Protons and Path Integrals

Landmark Simulation of Condensed Phase Proton Transfer

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Introduction

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- These reactions are ubiquitous in biology
- Transfer of H, H^+, and H^- is a major synthetic motif
- Cutting-edge materials for energy storage and transport

The Proton Transfer Problem

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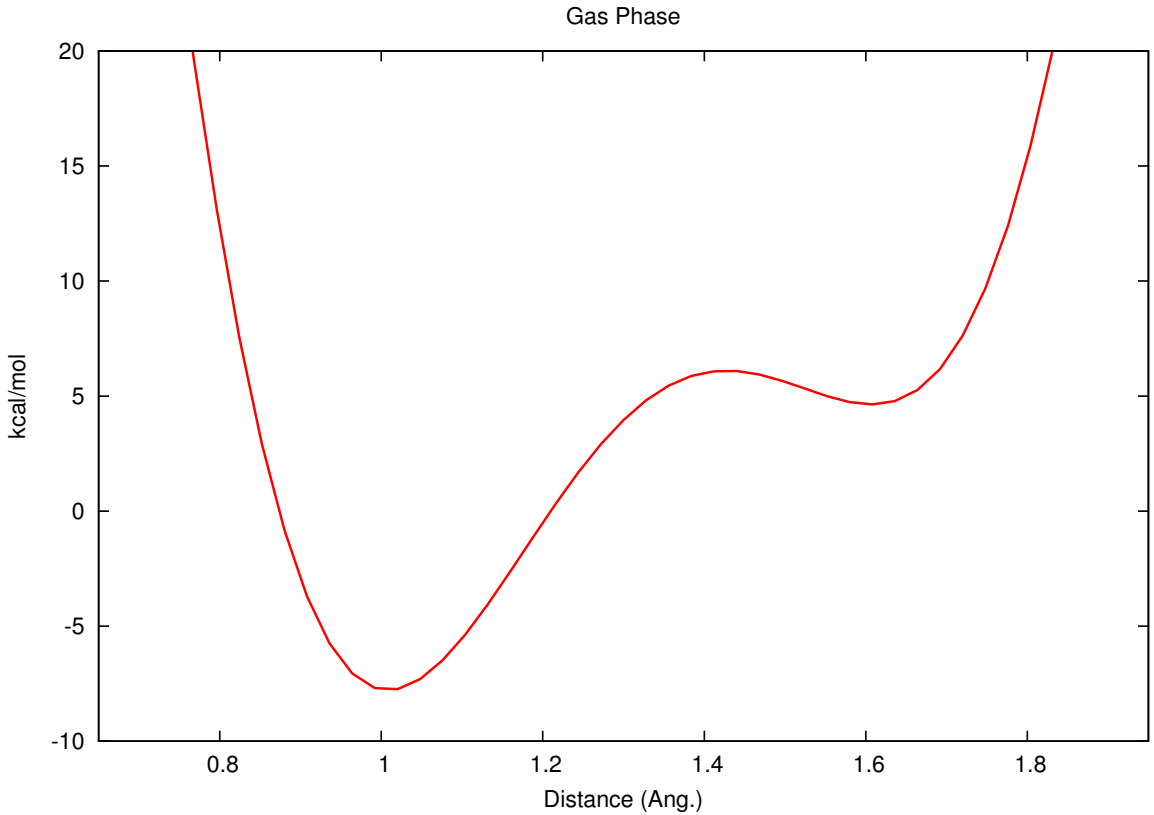

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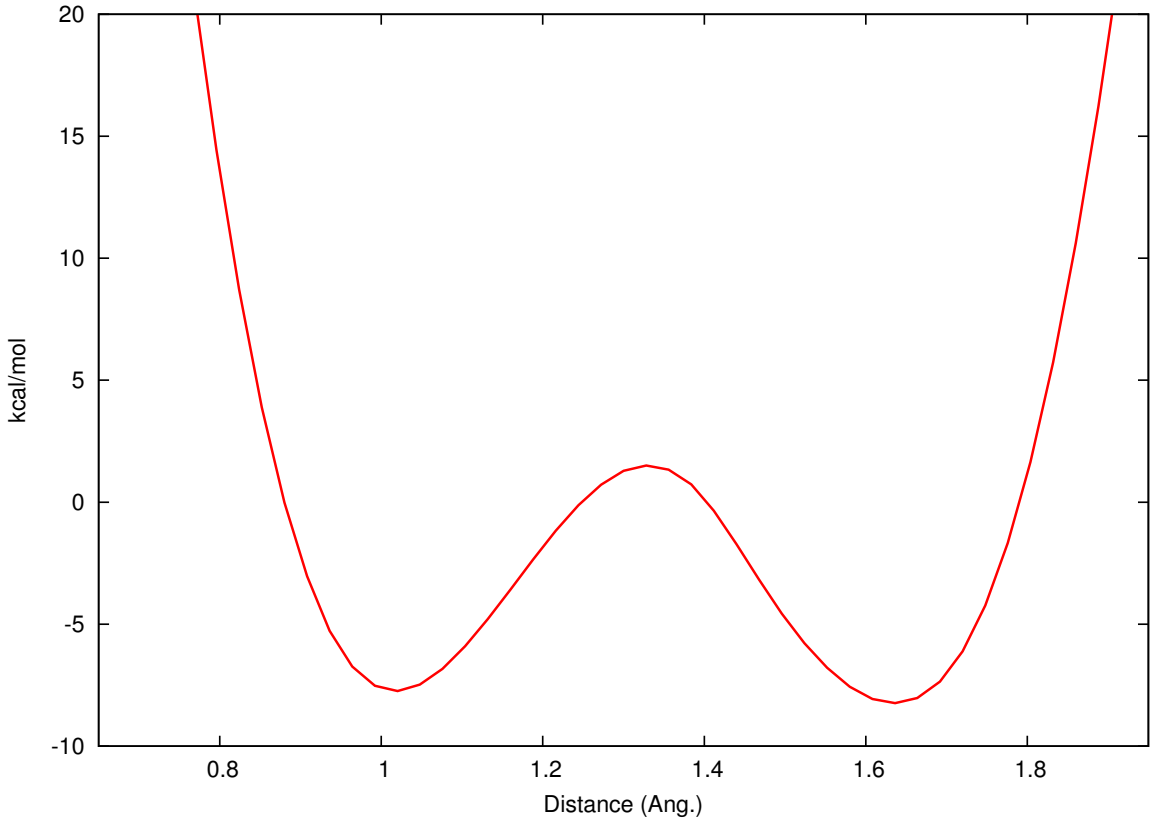

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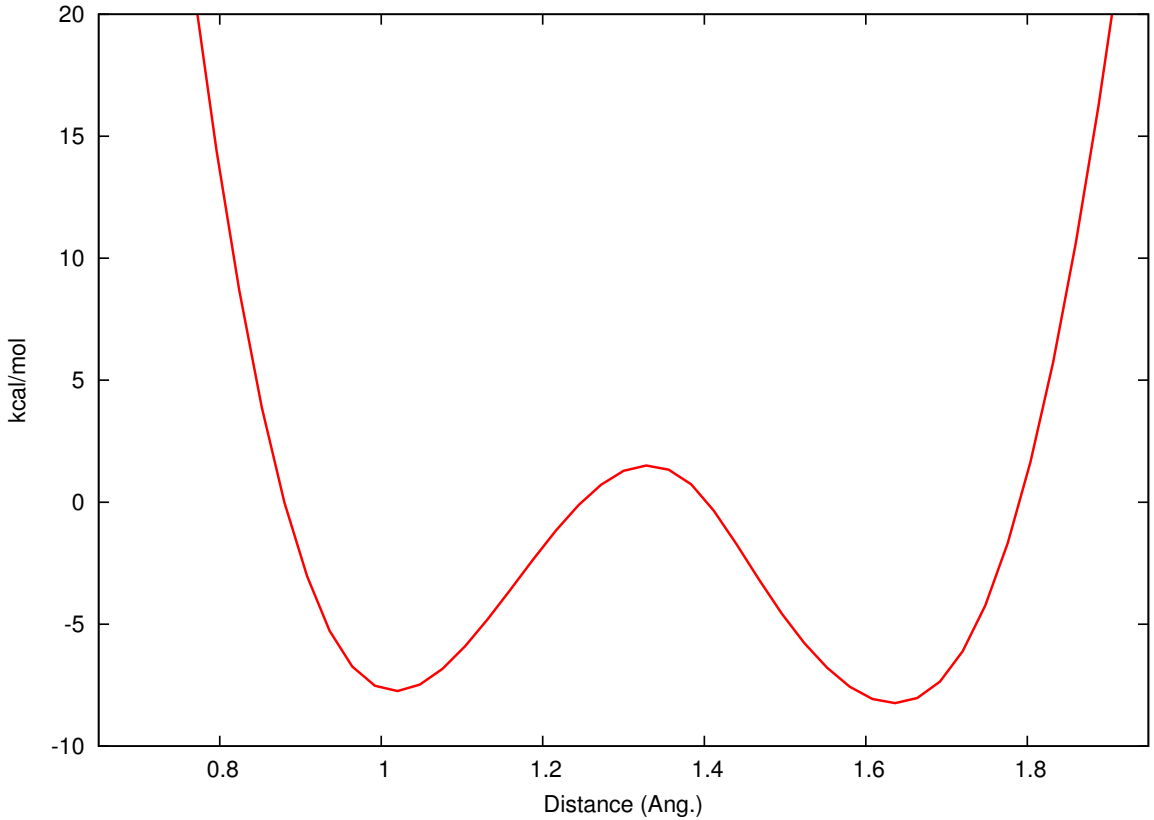

- Many degrees of freedom, transfering species is quantum mechanical
- Separation into interacting system and environment is key

Quantum-Classical Approaches

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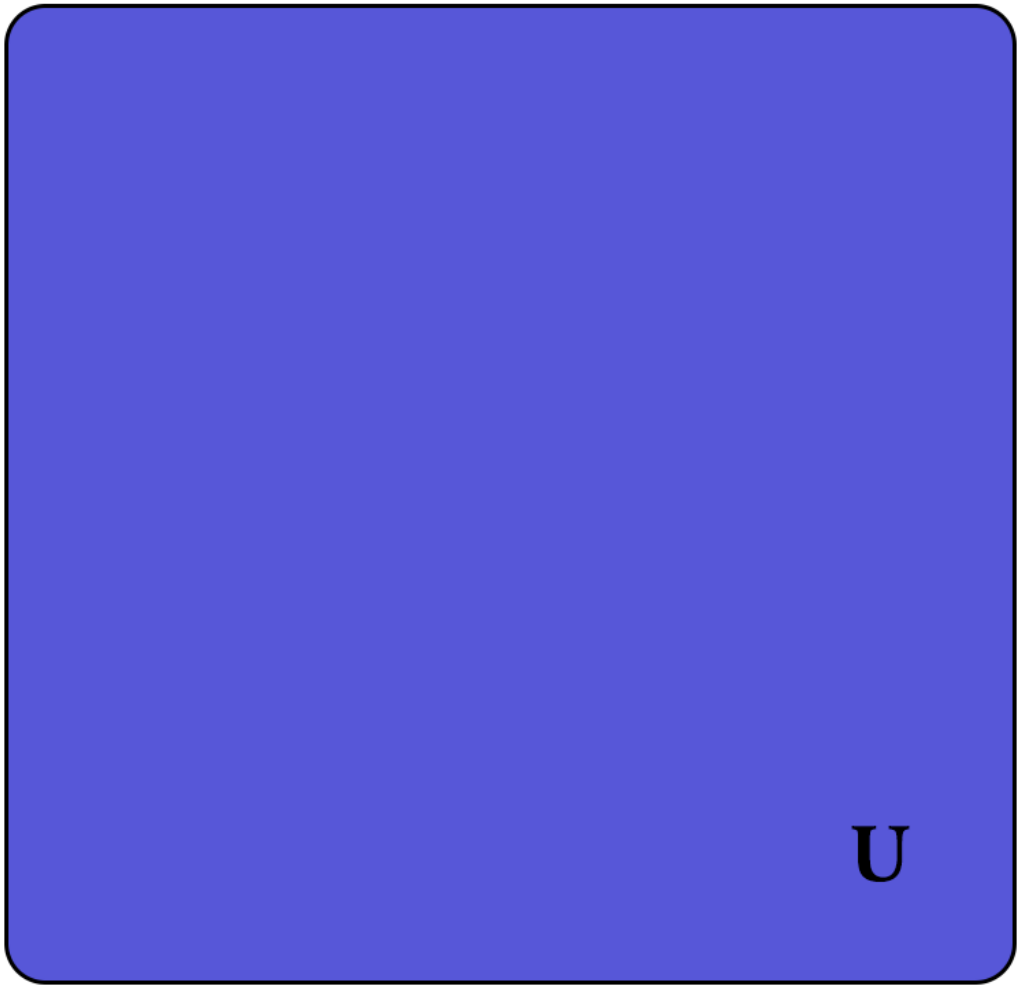
- We desire a rigorous method that works across many regimes of behavior
- Capturing full system-bath interaction is especially important
- The Quantum-Classical Path Integral formalism is designed to achieve these goals

QCPI in a Nutshell



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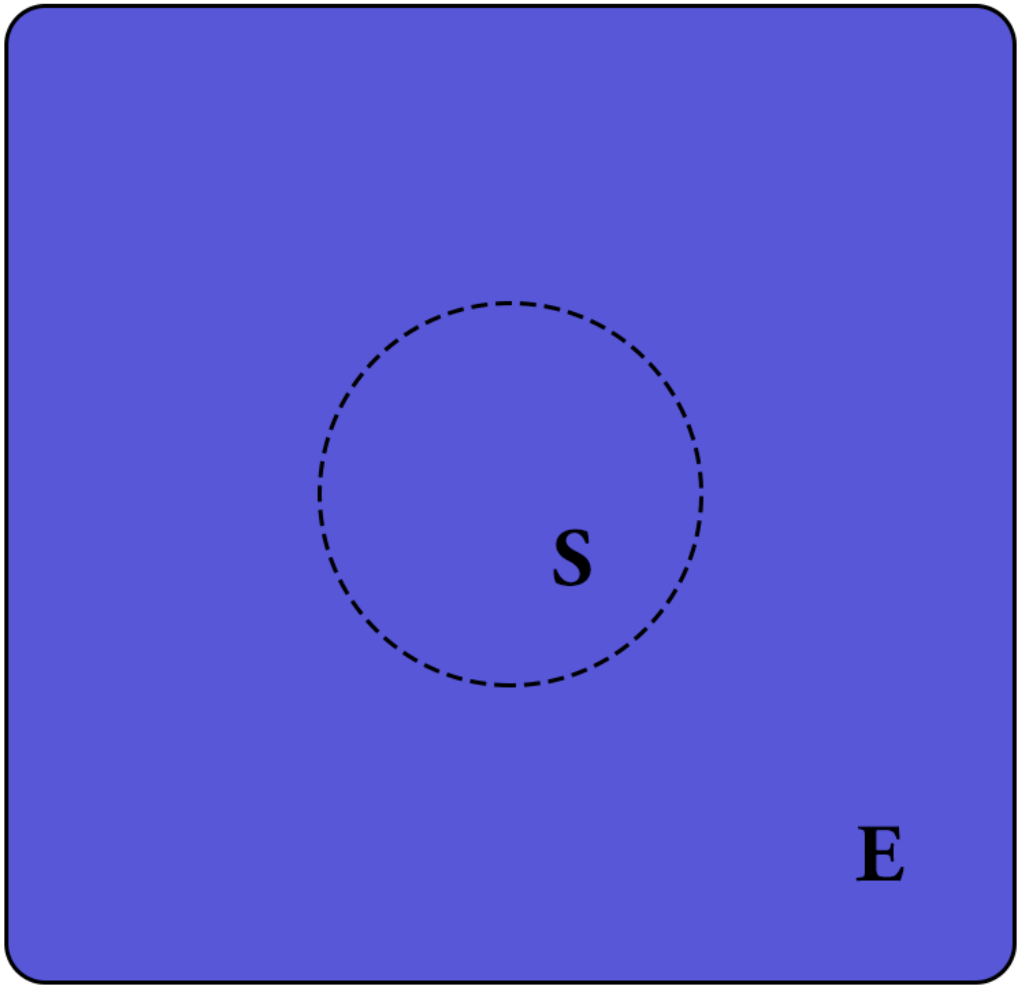

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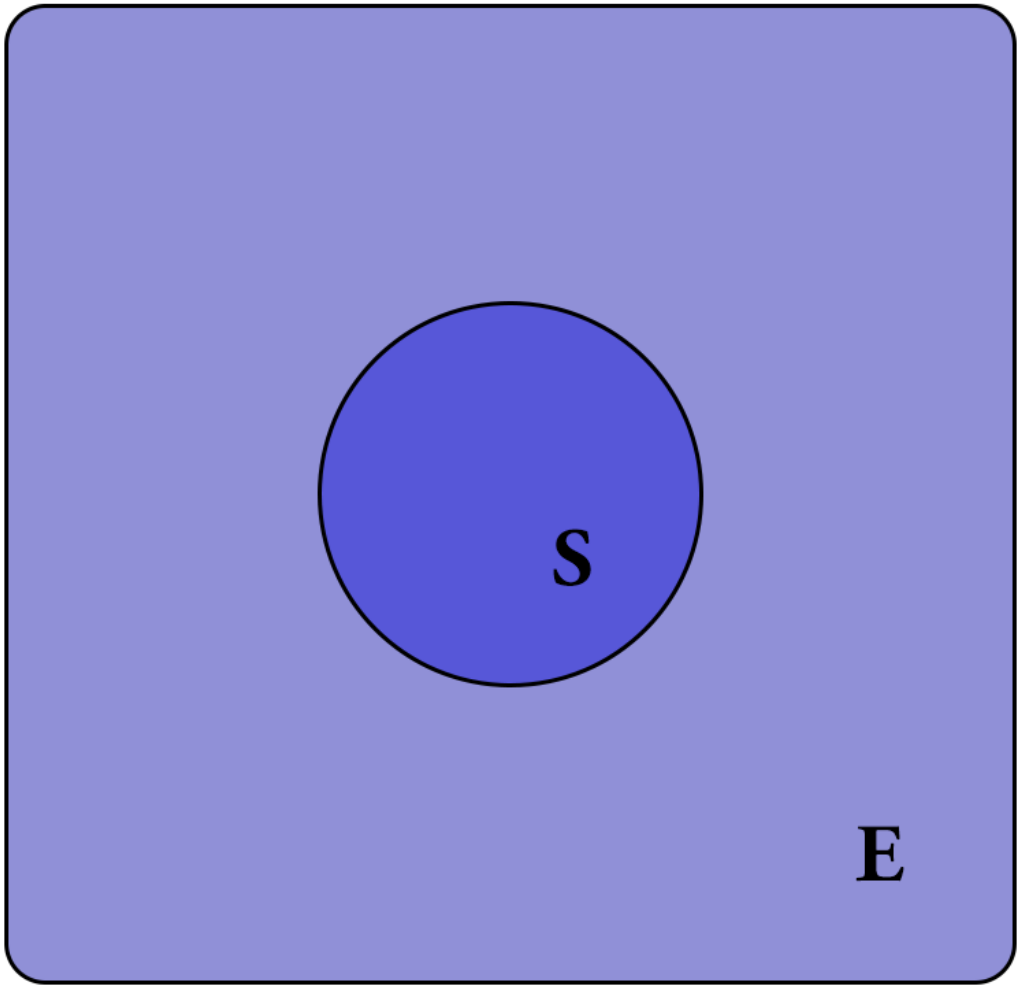

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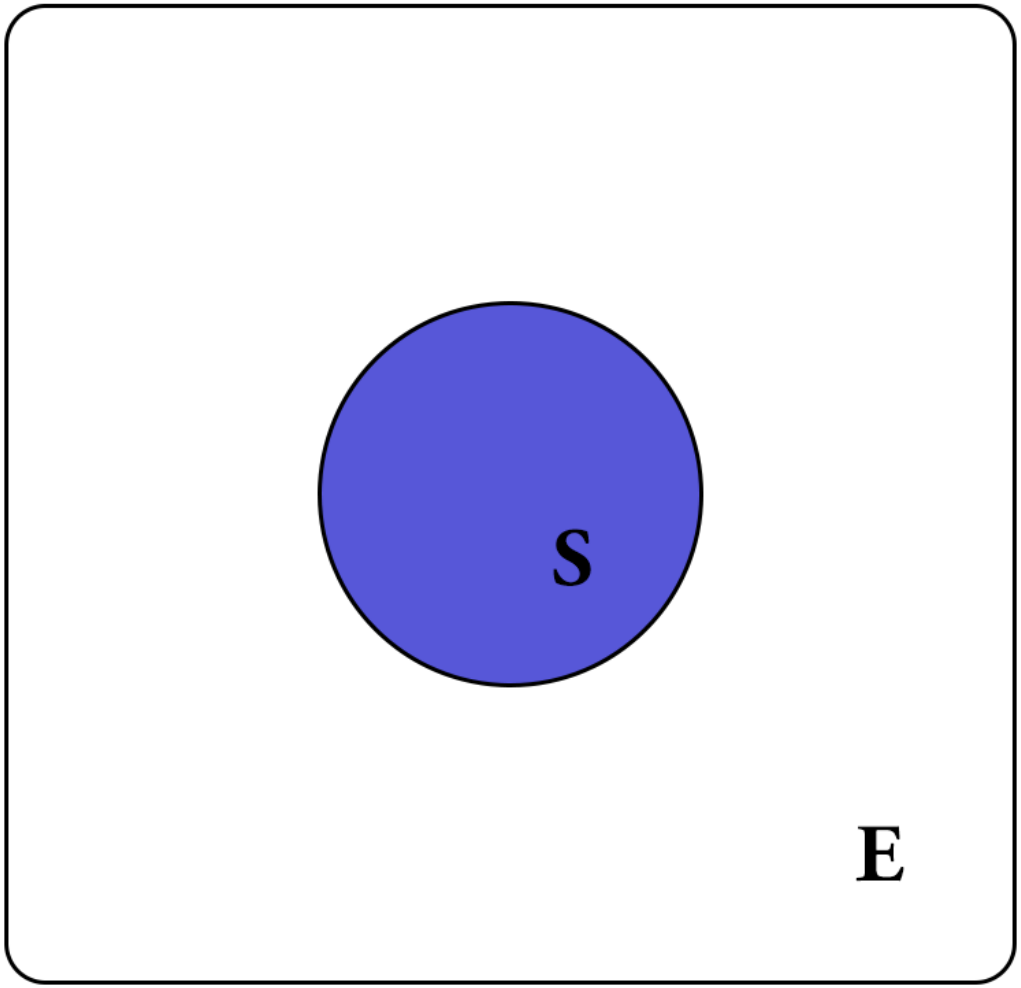

QCPI Equations

$$\hat{\rho}_{red}(s_N^{\pm}; N\Delta t) = \int dx_N^{\pm} \left\langle s_N^{+} x_N^{+} \right| e^{-i\hat{H}N\Delta t/\hbar} \hat{\rho}(0) e^{i\hat{H}N\Delta t/\hbar} \left| s_N^{-} x_N^{-} \right\rangle$$

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

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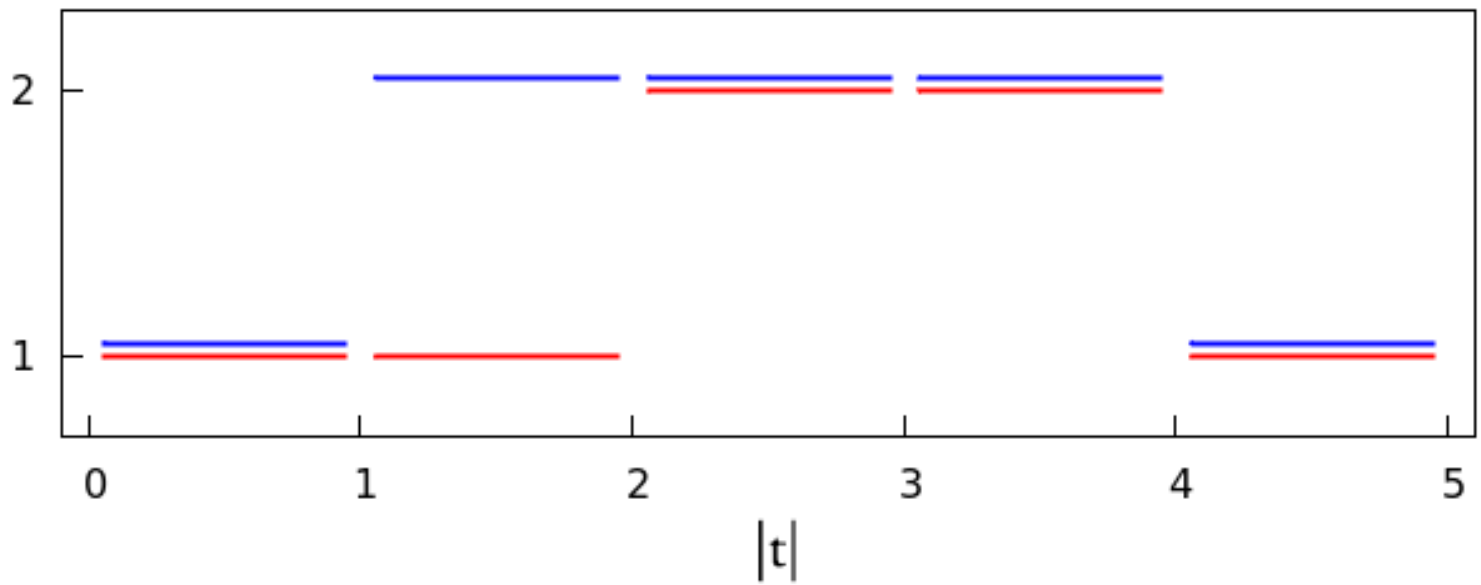

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The Azzouz-Borgis Model

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H. Azzouz, D. Borgis, *J. Chem. Phys.* **98**, 7361 (1993)

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- A test system for our method should have several properties
  - Simple MD description
  - Realistic interactions and energetics
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- Our goal is to extend previous work to treat atomistic systems
- A test system for our method should have several properties
  - Simple MD description
  - Realistic interactions and energetics
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- The Azzouz-Borgis model of proton transfer is just such a system

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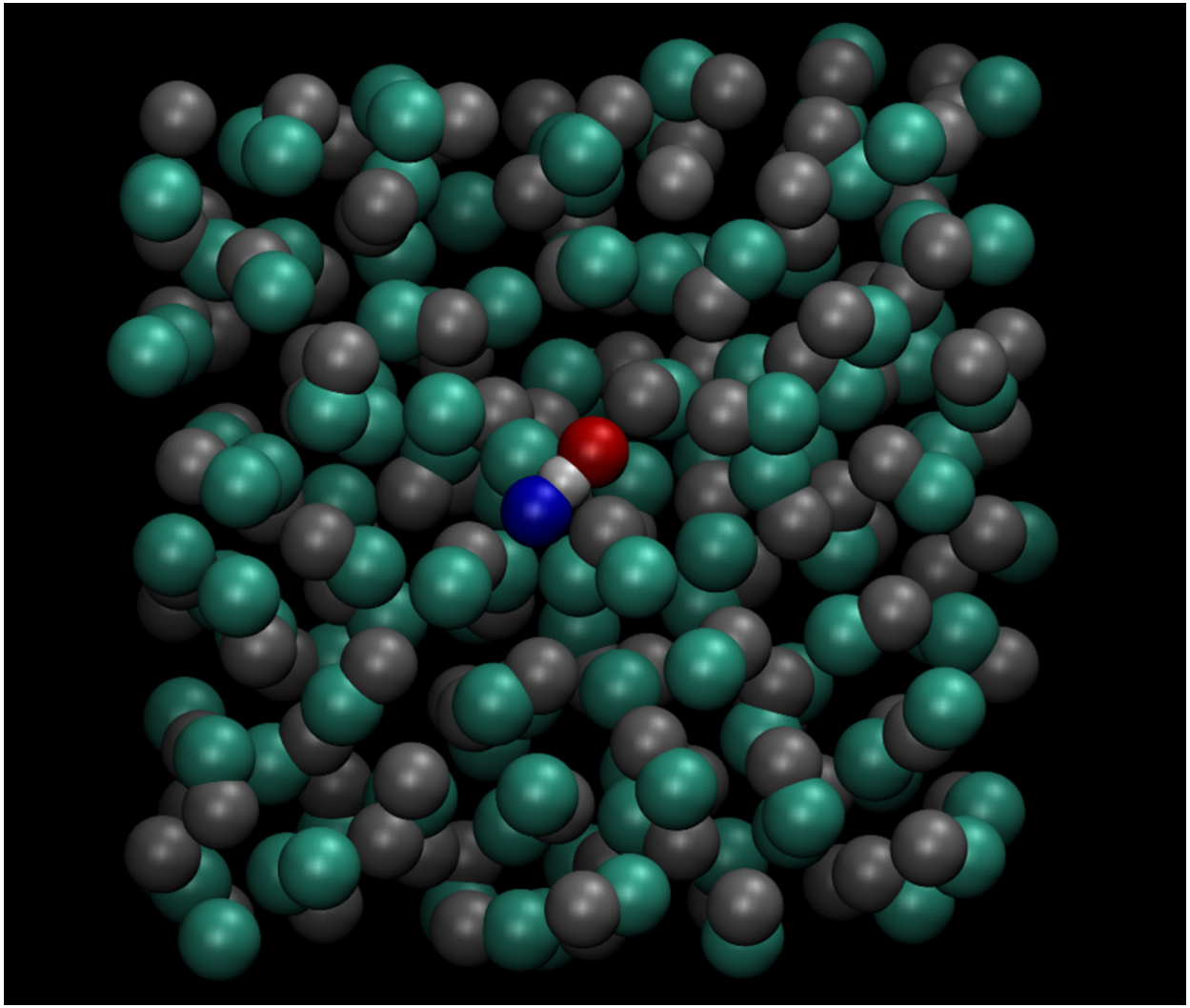
The Azzouz-Borgis Model



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QCPI Challenges

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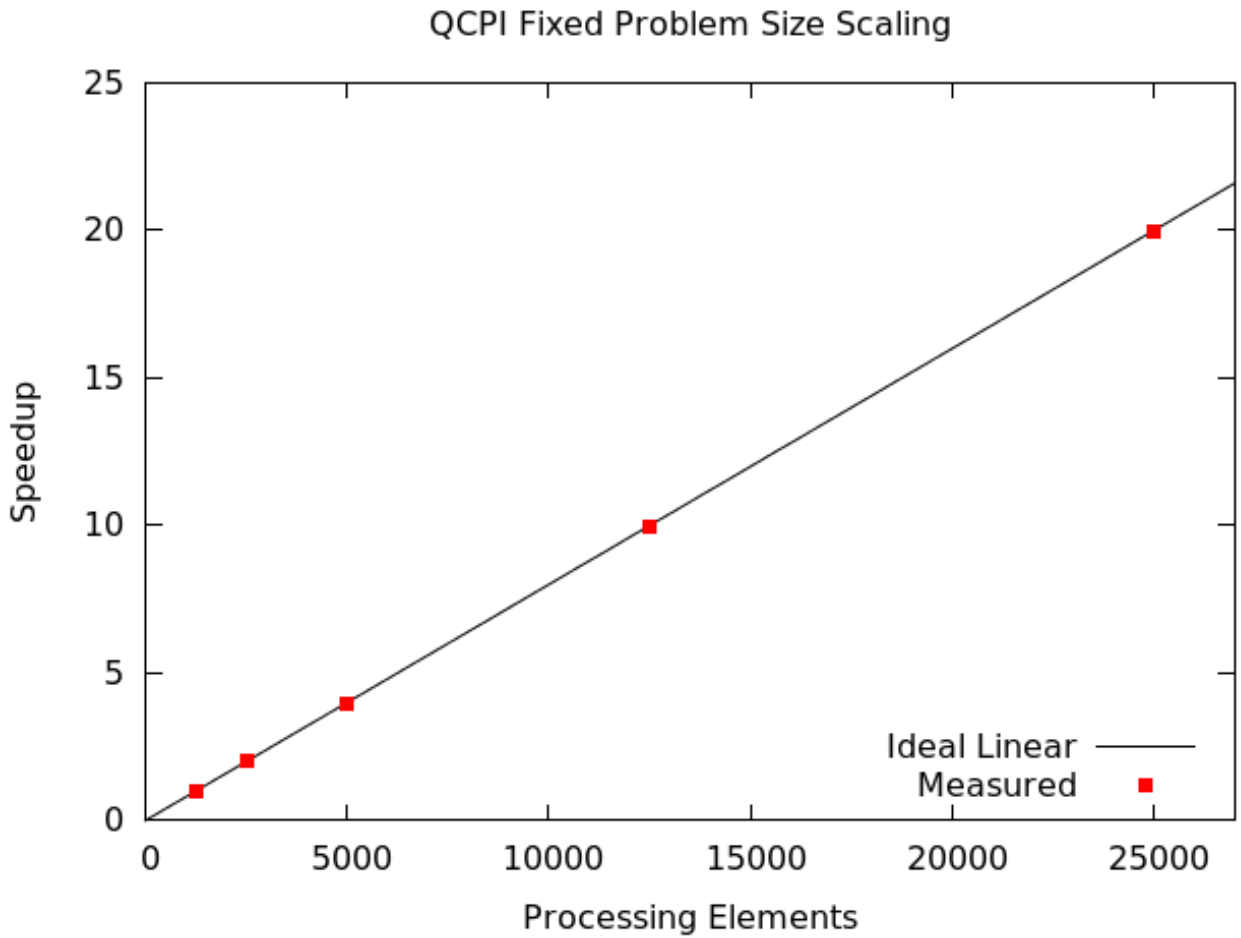

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- Further refinements suggested by BW staff
  - Using memory for file storage
  - Investigating multi-level parallelism

Results

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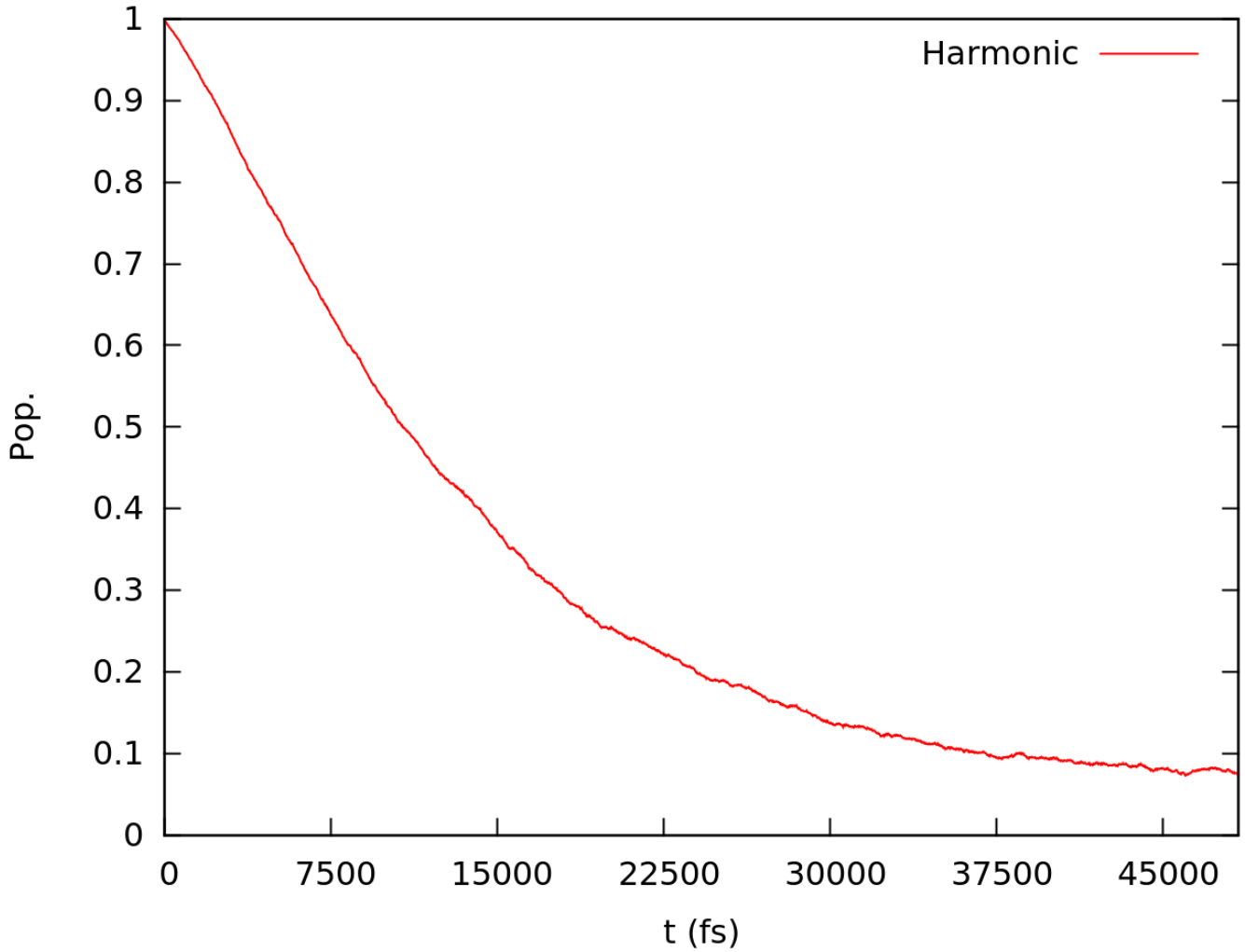
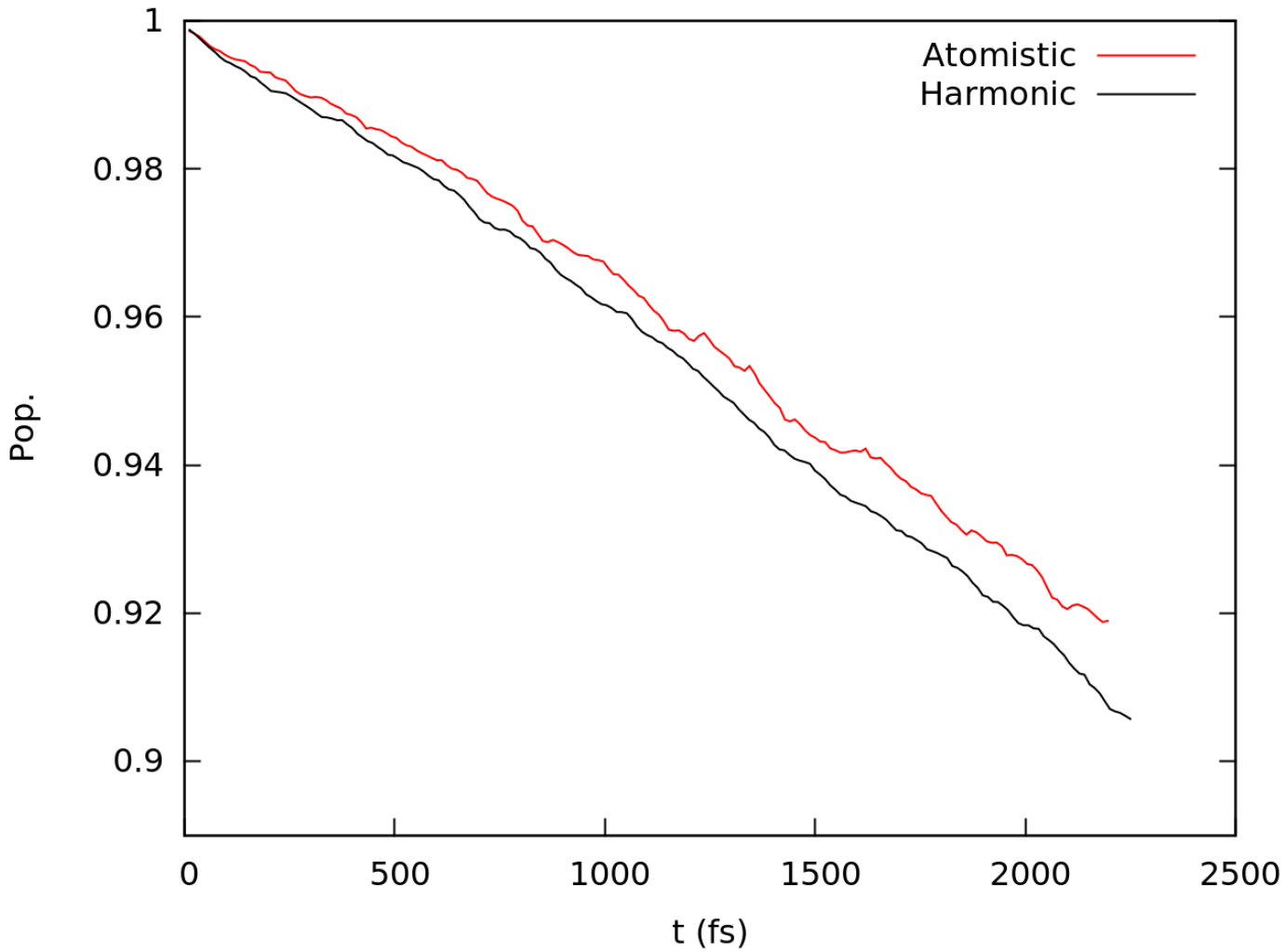

Harmonic
Pop.
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
7500
15000
22500
30000
37500
45000
t (fs)

Results


Atomistic
Harmonic
Pop.
1
0.98
0.96
0.94
0.92
0.9
0
500
1000
1500
2000
2500
t (fs)

Future Directions

- Complete converged anharmonic calculations
- Investigate bath ensemble properties
- Extending results to complex systems, including proteins and biomolecules
  - Although these systems are larger, their couplings may be more manageable

Acknowledgements

BLUE WATERS
SUSTAINED PETASCALE COMPUTING

NCSA

NSF