Atom-Centered Density Matrix
Propagation of an $S_{N2}$ Reaction

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ADMP

- Atom-Centered Density Matrix Propagation
- Begins with transition state geometry
- Assigns random velocities to all atoms following Newtonian physics
- Nuclear kinetic energies assigned so the total kinetic energy is equal to a supplied value
Calculates electronic energy of the molecule using the Schrödinger Equation at certain time intervals (between 0.1-0.25 fs)

Process is then repeated using new initial random velocities
Computational Methods

- MPW1K level of theory
- MIDIY+ basis set
- PCM solvation model
  - Water
- UFF topological model
Our \( S_{N2} \) Reaction

\[
\text{NH}_3 + \text{CH}_3\text{Cl} \rightleftharpoons \text{NH}_3\text{CH}_3 + \Theta\text{Cl}
\]

\( \Delta E = 117.00 \text{ kcal/mol, gas phase} \)

\( \Delta E = -21.27 \text{ kcal/mol, aqueous solution} \)
Our Transition State!
Why We Chose this Reaction

- Small molecules allow the runs to go quickly
- ΔE(gas) and ΔE(aq) are very different
- A good test case to see if ADMP works in conjunction with PCM - should see dramatically different gas phase and aqueous phase trajectories
Why We Care About Quantum Dynamics

- Allows us to follow reaction over time
- Dynamic surface looks different from the Born-Oppenheimer surface of quantum mechanics
- When there are several competing pathways, quantum dynamics can determine the ratios of pathway frequency
Born-Oppenheimer Surface

Reaction Coordinate for NH3 + CH3Cl

Relative E (kcal/mol)

Reaction Coordinate

Gas
Aqueous
Representative of the Gas Phase Dynamic Surface
Representative of the Aqueous Phase Dynamic Surface
Conclusions

* Aqueous Phase*: 51.6% go to reactants
48.4% go to products

* Gas Phase**: 84.0% go to reactants
16.0% go to products

* Out of 93 trajectories
** Out of 94 trajectories
Eventually….

- We want to apply quantum dynamics to the alkaline hydrolysis and perhydrolysis of VX
- Determine the actual reaction pathways for these reactions
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