

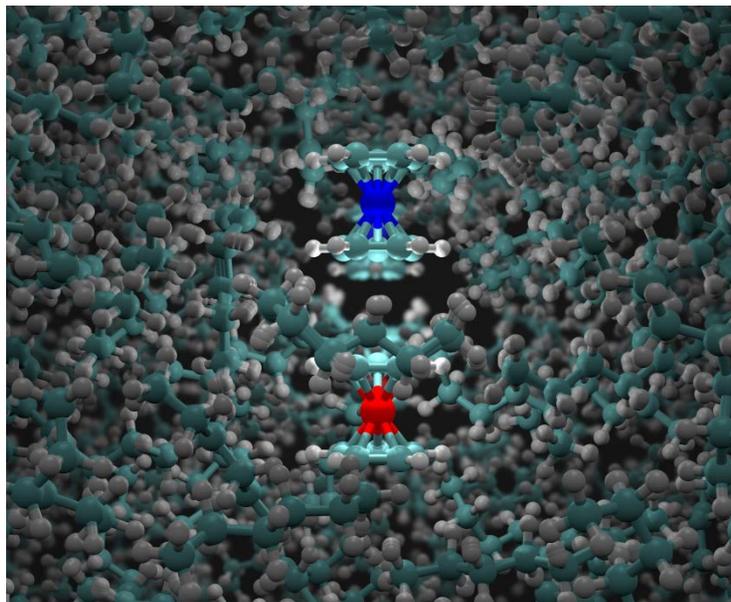
Quantum-classical path integral simulation of ferrocene-ferrocenium charge transfer in solution



Peter Walters (PI: Nancy Makri)

University of Illinois

6/13/16

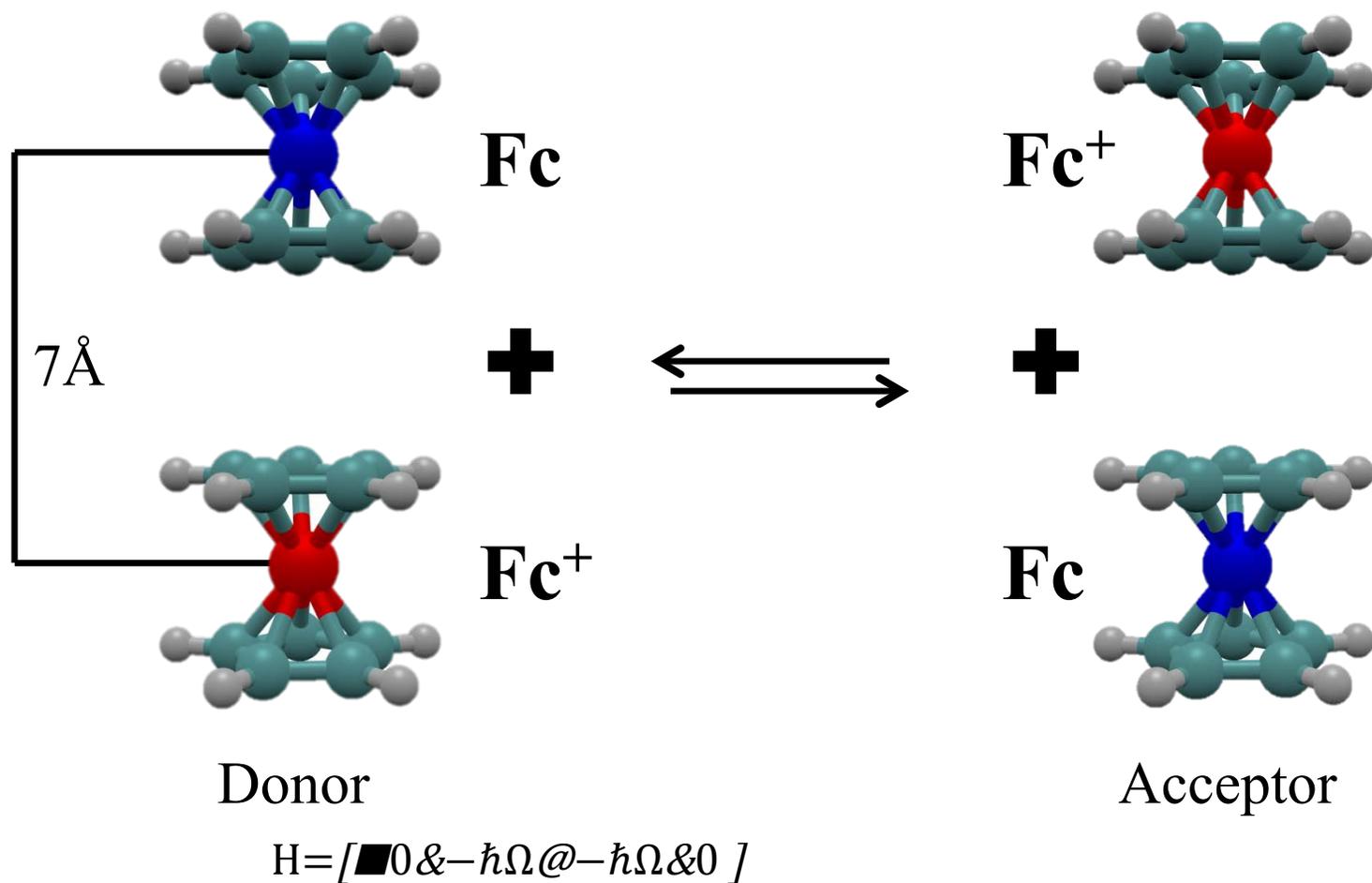


Condensed phase electron transfer reactions

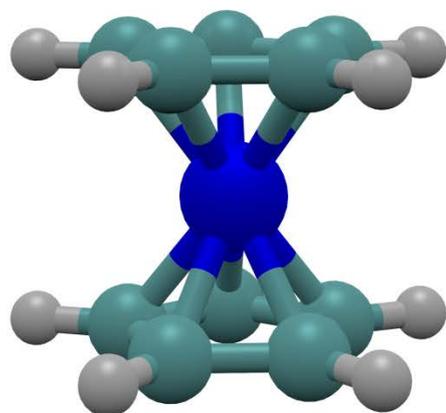
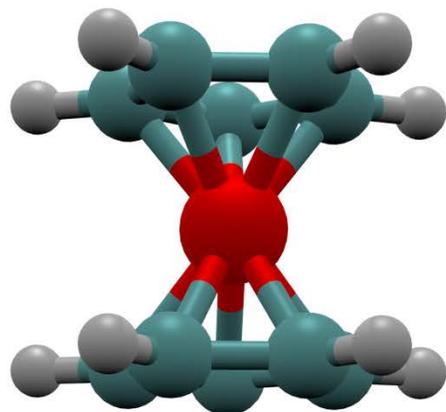


- Prototypical example of condensed phase electron transfer
- Most biological/synthetic energy pathways involve condensed phase electron transfer
- Accurate simulations are extremely demanding
 - Involve thousands of complexly coupled atoms
 - Quantum effects can't be ignored

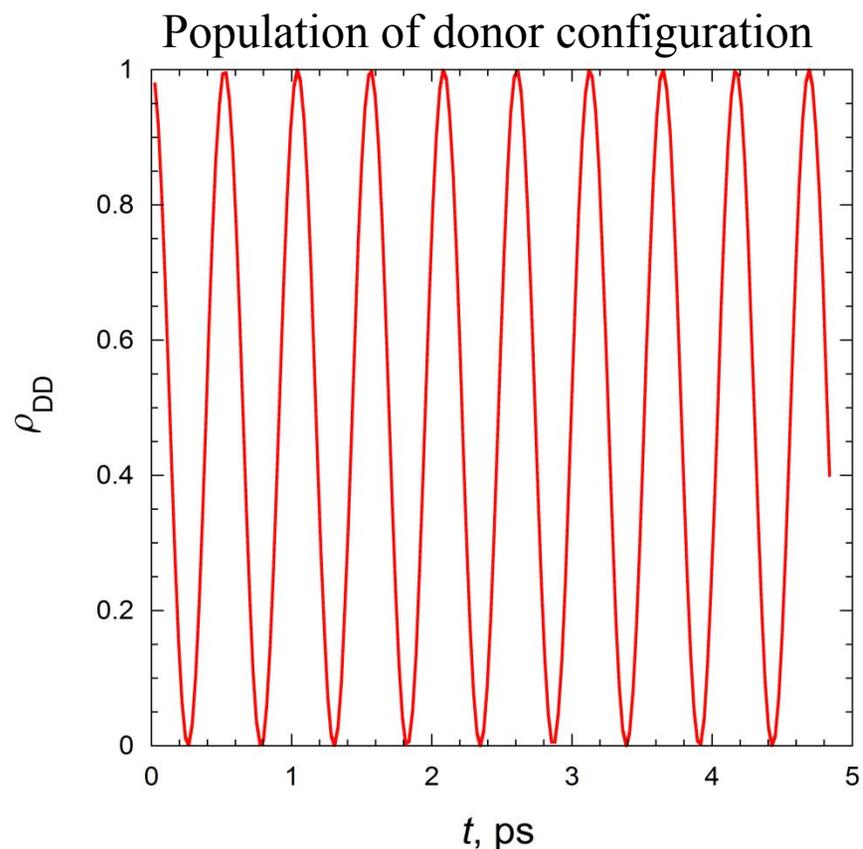
Ferrocene-Ferrocenium



Ferrocene-Ferrocenium in vacuum

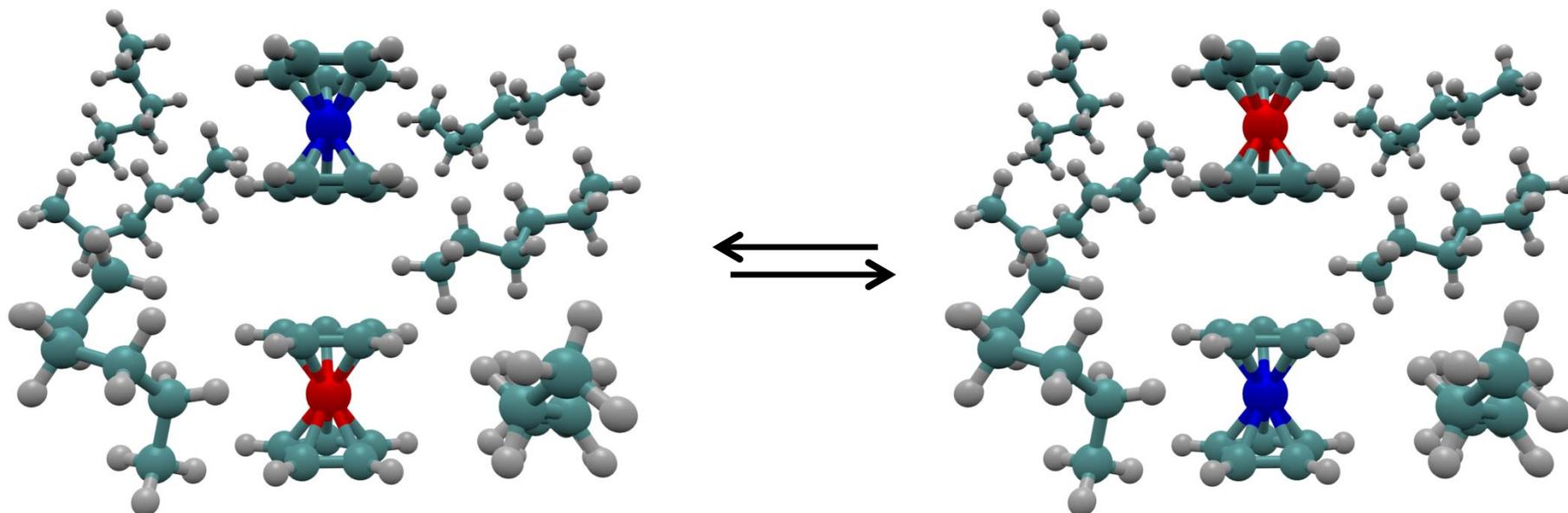


Donor
Acceptor



- Oscillations don't dissipate without solvent
- Oscillation frequency depends on coupling

Ferrocene-Ferrocenium in solution



$$H = [H_{\downarrow D}(\mathbf{p}, \mathbf{q}) - \hbar\Omega @ -\hbar\Omega + H_{\downarrow A}(\mathbf{p}, \mathbf{q})]$$

Ferrocene-Ferrocenium in solution



Donor population dynamics

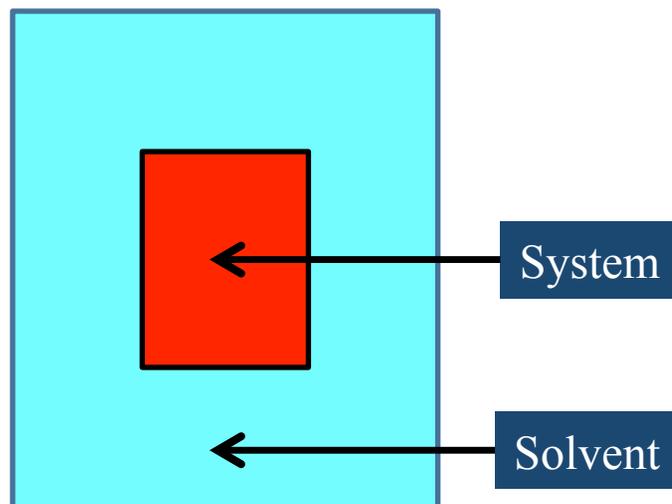


Impossible to simulate?



- Impossible to simulate using traditional quantum methods
- Cost scales exponentially with the number of degrees of freedom
- Not all degrees of freedom require full quantum treatment
- Judicious application of quantum mechanics makes simulation possible

System solvent decomposition



- The system (ferrocene-ferrocenium) is treated using quantum mechanics
- The solvent (hexane) is treated classically
- System solvent interaction?

System solvent interaction

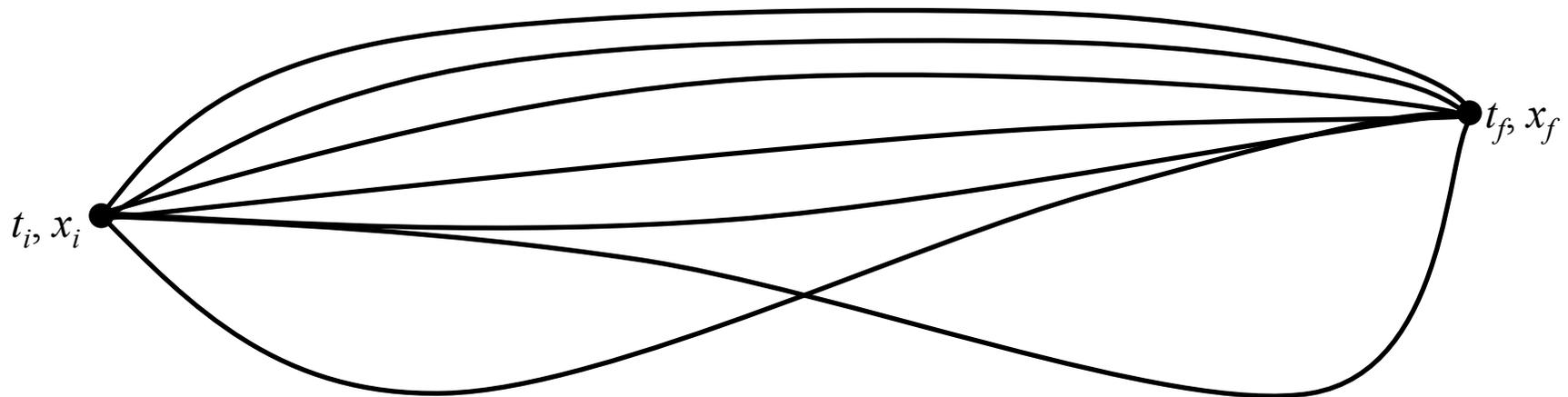


- Goal: couple quantum system to classical solvent
- Can't be done accurately if wavefunctions are involved
- The nonlocality of wavefunctions is incompatible with classical mechanics
- Need something local in nature but able to capture the effects of quantum nonlocality

Feynman path integral



- Sums over all possible paths connecting the initial and final configurations



- The paths are local in space
- Summation leads to quantum nonlocality

Quantum-classical path integral (QCPI)



- Combines a path integral representation of the system with a classical treatment of the solvent
- Rigorously describes the interaction between the quantum system and the classical solvent
 - Each path applies a unique sequence of forces to the solvent
 - The solvent, in turn, contributes a phase to the path sum
- Results in a quantum superposition of the classically propagated solvent

QCPI



$$\rho_{\text{red}}(s^{\pm}; N\Delta t) = \int d\mathbf{q}_0 \int d\mathbf{p}_0 P(\mathbf{q}_0, \mathbf{p}_0) Q(\mathbf{q}_0, \mathbf{p}_0; s^{\pm})$$

s is the coordinate of the system

\mathbf{q} is a vector of the solvent's coordinates

\mathbf{p} is a vector of the solvent's momenta

$$\rho_{\text{red}}(s^{\pm}; t) = \int d\mathbf{q} \langle \mathbf{q} | \rho(t) | \mathbf{q} \rangle$$

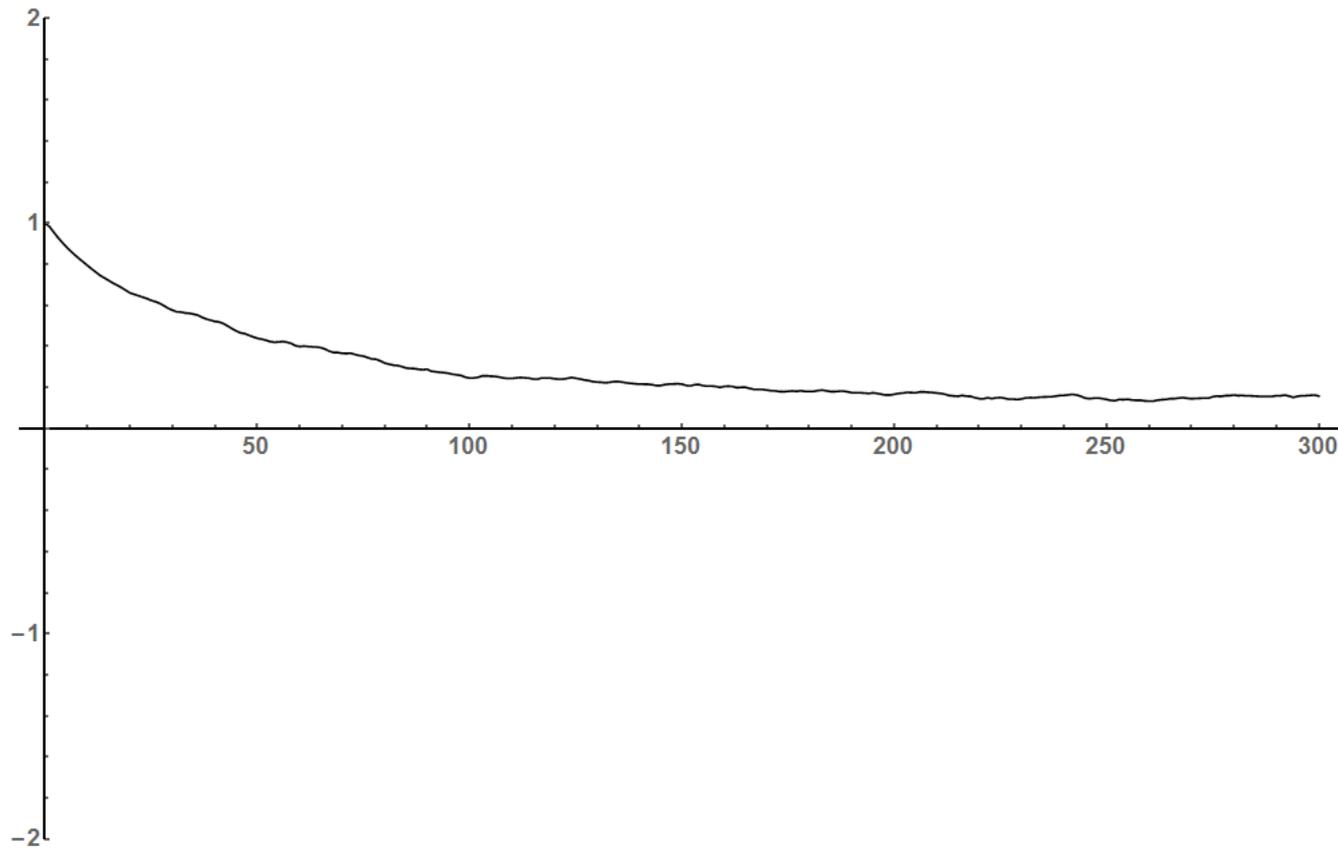
$P(\mathbf{q}_0, \mathbf{p}_0)$ solvent's initial distribution

$Q(\mathbf{q}_0, \mathbf{p}_0; s^{\pm})$ quantum influence function

QCPI

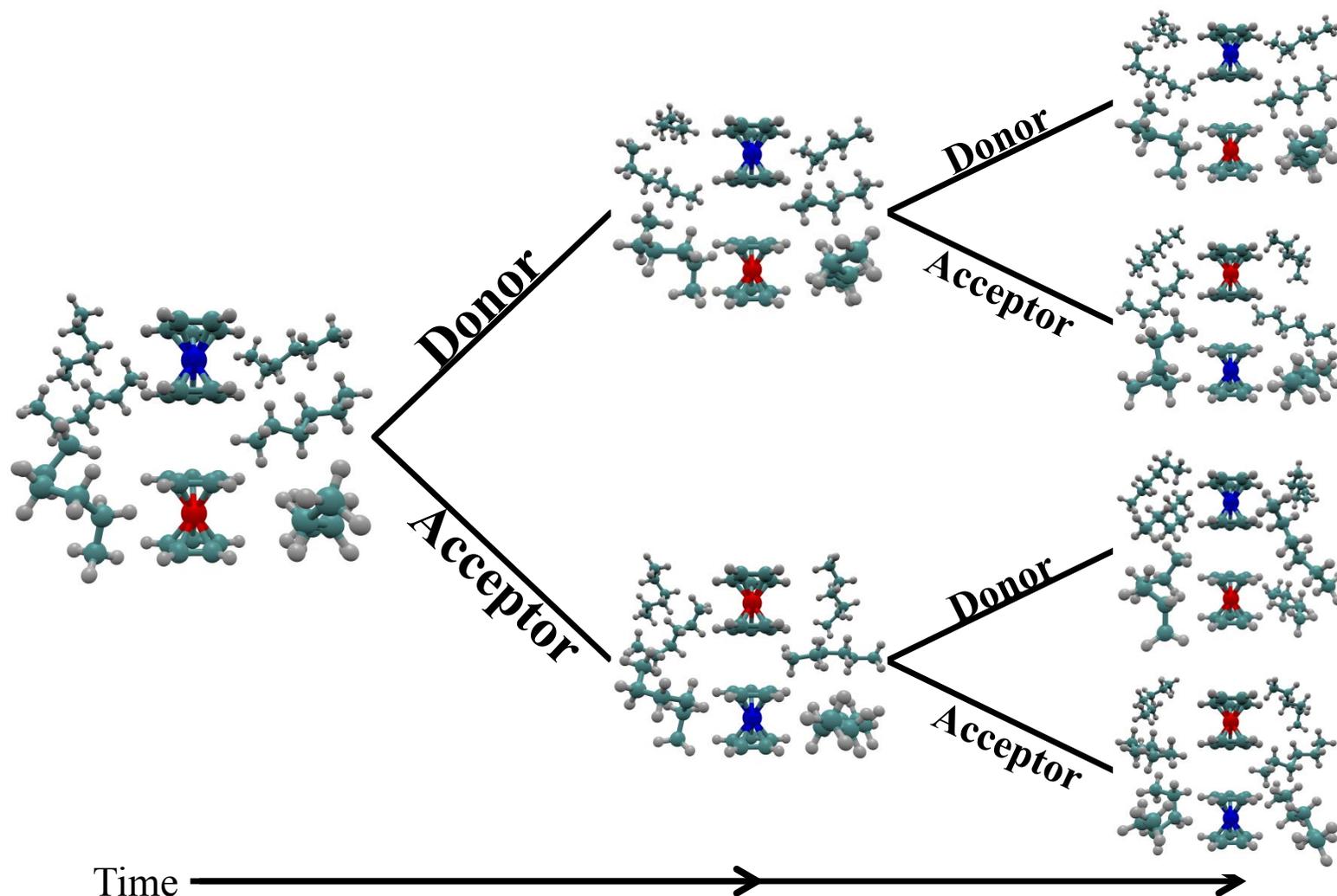


$$\rho_{\text{red}}(s^{\pm}; N\Delta t) = \int d\mathbf{q}_0 \int d\mathbf{p}_0 P(\mathbf{q}_0, \mathbf{p}_0) Q(\mathbf{q}_0, \mathbf{p}_0; s^{\pm})$$

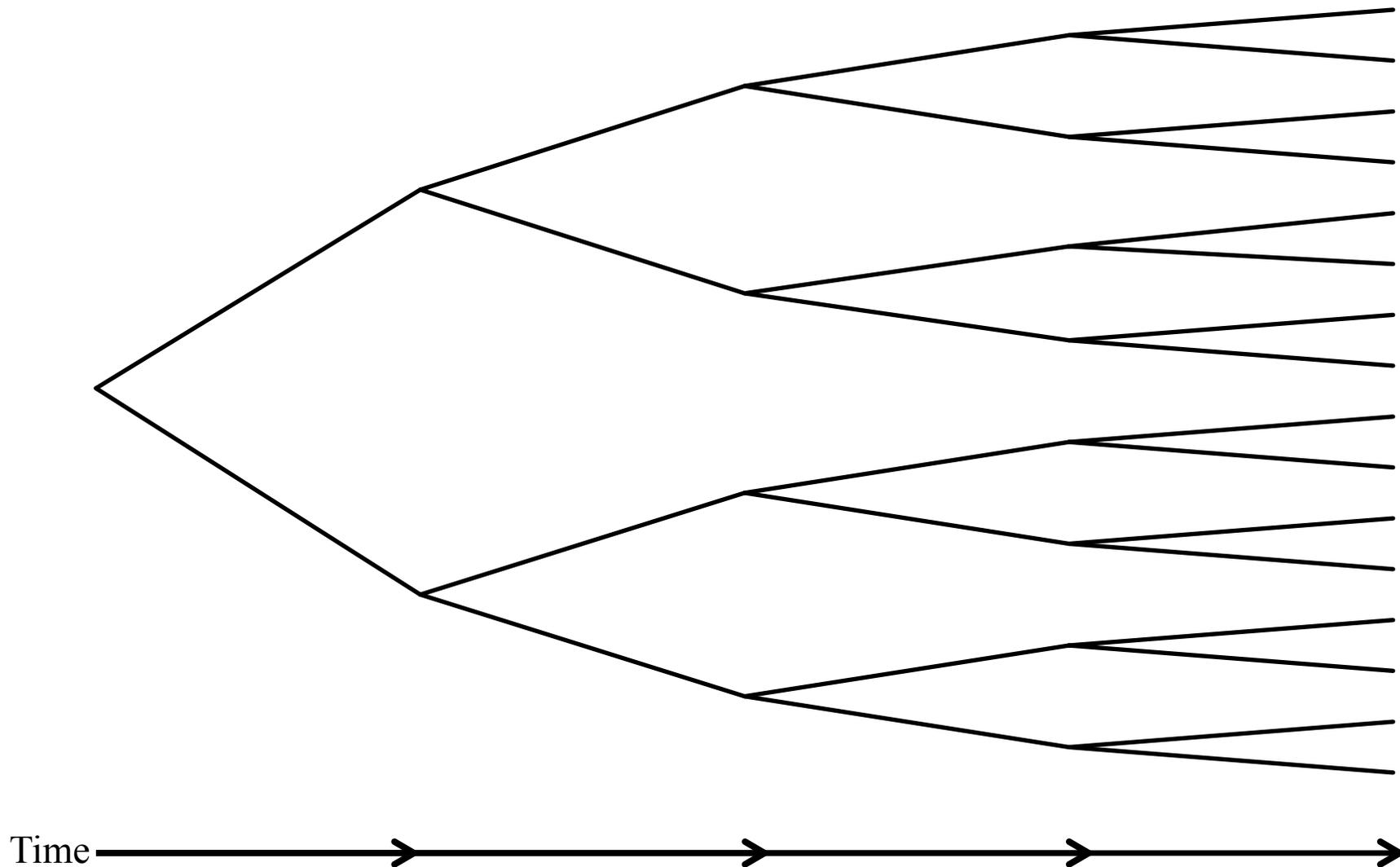




Solvent trajectories



Solvent trajectories

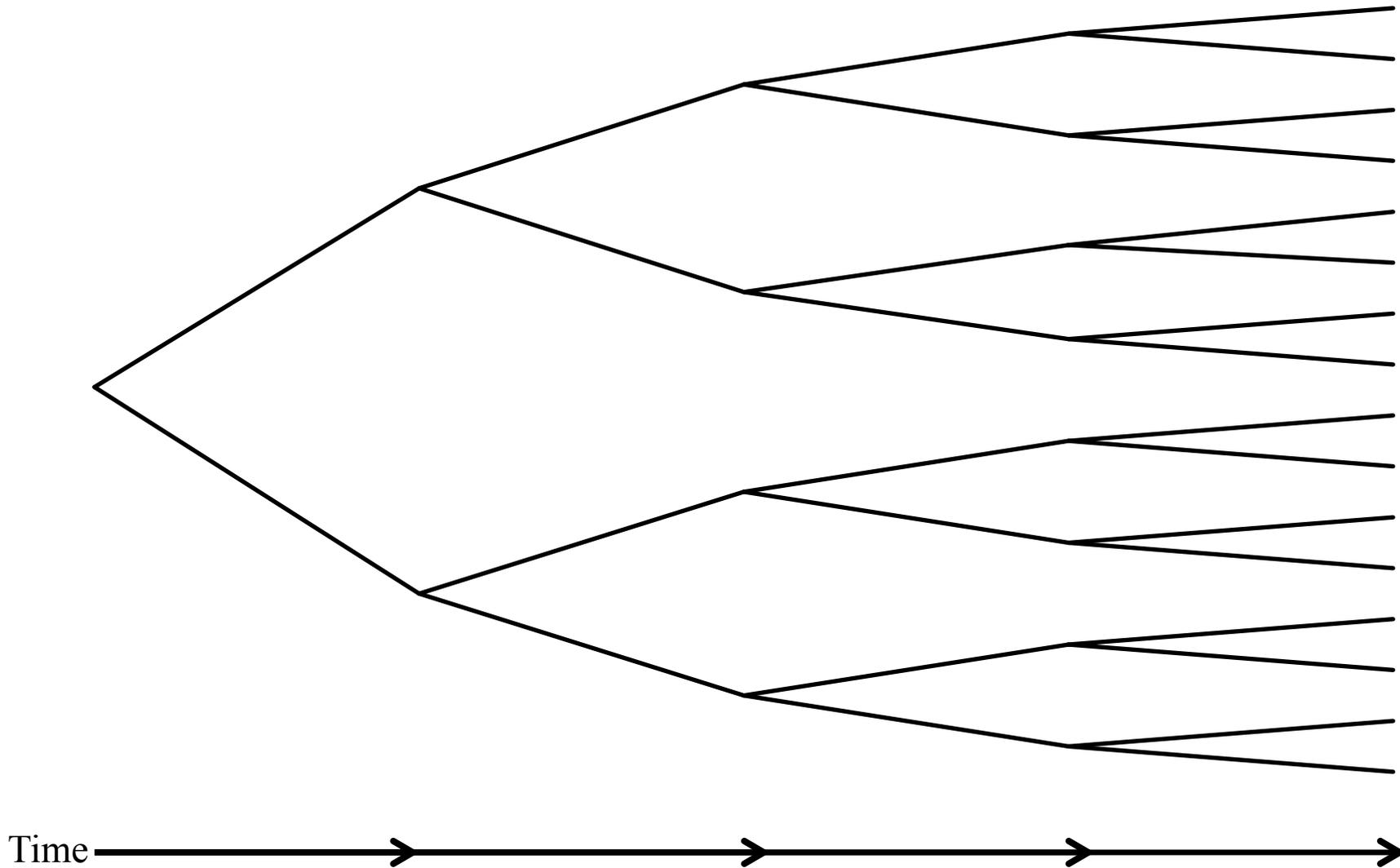




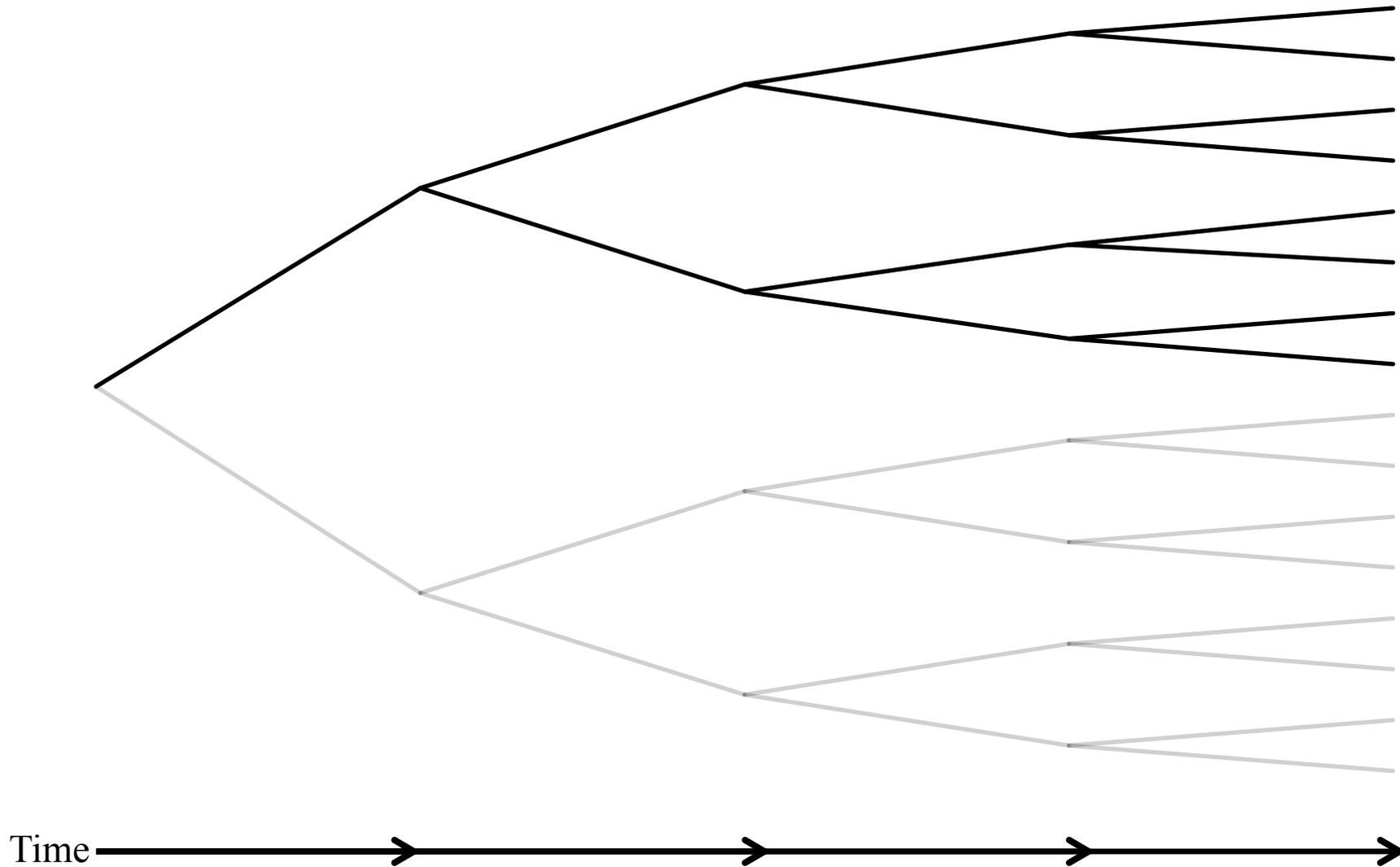
Temporal nonlocality

- In principle all time points are coupled
- System-solvent interaction described by (multi-) time correlation functions
- Correlation functions decay irreversibly
- Memory time: $\tau \downarrow m = L\Delta t$
- Iteration is possible

Graphically



Graphically





Advantages of QCPI

- Makes no ad hoc approximations
- Places no restrictions on the solvent's potential or its coupling to the system
- Can use preexisting MD packages for classical integration
- It is highly parallelizable



Ferrocene-ferrocenium electron transfer reaction in hexane

Detailed atomistic description



- Solvent-solvent interactions
 - Bonded
 - Bonds, angles, dihedrals
 - Non-bonded
 - Lennard-Jones, electrostatic

- System-solvent interactions
 - Non-bonded
 - Lennard-Jones, electrostatic



Force Field Parameters

- Standard CHARMM parameters for hexane
- Ferrocene/Ferrocenium must be parameterized
- Fit to *ab initio* calculations
- Using VMD plugins FFTK¹ and Paratool
- Following CGenFF² guidelines

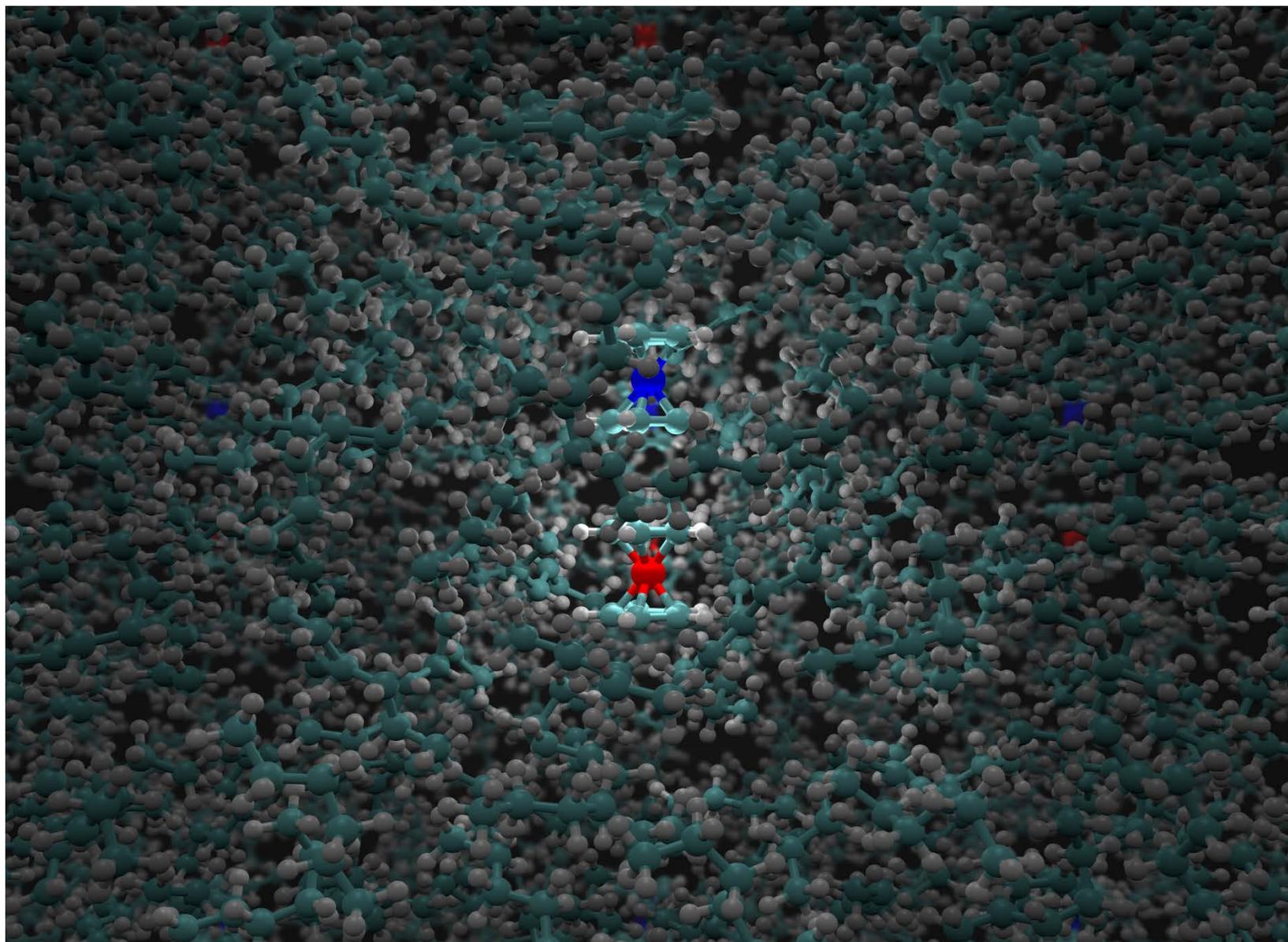
1. C.G. Mayne, et al., J. Comput. Chem., 32, 2757 (2013)
2. A.D. Mackerell JR., et al., J. Comput. Chem., 31, 671 (2010)



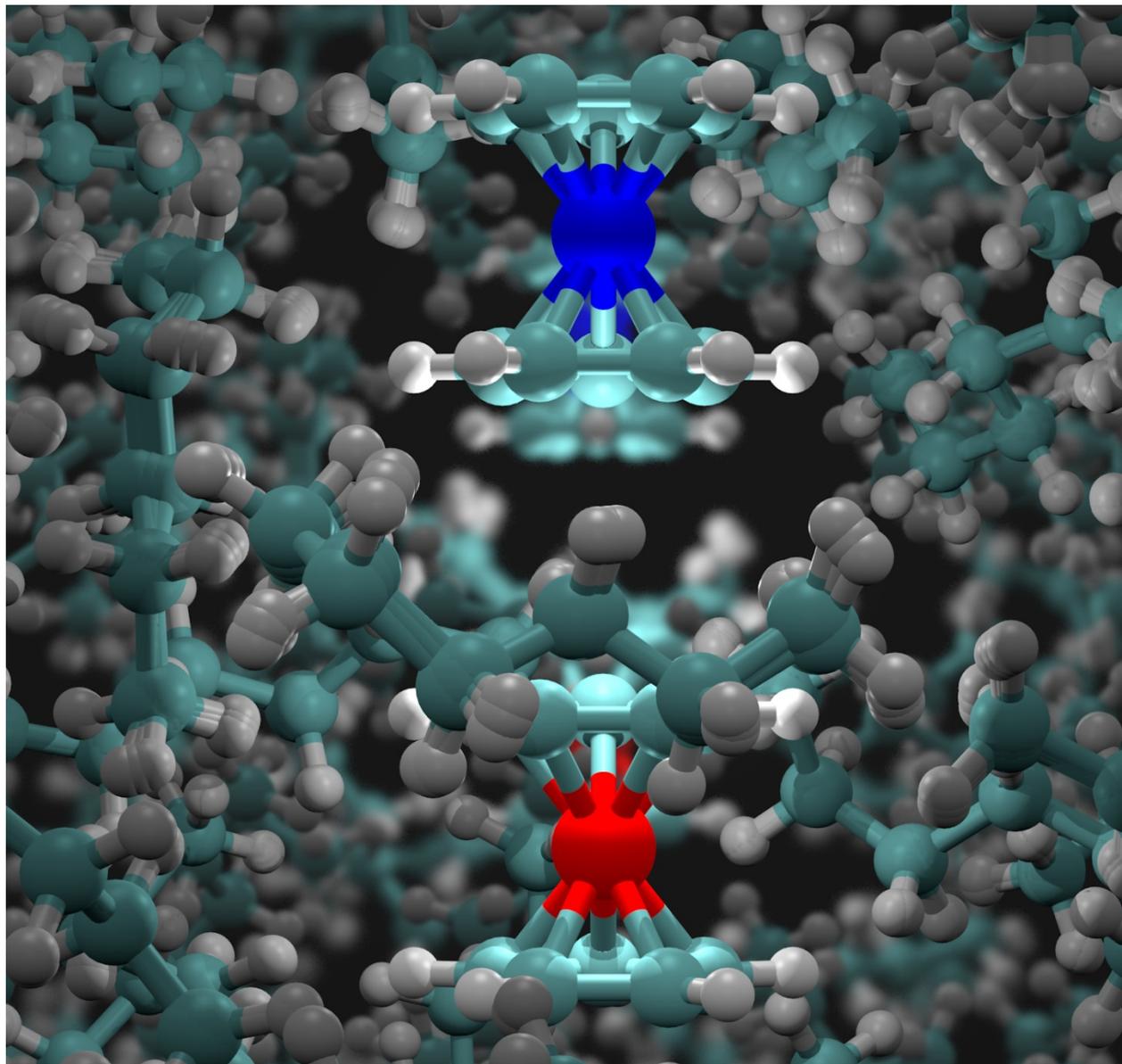
Simulation Details

- 13Å Shell of hexane (66 molecules)
- Periodic boundary conditions
- Electron transfer complex fixed
- Initial distribution: NPT ensemble 300K and 1 atm
- Classical time step: approximately 2 fs (NAMD)
- Quantum time step: 24.2 fs (12 classical steps)

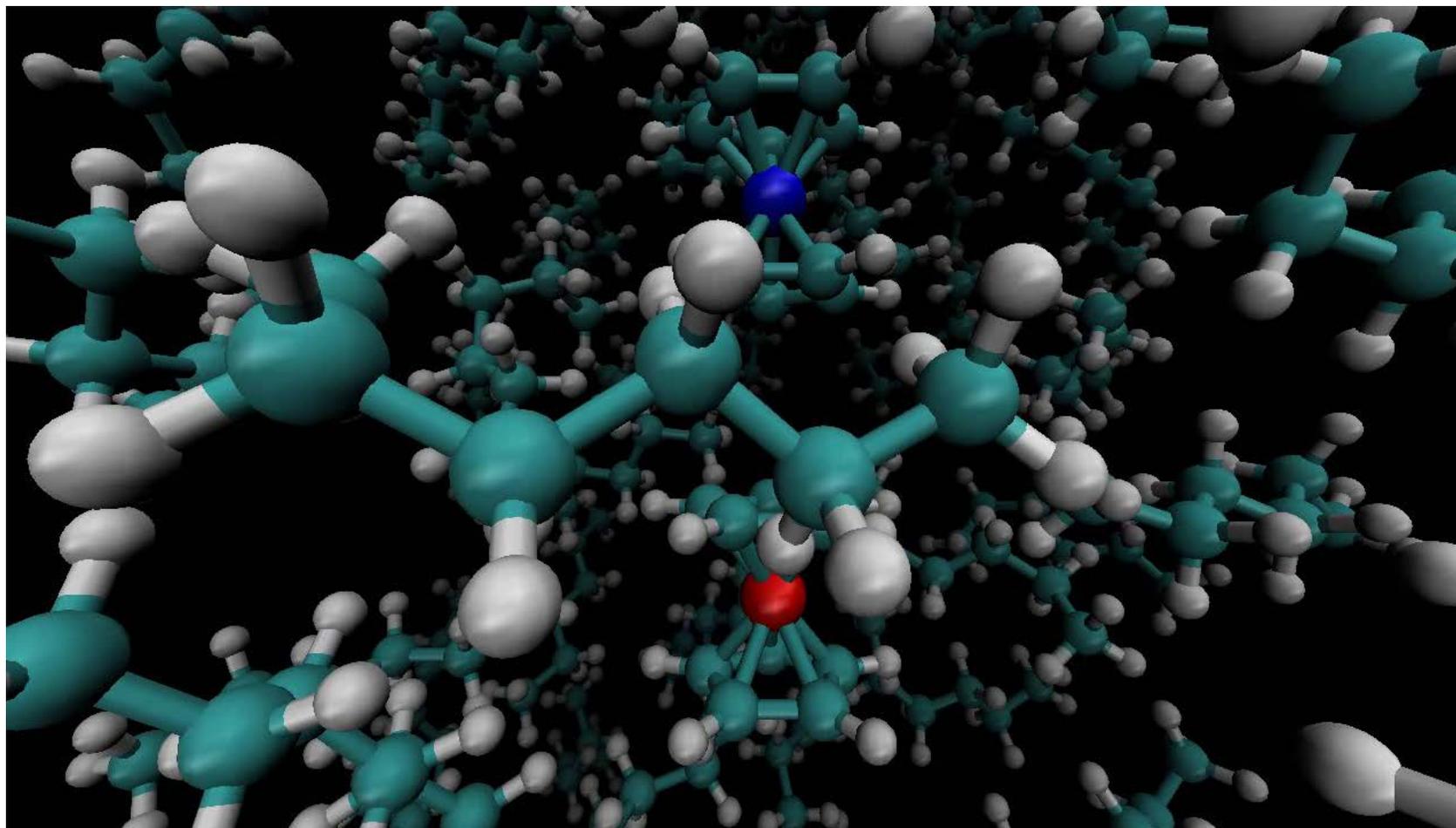
Ferrocene-Ferrocenium in hexane



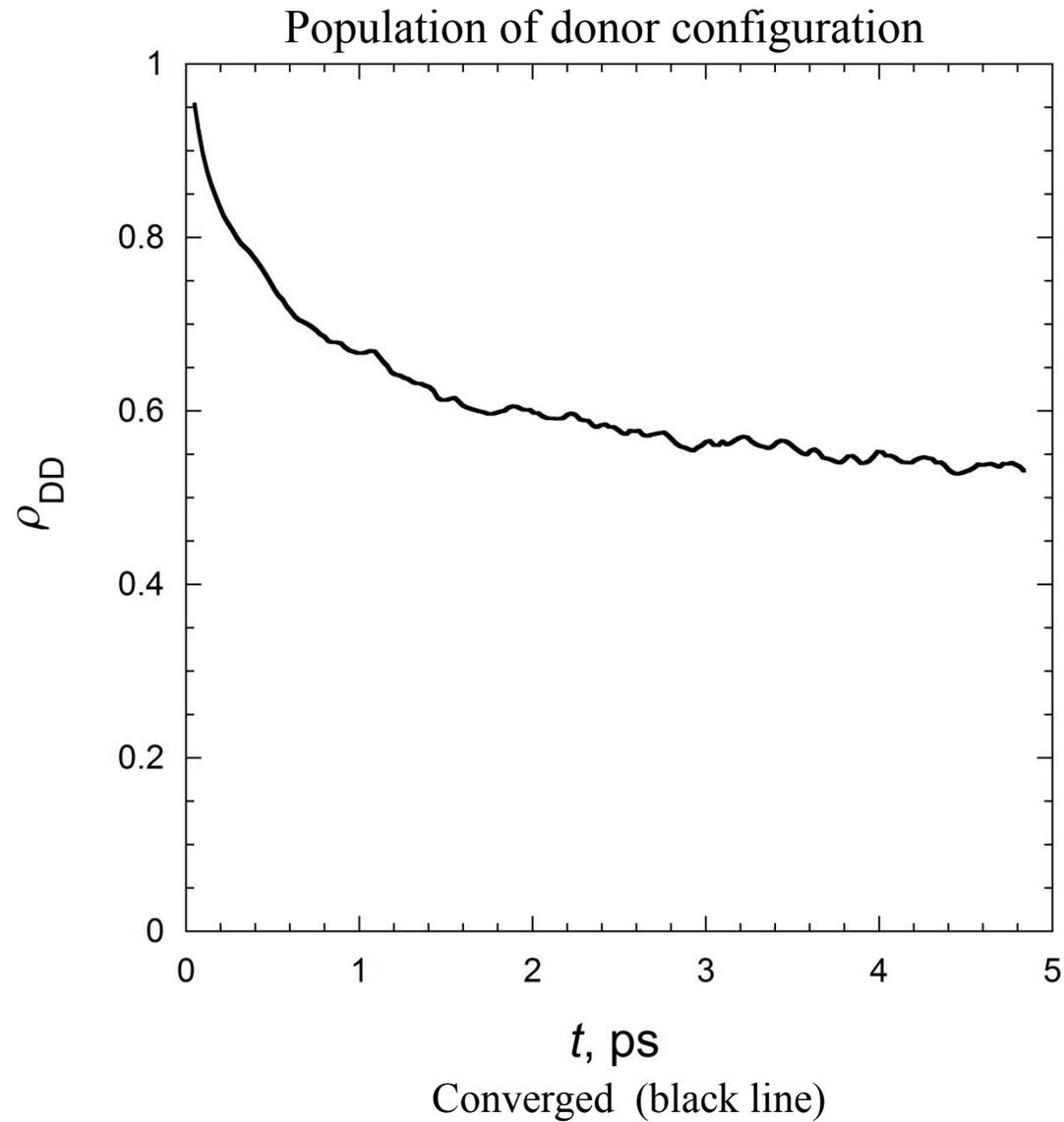
Solvent delocalization



Solvent delocalization



All-atom results



Harmonic approximation



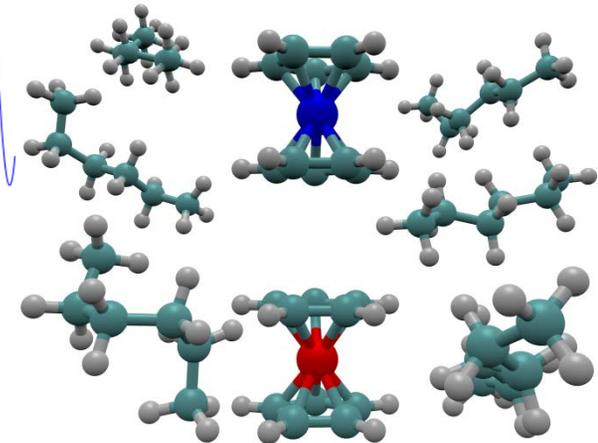
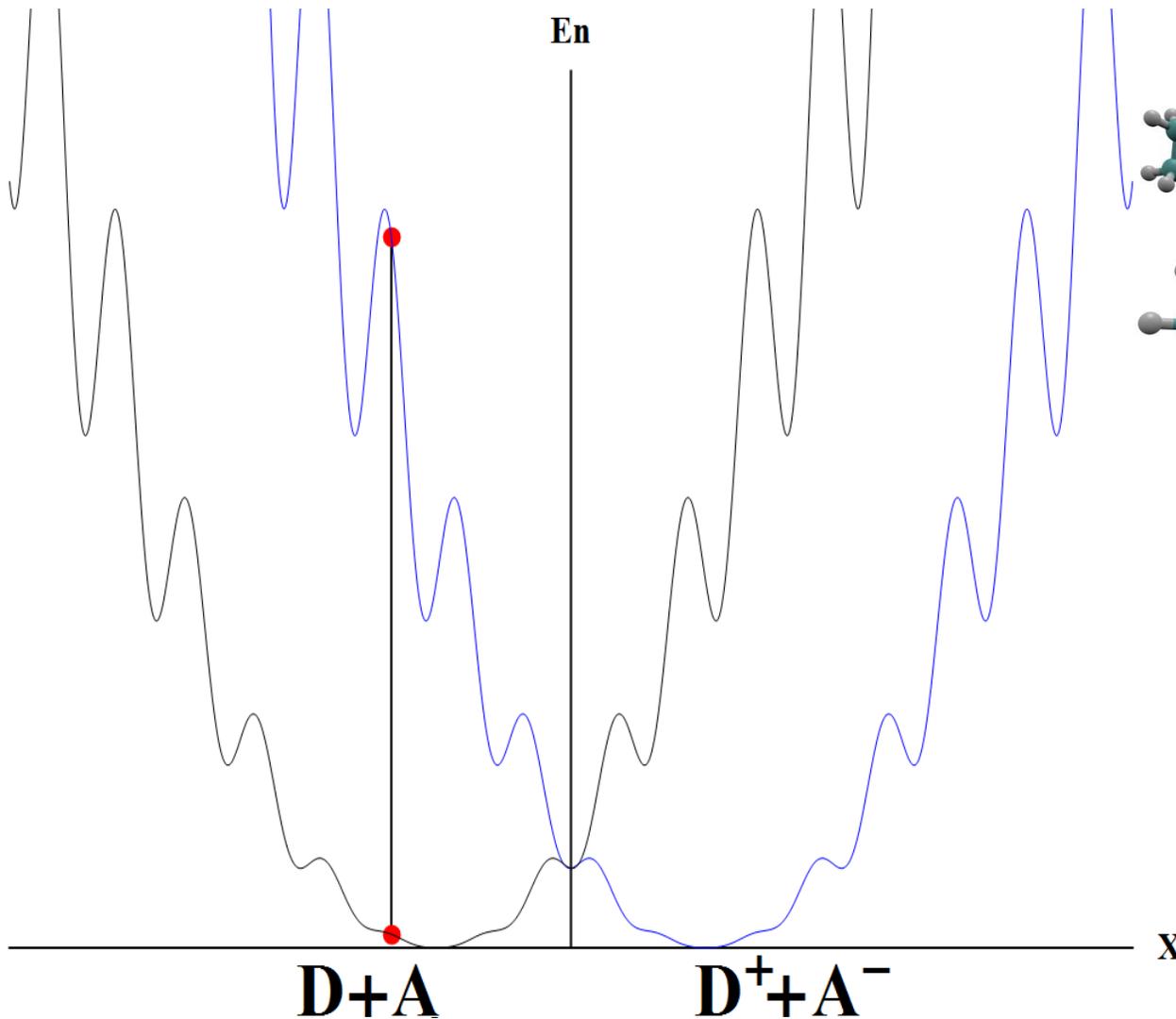
$$H_{DHA}(\mathbf{p}, \mathbf{x}) = \sum_j \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 x_j^2 \quad H_{SHA}(\mathbf{p}, \mathbf{x}) = \sum_j \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 x_j^2$$

- Extremely useful
- Reproduce the effective system-solvent interaction
- Not a Taylor series
- Can be highly accurate



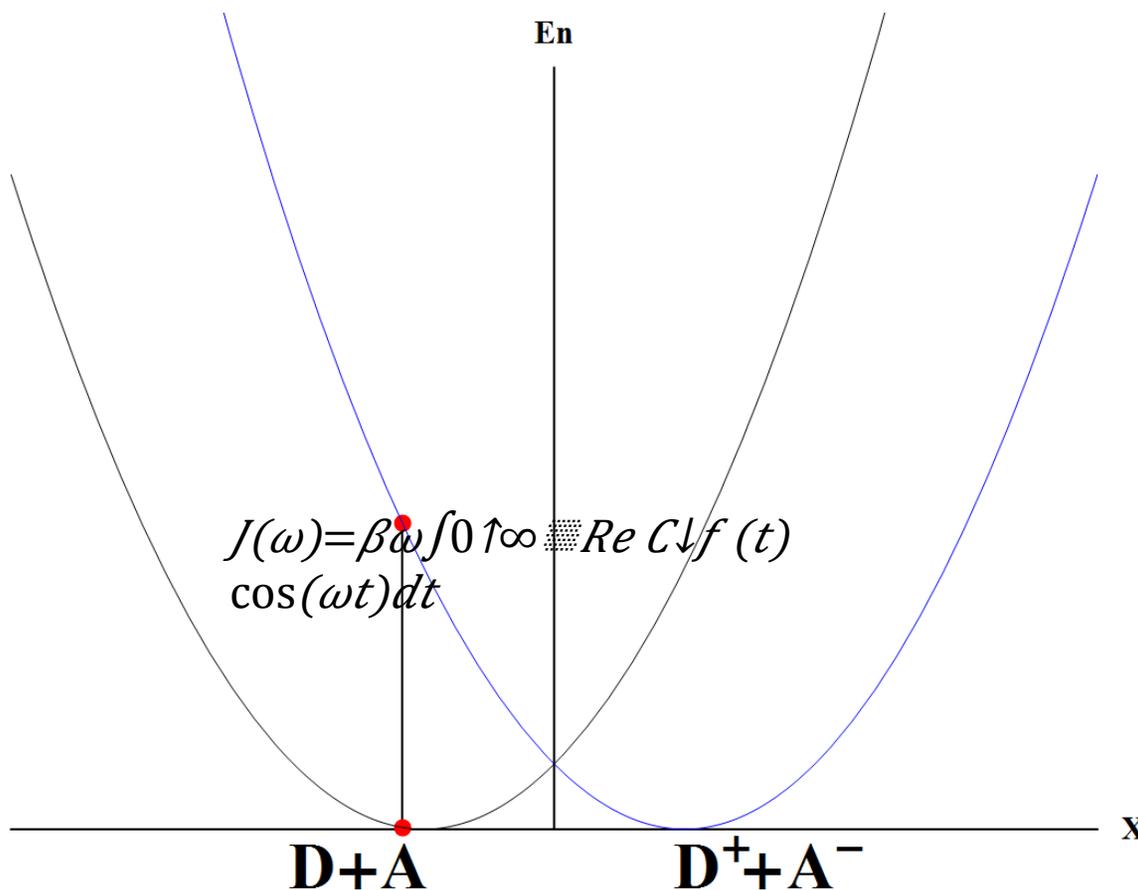
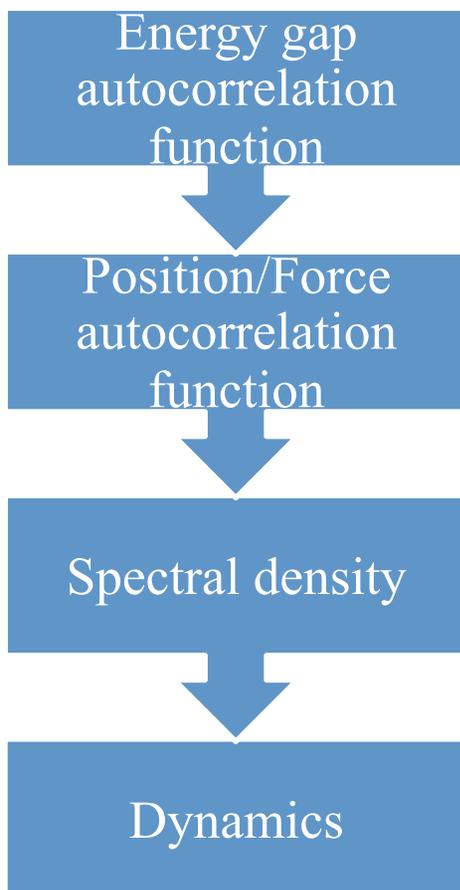
Mapping an atomistic solvent to a harmonic bath

Energy Gap Function



- Donor (Black)
- Acceptor (Blue)
- Configuration (Red)

Energy Gap Autocorrelation Function

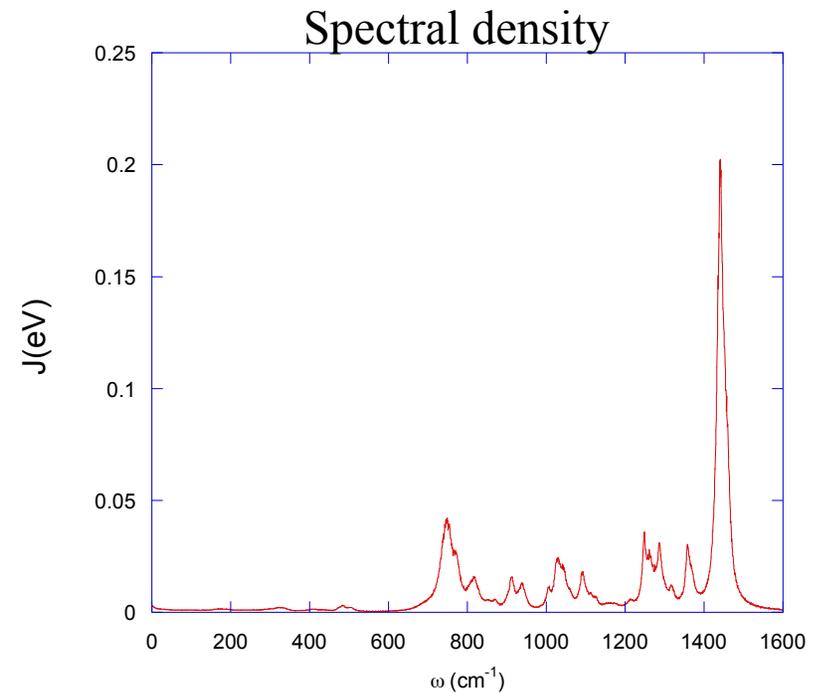
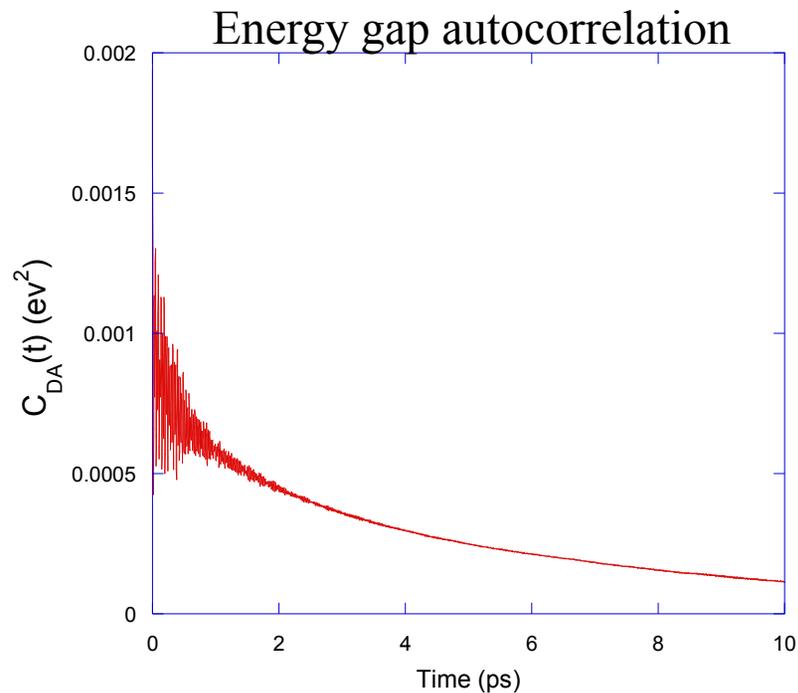




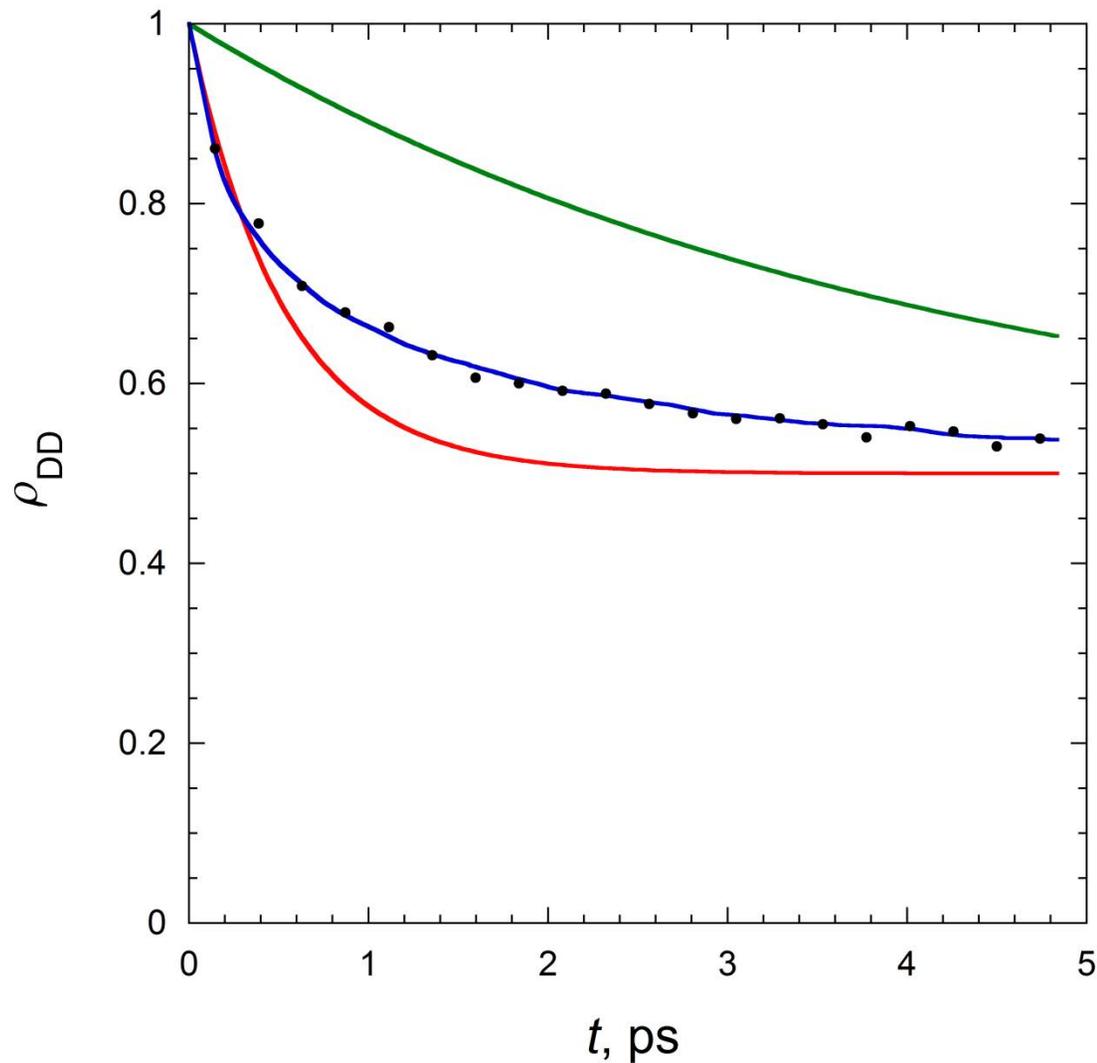
Harmonic bath approximation

$$H_{\text{th}} = [H_{\text{D}}(\mathbf{p}, \mathbf{x}) - \hbar\Omega + H_{\text{A}}(\mathbf{p}, \mathbf{x})]$$

$$H_{\text{D}}(\mathbf{p}, \mathbf{x}) = \sum_j \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 (x_j - x_{j0})^2 \quad H_{\text{A}}(\mathbf{p}, \mathbf{x}) = \sum_j c_j p_j x_j + \frac{1}{2} m_j \omega_j^2 x_j^2$$



Comparison with all-atom results



Converged donor population: all-atom results (black markers), harmonic results (blue line). Exponential decay: rate coefficient from long time limit (green line), from the Marcus expression (red line).

- Excellent agreement between the harmonic and all-atom results
- Decay is not exponential
- Need direct dynamics

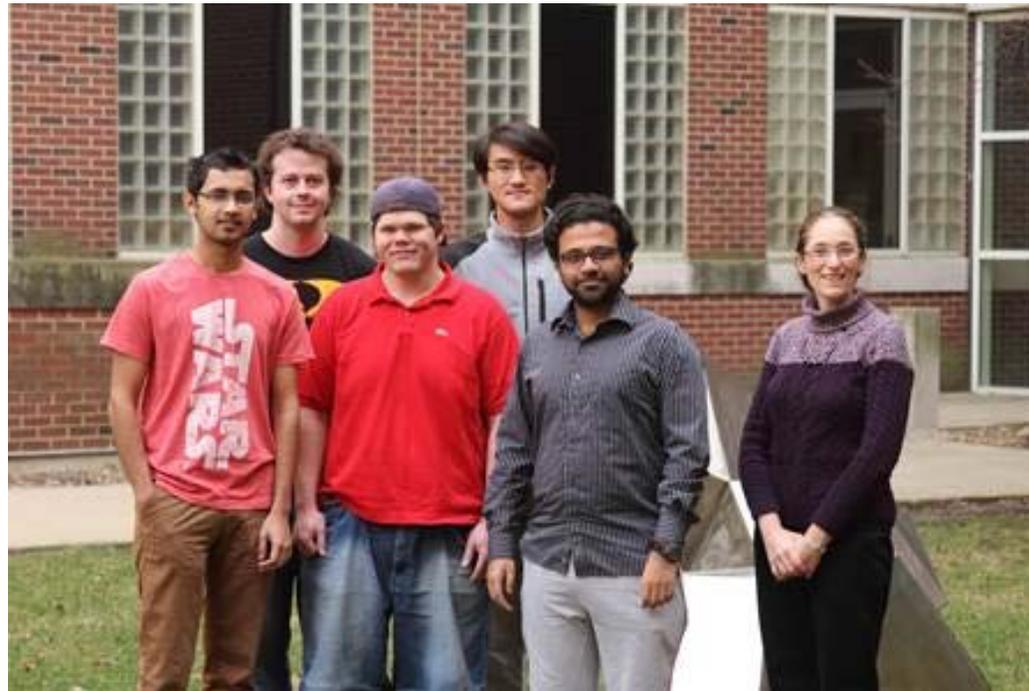


Summary

- Condensed phase quantum dynamics is an extraordinarily difficult problem that can't be solved by traditional methods
- QCPI can simulate the dynamics of a quantum system immersed in a condensed phase environment accurately
- Despite its simplicity, linear response can be extremely accurate



Acknowledgements





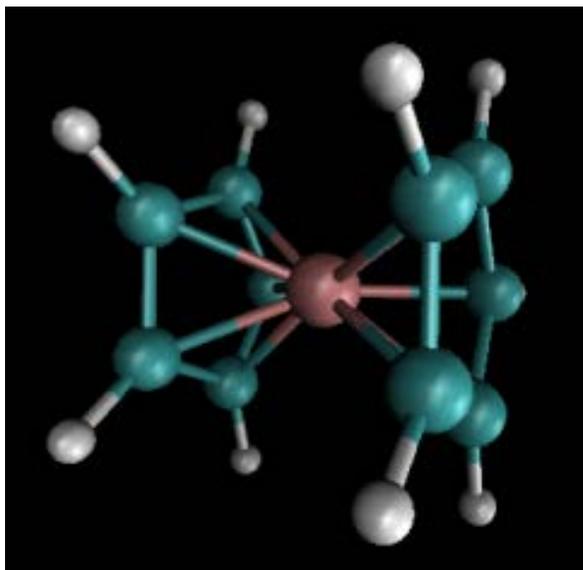
Additional slides

Optimized Structure

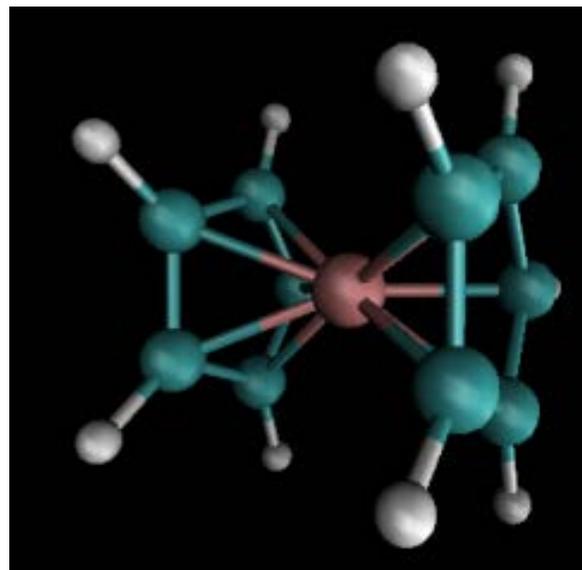


- Gaussian09 was used for all electronic structure calculations
- The geometry was optimized at the MP2/ 6-31G(d) level of theory
- In both cases the most stable conformer is eclipsed

Ferrocene



Ferrocenium



Comparison with Experiment



Ferrocene	Experiment ¹	MP2/ 6-31G(d)
Fe-Cp distance (pm)	166.1	146.6
Fe-C distance (pm)	205.4	191.0
Ferrocenium	Experiment ²	MP2/ 6-31G(d)
Fe-Cp distance (pm)	168.9	153.2
Fe-C distance (pm)	206.9	196.0

1. S. Coriani, et al.,
ChemPhysChem, 7, 245
(2006)
2. R. Martinez & A. Tiripicchio,
Acta Cryst., C46, 202 (1990)

Ferrocene

Ferrocenium

- The distances are underestimated
- The general trends are reproduced at this level
- The CCSD(T) level of theory matches the experimental values¹, but its prohibitively expensive



Force Field Parameters

- Not in the standard CHARMM database
- Were obtained from *ab initio* calculations
- Using VMD plugins FFTK¹ and Paratool
- Loosely following CGenFF² guidelines
- Bonded parameters
 - Low importance
 - Approximated from MP2/ 6-31G(d) Hessian matrix
 - Improper dihedral terms neglected

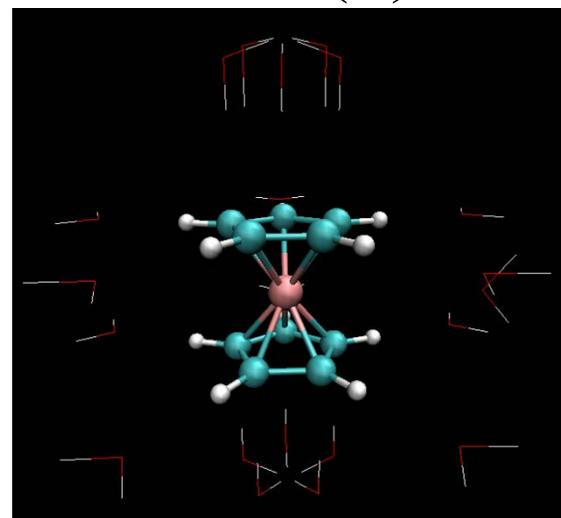
1. C.G. Mayne, et al., J. Comput. Chem., 32, 2757 (2013)

2. A.D. Mackerell JR., et al., J. Comput. Chem., 31, 671 (2010)

Non-bonded Parameters



- Lennard-Jones parameters obtained by analogy
- Partial atomic charges are fit to *ab initio* data
- Chosen to reproduce interactions with water and the dipole moment
- For CHARMM compatibility HF/ 6-31G(d) interaction energy is used



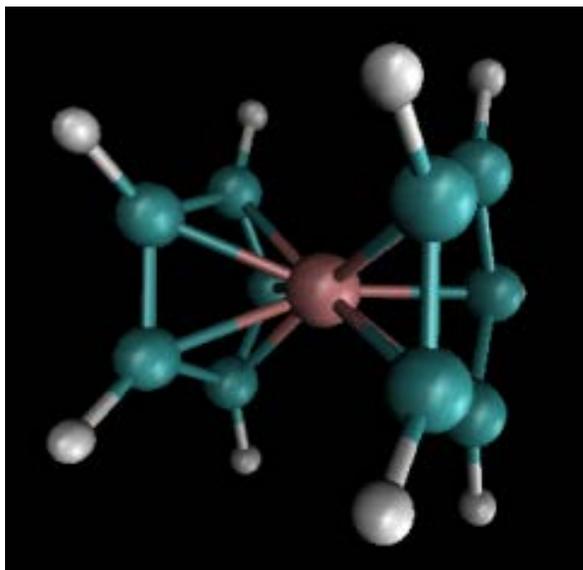


Optimized Charges

	Ferrocene	Ferrocenium
C	-0.213	-0.140
H	0.062	0.122
Cp	-0.745	-0.090
Fe	1.510	1.180

- Excess positive charge distributed in the rings
- Highly delocalized electrons

Ferrocene



Ferrocenium

