximations, statistical exchange can be easily included for bosons.



Real-time dynamics: “Sign Problem” 😞

Positive and negative regions occupy almost equal volumes. Monte Carlo methods converge extremely slowly, producing results buried in noise.

A pragmatic approach

Treat a few degrees of freedom (charge transfer pair, proton,...) by quantum mechanics, and all remaining atoms by classical trajectories.

Unfortunately...

Classical mechanics is based on local trajectories, while the wavefunction of the quantum particle is delocalized. This means the classical particles will experience a force that is averaged with respect to the wavefunction of the quantum particle. This is a major flaw that leads to incorrect product distributions. Available quantum-classical methods are based on various assumptions and uncontrolled approximations.

Resolving the inconsistency:

To remove the incompatibility of quantum and classical mechanics, we need to adopt a **local** description of the quantum system. This is possible within the path integral formulation of quantum mechanics.

Quantum-Classical Path Integral (QCPI)

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

For the (few) quantum degrees of freedom, sum over *all* paths

For the (many) classical degrees of freedom, include only *classical* paths

The path integral approach offers a unique advantage:

Paths are *local*, just like trajectories, so there is no averaging with respect to delocalized wavefunctions.

Basic QCPI Formulation

$$\rho(t) = \int d\mathbf{q}_0 \int d\mathbf{p}_0 P(\mathbf{q}_0, \mathbf{p}_0) \sum_{\text{all system paths } k} e^{\frac{i}{\hbar} \Phi_k^{\text{sys}}} e^{\frac{i}{\hbar} \Phi_k^{\text{env}}(\mathbf{q}(t'), \mathbf{p}(t'))}$$

The quantum system ‘drives’ the solvent; i.e., the instantaneous position (state) of the system along one of its paths determines the force on the solvent trajectory. Thus, for each initial condition of the solvent phase space, there is a different trajectory along each system path. (This is the “back reaction”.)

In turn, a classical trajectory supplies a phase that modifies the amplitude of the quantum system. All the effects of the solvent on the system come from this phase.

All correlations are included exactly. No assumptions or approximations required.

Decoherence arises naturally from phase cancellation.

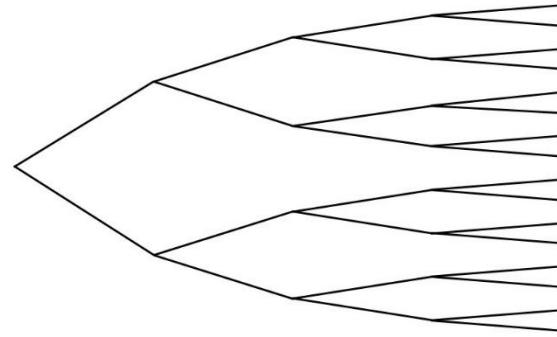
How many paths are there?

$$\text{QCPI expression: } \rho(t) = \int d\mathbf{q}_0 \int d\mathbf{p}_0 P(\mathbf{q}_0, \mathbf{p}_0) \sum_{\text{all system paths } k} e^{\frac{i}{\hbar} \Phi_k^{\text{sys}}} e^{\frac{i}{\hbar} \Phi_k^{\text{env}}(\mathbf{q}(t'), \mathbf{p}(t'))}$$

There are $[n(n+1)/2]^N$ trajectories from each initial condition, where n is the number of system states and N is the number of time steps.

For a 2-state (donor “D” and acceptor “A”) charge transfer reaction, in order to propagate by 1000 time steps, one must integrate 4^{1000} solvent trajectories for each sampled initial condition.

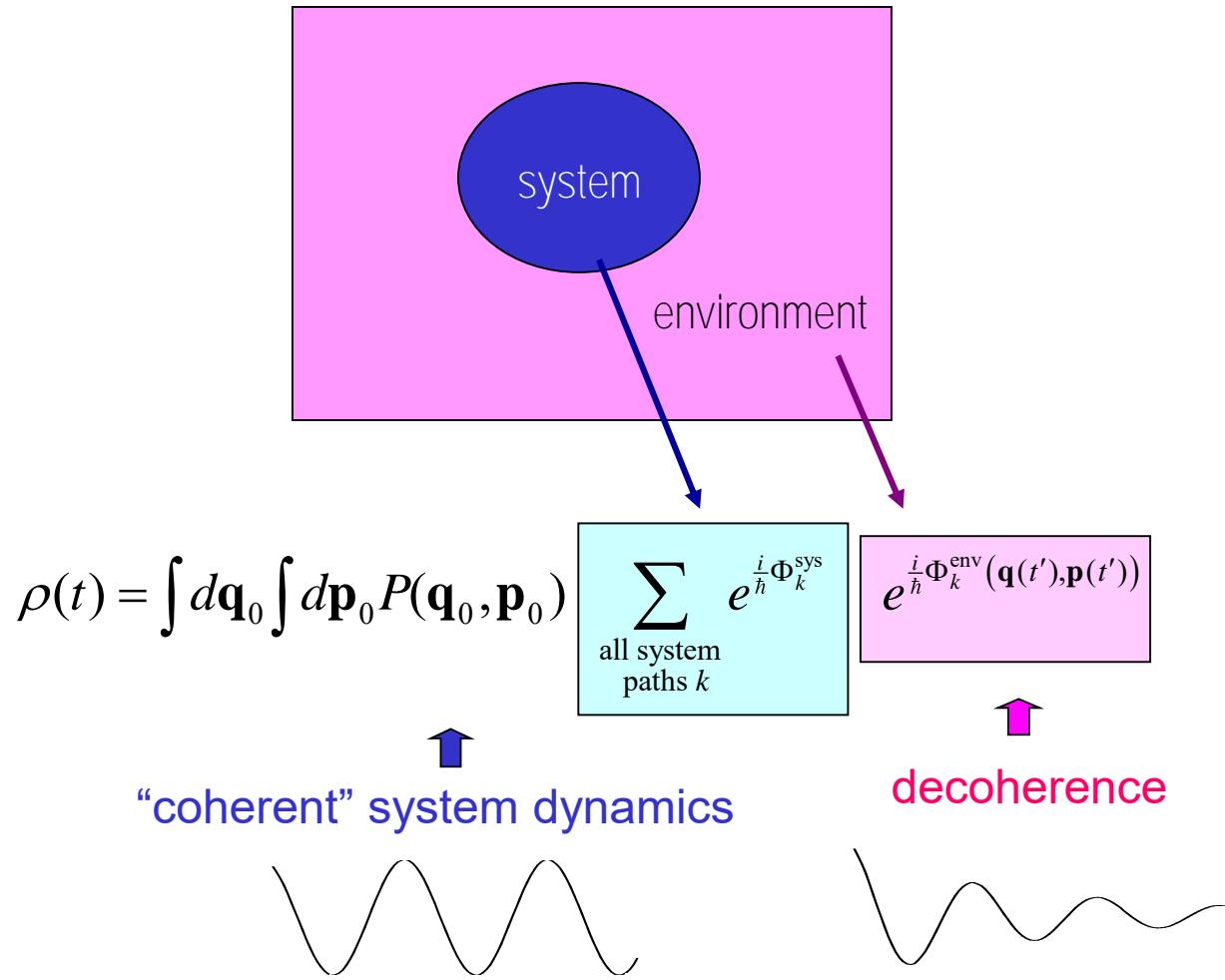
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Monte Carlo methods fail because of the oscillatory nature of the integrand (the sign problem).

- Can we disentangle the QCPI sum by exploiting the physics?

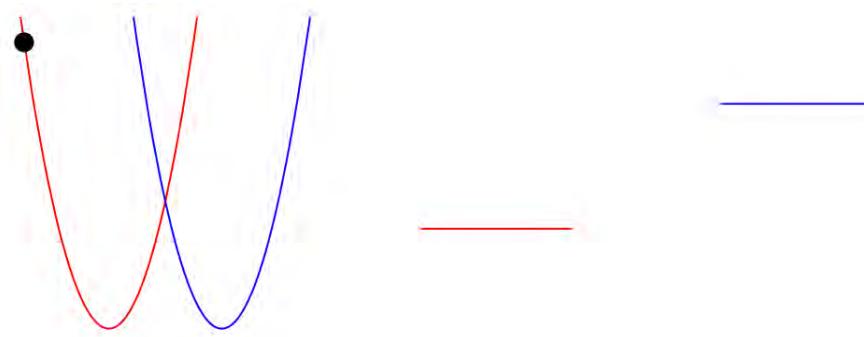
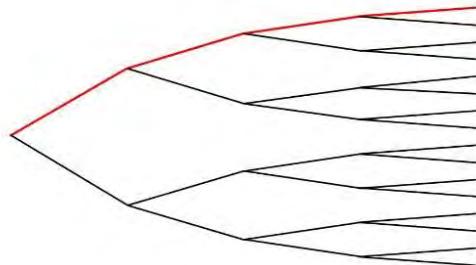
The Mechanism of Decoherence



How does it work?

The mechanism of decoherence

A single solvent trajectory from each initial condition (i.e. a trajectory that neglects the state changes of the quantum system) causes fluctuation of the system's energy levels, leading to **absorption and stimulated emission** of phonons.

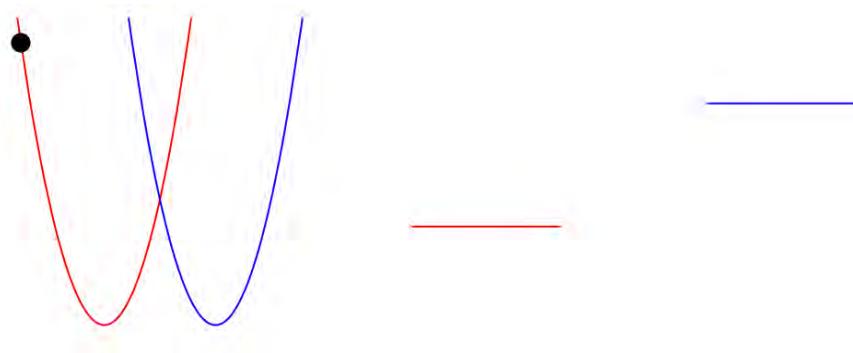
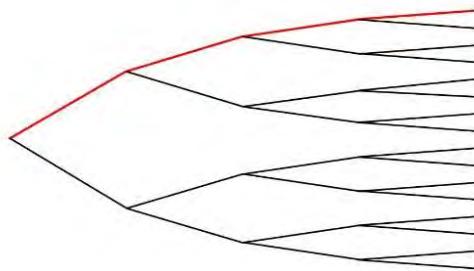


The ensemble average of these events damps the coherence of the quantum system. This "**classical decoherence**" is the main solvent effect at high temperature.

N. Makri, *Chem. Phys. Lett.* **593**, 93-103 (2014)

The mechanism of decoherence

All other classical trajectories arise from the changes of system state along each quantum path (the “**back reaction**”). These trajectories are responsible for spontaneous phonon emission (the “**quantum decoherence**”), which is essential for detailed balance.



The dependence of each classical trajectory (and phase) on the entire system path is a **quantum memory**. This quantum memory needs to be fully accounted for.

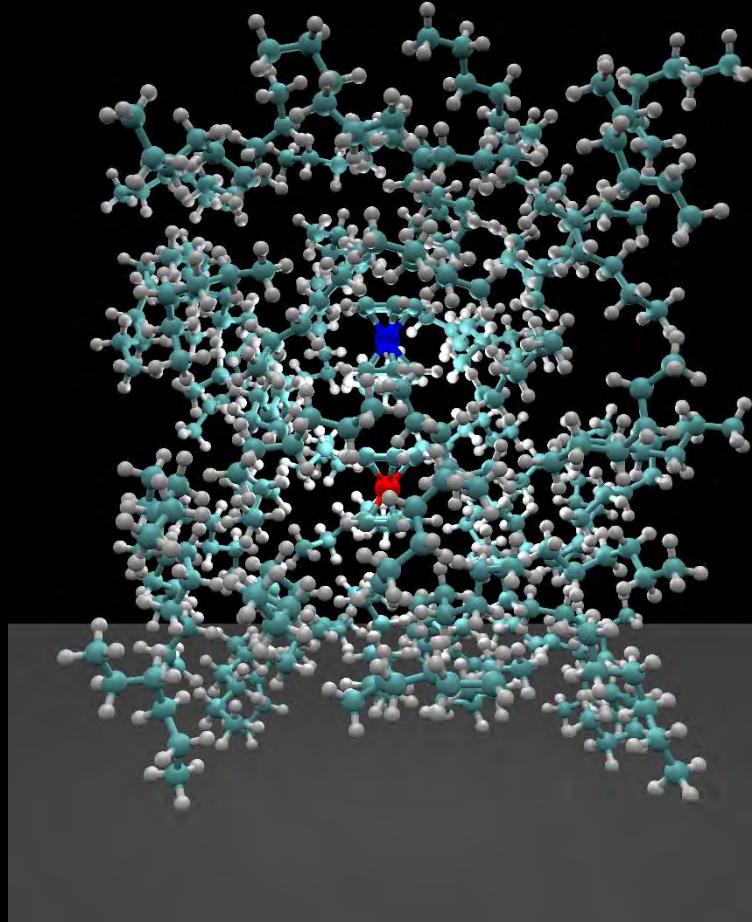
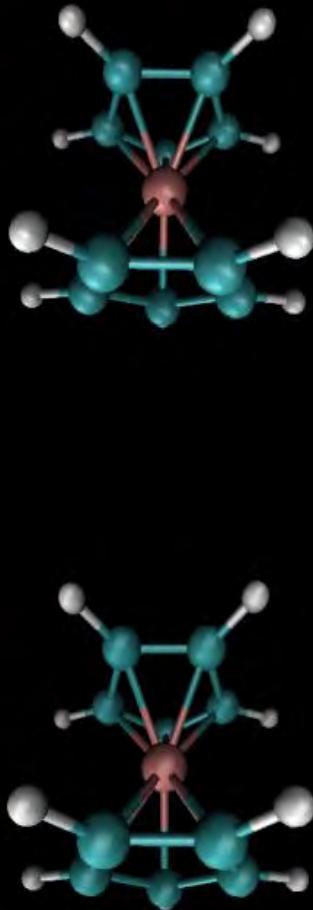
Efficient QCPI Methodology

- *Pre-treat the most important classical decoherence*; i.e., incorporate all classical decoherence via system-independent (e.g., fixed charge) solvent trajectories into effective system propagators that capture the bulk of the effects induced by the solvent on the system.
- Perform the full path sum to add the effects of quantum decoherence. *Quantum memory* usually short-lived, allowing *iterative decompositions of the path integral*, make this task feasible.
- Elimination of paths that carry exponentially small weights leads to further acceleration. Many path combinations are eliminated by virtue of destructive interference.
- Quantum decoherence is a vacuum effect. This can be exploited to eliminate the vast majority of trajectories, leading to an algorithm with molecular dynamics scaling.
 - No sign problem
 - Linear scaling with propagation time
 - MD scaling with number of atoms
 - Fully parallelizable, ideal for Blue Waters

Charge Transfer in Solution: Ferrocene-Ferrocenium in Hexane

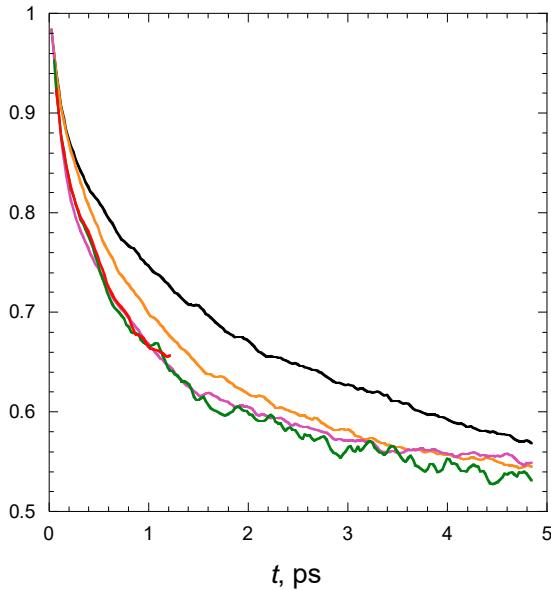


Peter Walters



1,320 solvent atoms (periodic boundary conditions) with CHARMM force fields

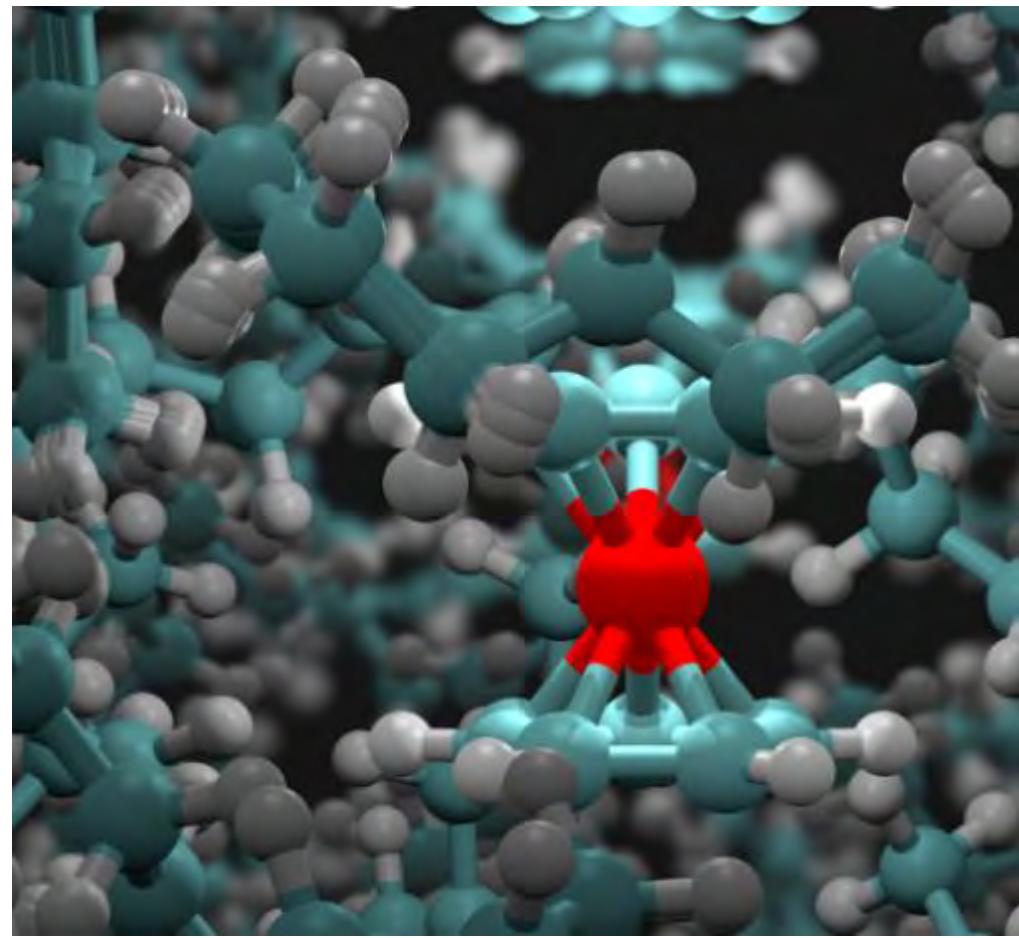
Convergence of all-atom QCPI



Results effectively include $10^4 \times 2^{400}$ trajectories; all phase interference included.

First of its kind!

Done on Blue Waters



quantum superposition
in a classical solvent!

Summary of QCPI methodology

QCPI is a **rigorous quantum-classical formulation**. It makes no *ad hoc* assumptions and uses no adjustable parameters. Yet it does not suffer from the sign problem.

Zero-point energy effects for the classical particles can be included, if desired, by using a quantized phase space density.

Quantum interference effects are fully included through the superposition of phases, which include the interaction between quantum and classical degrees of freedom. Quantum delocalization spreads to the classical particles.

All decoherence effects are automatically accounted for through these phases. There is no need for externally introduced ‘decoherence terms’.

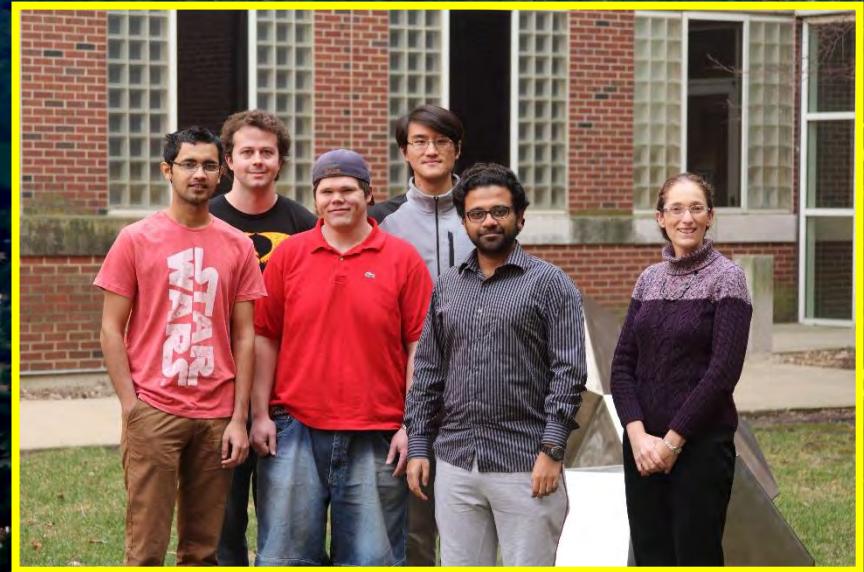
QCPI rigorously **satisfies detailed balance** through phases associated with spontaneous phonon emission.

QCPI is **exact for a system coupled to a harmonic bath**.

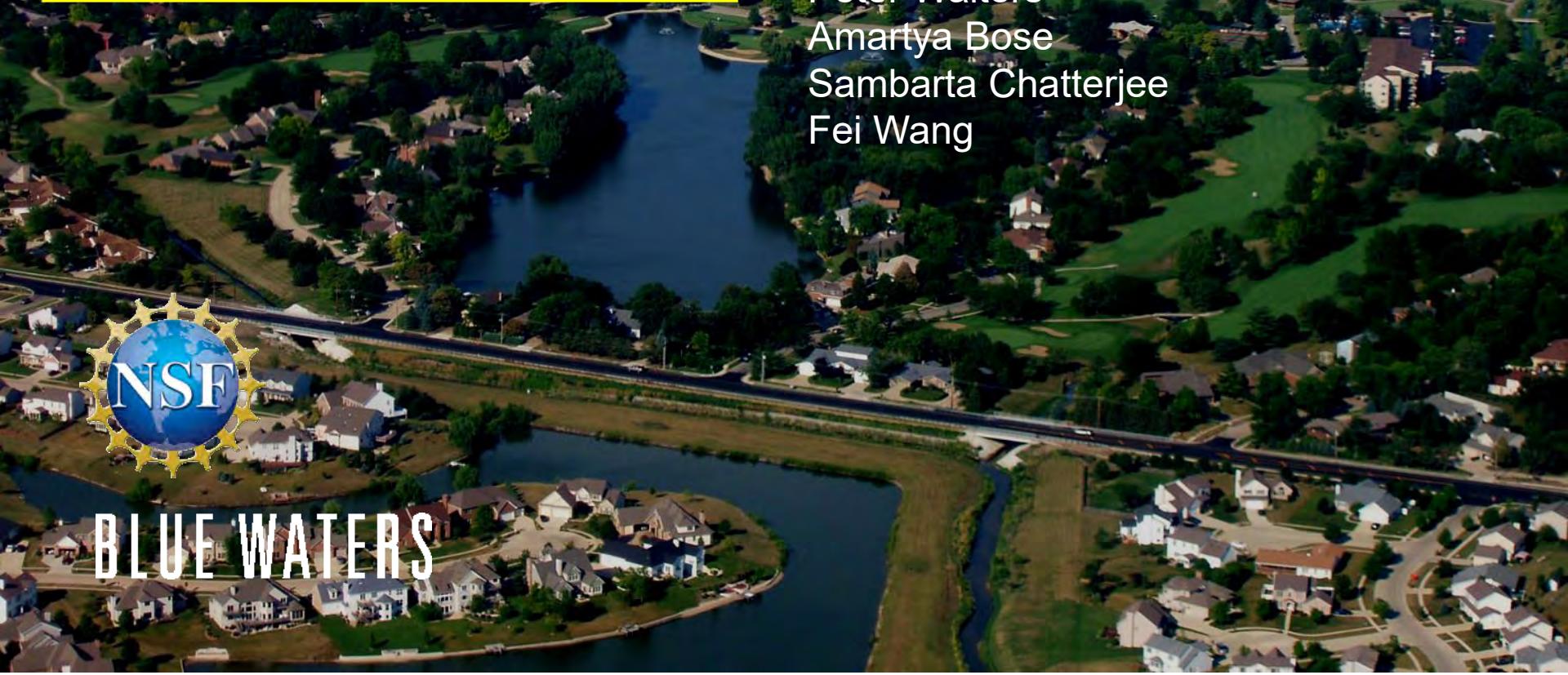
The QCPI algorithm can be used with **thousands of atoms**, described in full detail via available force fields or *ab initio* electronic structure.

External **time-dependent fields** and Langevin thermostats are easily included.

The method is characterized by **MD scaling** and is **fully parallelizable**.



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Amartya Bose
Sambartha Chatterjee
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