Protons and Path Integrals
Landmark Simulation of Condensed Phase Proton Transfer

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Charge transfer reactions are an important class of fundamental chemical reactions.
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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
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The Proton Transfer Problem

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Quantum-Classical Approaches

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  - Surface Hopping
  - Reduced Models (Spin-Boson, etc.)
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- Capturing full system-bath interaction is especially important

- The Quantum-Classical Path Integral formalism is designed to achieve these goals
\[ \hat{\rho}_{\text{red}}(s_{N}^{\pm}; N\Delta t) = \int dx_{N}^{\pm} \langle s_{N}^{+}x_{N}^{+} | e^{-i\hat{H}N\Delta t/\hbar} \hat{\rho}(0) e^{i\hat{H}N\Delta t/\hbar} | s_{N}^{-}x_{N}^{-} \rangle \]
\[
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\]

\[
\hat{\rho}_{\text{red}}(s_N^{\pm}; N\Delta t) = \int dx_0 \int dp_0 P(x_0, p_0) Q(s_N^{\pm}, x_0, p_0; N\Delta t)
\]
\[ \hat{\rho}_{\text{red}}(s_N^\pm; N\Delta t) = \int dx_N^\pm \langle s_N^+ x_N^+ | e^{-i\hat{H}N\Delta t/\hbar} \hat{\rho}(0) e^{i\hat{H}N\Delta t/\hbar} | s_N^- x_N^- \rangle \]

\[ \hat{\rho}_{\text{red}}(s_N^\pm; N\Delta t) = \int dx_0 \int dp_0 P(x_0, p_0) Q(s_N^\pm, x_0, p_0; N\Delta t) \]

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The Azzouz-Borgis model of proton transfer is just such a system.

The Azzouz-Borgis Model

\[ \hat{\rho}_{\text{red}}(s^{\pm}_N; N\Delta t) = \int dx_0 \int dp_0 \, P(x_0, p_0) Q(s^{\pm}_N, x_0, p_0; N\Delta t) \]
\[ \hat{\rho}_{\text{red}}(s_N^\pm; N\Delta t) = \int dx_0 \int dp_0 \, P(x_0, p_0) \, Q(s_N^\pm, x_0, p_0; N\Delta t) \]

- Huge number of calculations required
- It is possible to parallelize these efficiently
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QCPI Challenges

\[ \hat{\rho}_{\text{red}}(s_{\pm}^N; N\Delta t) = \int dx_0 \int dp_0 P(x_0, p_0) Q(s_{\pm}^N, x_0, p_0; N\Delta t) \]

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- Forward-Backward paths must interface with MD
  - BW staff and LAMMPS developers helped incorporate this behavior efficiently
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- Further refinements suggested by BW staff
  - Using memory for file storage
  - Investigating multi-level parallelism
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

[Image of people enjoying a meal]

[Logos for Blue Waters, NCSA, and NSF]