Cornell University
Chemistry and Chemical Biology

PATH INTEGRAL METHODS FOR NONADIABATIC DYNAMICS:

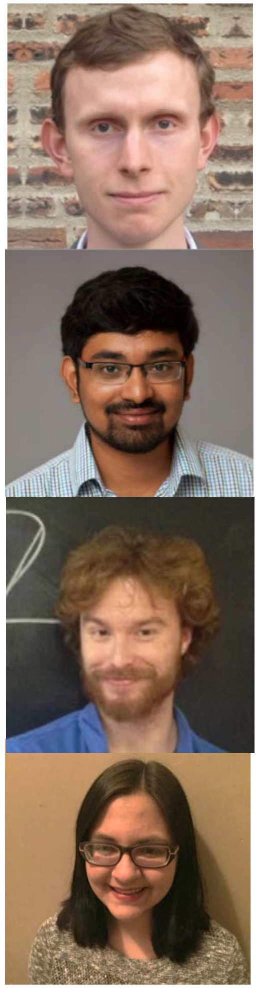
QUANTUM TRANSITIONS FROM CLASSICAL TRAJECTORIES

NANDINI ANANTH

ICTP, 7TH JULY 2017

Cornell University
Chemistry and Chemical Biology

ACKNOWLEDGEMENTS



Collaborators: Luis Campos and Xiaoyang Zhu (Columbia University), Matt Sfeir (Brookhaven National Lab), Roald Hoffmann (Cornell University)

NSF

Science to Shape the Future of the Army
Army Research Office
1951

Department of Energy
United States of America

Department of Defense
United States of America

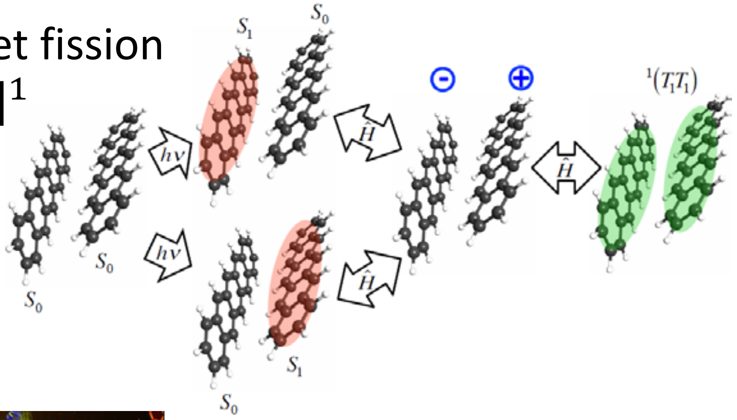
Alfred P. Sloan Foundation
1934

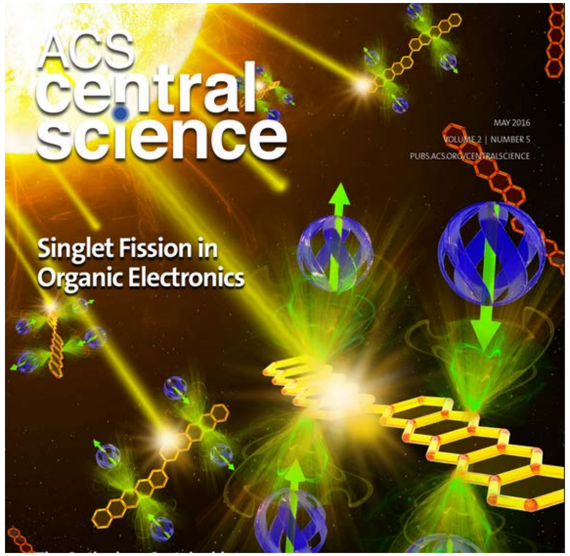
RESEARCH CORPORATION
for SCIENCE ADVANCEMENT

CHARGE AND ENERGY TRANSFER REACTIONS

Mechanisms of singlet fission

$$S_0S_1 \leftrightarrow [TT]^1$$




ACS central science

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VOLUME 2 | NUMBER 5
PUBS.ACS.ORG/CENTRALSCIENCE

Singlet Fission in Organic Electronics

T. Zeng, R. Hoffmann, and N. Ananth, J. Am. Chem. Soc. (2014)

T. Zeng, N. Ananth, and R. Hoffmann, J. Am. Chem. Soc. (2014)

E. G. Fuemmeler, N. Ananth et al, ACS Cent. Sci. (2016)

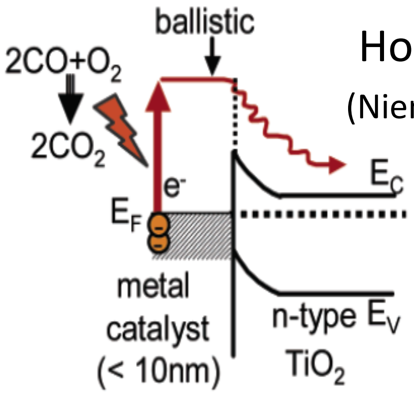
T. J. H. H, E. G. Fuemmeler, N. Ananth et al, *Manuscript Under Review* (2017)

In collaboration with

Luis M. Campos, Columbia Univ.

X. Y. Zhu, Columbia Univ.

M. Sfeir, BNL



Hot electron at metal surfaces

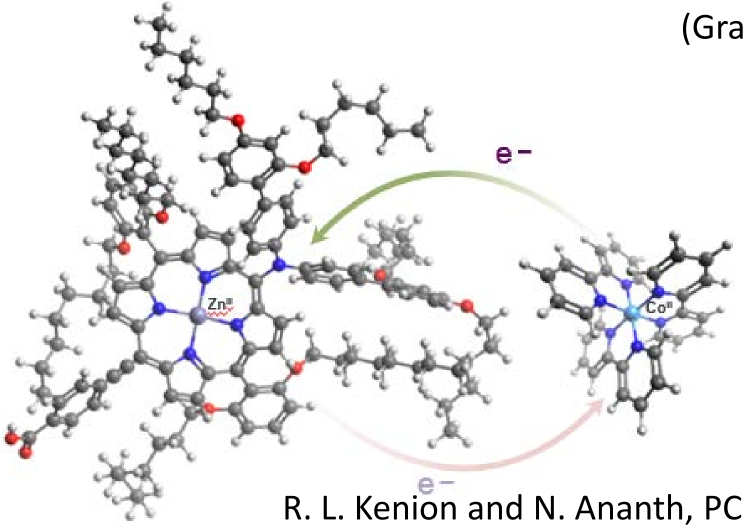
(Nienhaus, 2002; Somorjai 2006, Wodtke 2002)

S. V. Antipov, Z. Ye, and N. Ananth, J. Chem. Phys.(2015)

M. S. Church, S. V. Antipov, and N. Ananth, J. Chem. Phys., *Accepted* (2017)

Redox process in dye-sensitized solar cell

(Gratzel, 2011)



R. L. Kenion and N. Ananth, PCCP (2016)

- Coupled motions across different timescales and lengthscales
- Important quantum effects: Tunneling, Zero-Point Energy, Coupled electron-nuclear dynamics, Coherences…

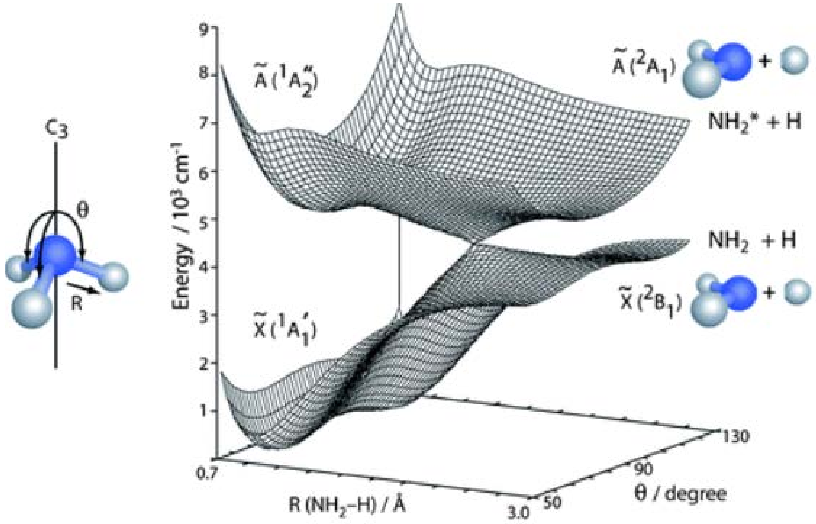
A BRIEF PEDAGOGICAL INTERLUDE

System defined by a Hamiltonian: $H(R, P, x, p) = T_N(P) + H_{el}(x, p, R)$

Electronic Hamiltonian $H_{el}(x, p, R) = T_e(p) + V_{ee}(r) + V_{eN}(r, R) + V_{NN}(R)$

For a given nuclear geometry, R, solve Schrödinger Equation for i^{th} energy level

$$\hat{H}_{el}\phi_i(x; R) = E_i(R)\phi_i(x; R)$$



Ground and first excited state potential energy surfaces of Ammonia

F. Crim, Faraday Discuss. 157, 9 (2012).

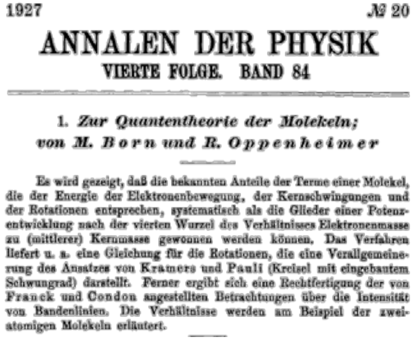
BORN-OPPENHEIMER AND BEYOND

Solution to the full system Schrödinger Equation: $\Psi(x, R, t) = \sum_i \chi_i(R, t)\, \phi_i(x; R)$

Substituting into the TDSE: $i\hbar \frac{\partial}{\partial t}\chi_i(R, t) = [T(P) + E_i(R)]\chi_i(R, t) + \sum_j C_{ij}\chi_j(R, t)$

where the nonadiabatic coupling operator is

$$C_{ij} = \langle \phi_i | T(P) | \phi_j \rangle - \frac{\hbar^2}{M}\langle \phi_i | \nabla_R | \phi_j \rangle \nabla_R$$



1927 № 20

ANNALEN DER PHYSIK

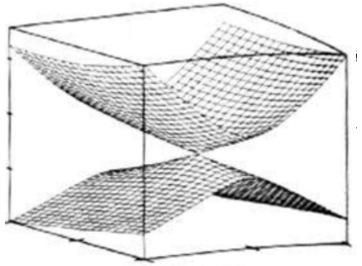
VIERTE FOLGE. BAND 84

1. *Zur Quantentheorie der Molekeln;*
von M. Born und R. Oppenheimer

Es wird gezeigt, daß die bekannten Anteile der Terme einer Molekel, die der Energie der Elektronenbewegung, der Kernschwingungen und der Rotationen entsprechen, systematisch als die Glieder einer Potenzentwicklung nach der vierten Wurzel des Verhältnisses Elektronenmasse zu (mittlerer) Kernmasse gewonnen werden können. Das Verfahren liefert u. a. eine Gleichung für die Rotationen, die eine Verallgemeinerung des Ansatzes von Kramers und Pauli (Kreisel mit eingebautem Schwungrad) darstellt. Ferner ergibt sich eine Rechtfertigung der von Franck und Condon angestellten Betrachtungen über die Intensität von Bandenlinien. Die Verhältnisse werden am Beispiel der zweiatomigen Molekeln erläutert.

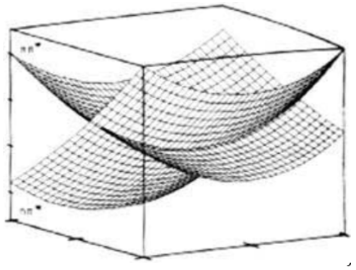
Born-Oppenheimer Dynamics: $C_{ij} = 0$

Beyond Born-Oppenheimer (Nonadiabatic Dynamics): $C_{ij} \neq 0$



A note on representation: Adiabatic states, $\{\phi_i\}$, are eigenstate of H_{el}

Adiabatic potential energy surfaces are $E_i(R)$



Diabatic states $\{\psi_i\}$ obtained by unitary transforming into a basis where $C_{ij} = 0$

Diabatic potential energy matrix elements are $V_{ij}(R) = \langle \psi_i | H_{el} | \psi_j \rangle$

SIMULATING NONADIABATIC DYNAMICS

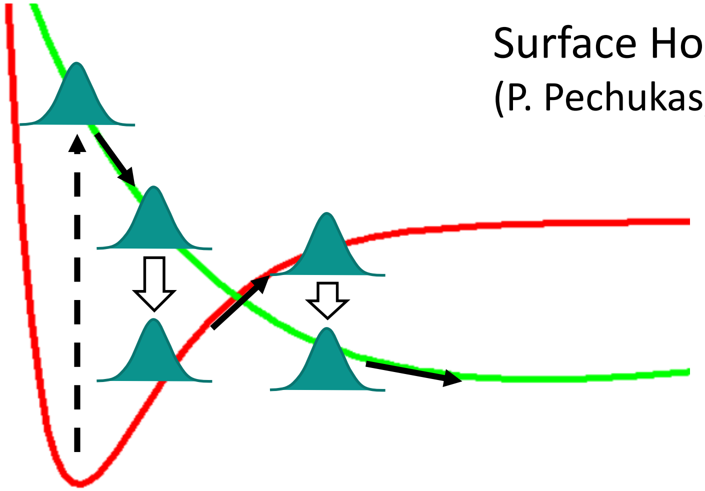
“whether the molecules can get from a higher potential-energy surface to a lower one, transforming in this way electronic excitation energy into kinetic energy and finally into heat.”

E. Teller, J. Phys. Chem 41, 109 (1937).

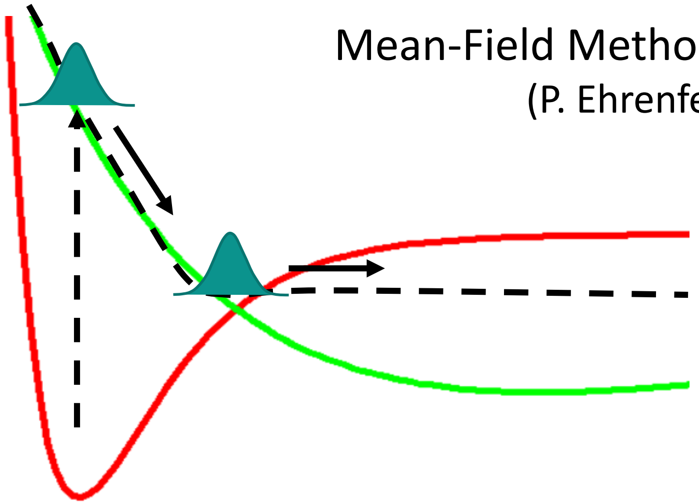
“It is now widely accepted that conical intersections play a key mechanistic role in photochemistry and photobiology”

D. Yarkony, Ann. Rev. Phys. Chem. 63, 325 (2012).

Popular Mixed Quantum-Classical Methods:



Surface Hopping
(P. Pechukas, J. C. Tully)



Mean-Field Methods
(P. Ehrenfest)

However, multi-physics approaches (quantum electron, classical nuclei) lead to <u>uncontrolled approximations</u>

- **Path Integral based methods provide a uniform dynamic framework**

J. Caro, and L. L. Salcedo, Phys. Rev. A 60, 842 (1999).

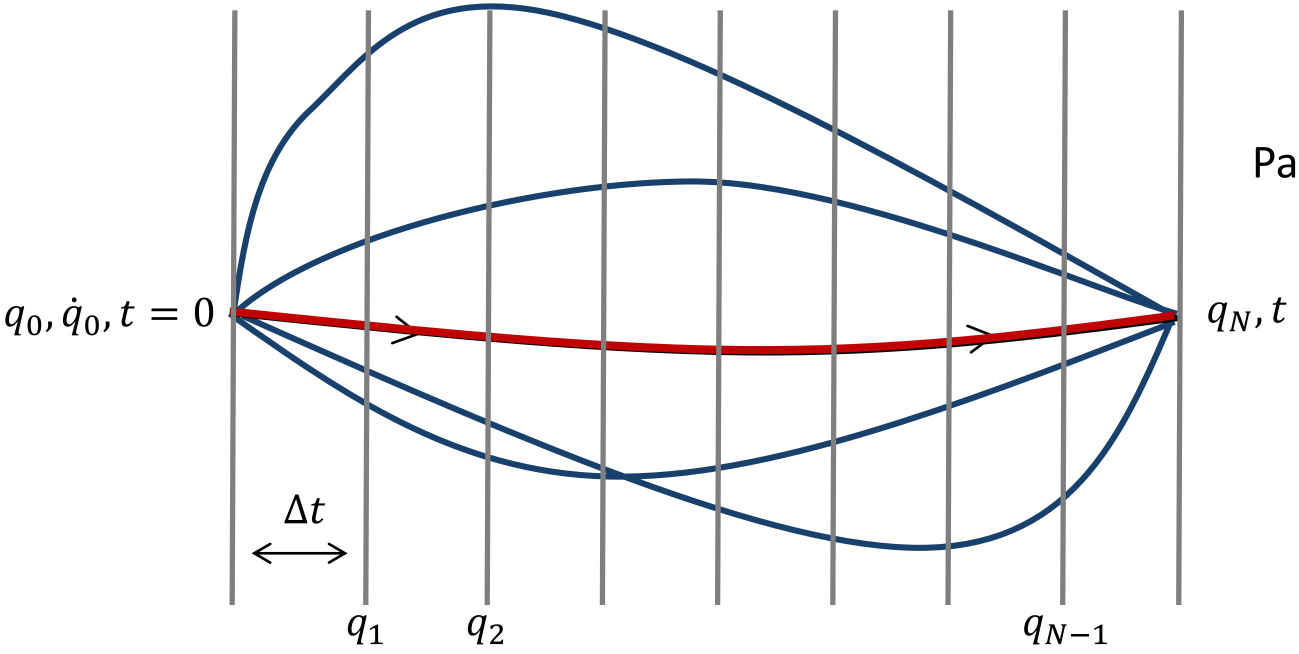
PATH INTEGRALS IN REAL-TIME

The quantum propagator: probability of going from initial position q_0 to final position q_N in time t

$$P_{q_N \leftarrow q_0}(t) = \left|\langle q_N|\, e^{-i\hat{H}t/\hbar}|q_0\rangle\right|^2$$

where $\langle q_N|\, e^{-i\hat{H}t/\hbar}|q_0\rangle = \sqrt[N]{A}\sum_{all\ paths} e^{iS_{path}/\hbar}\, \sqrt[N]{A} \;\; \propto \; \int \mathfrak{D}[q(t)]e^{iS_{path}/\hbar}$

Feynman and Hibbs, Quantum Mechanics and Path Integrals (1965)



Path $q(t) = \{q_0(0), q_1(\Delta t), \ldots q_N(N\Delta t)\}$

Exact quantum dynamic simulations for system + environment

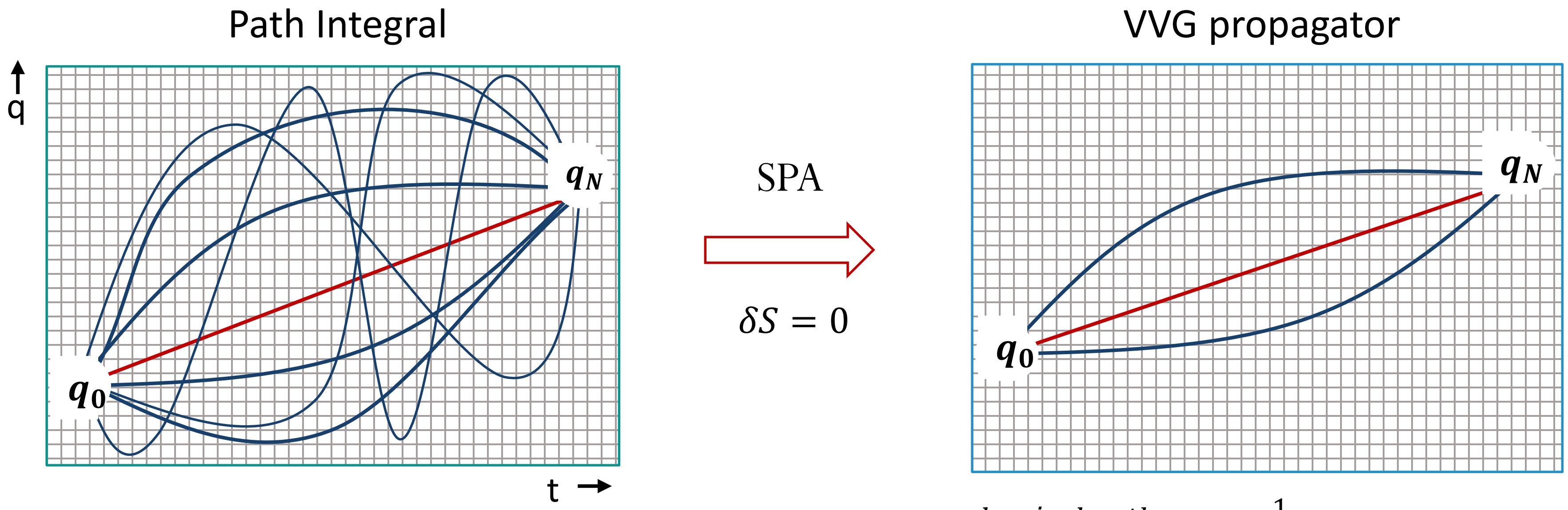
M. Topaler and N. Makri, Chem. Phys. Lett. (1993)

THE SEMICLASSICAL APPROXIMATION

We will focus on the SC Initial Value Representation (SC-IVR) and its many flavors

W. H. Miller, J. Phys. Chem. A (2001)

The Van-Vleck-Gutzwiller (VVG) derived as a stationary phase approximation to the Feynman propagator



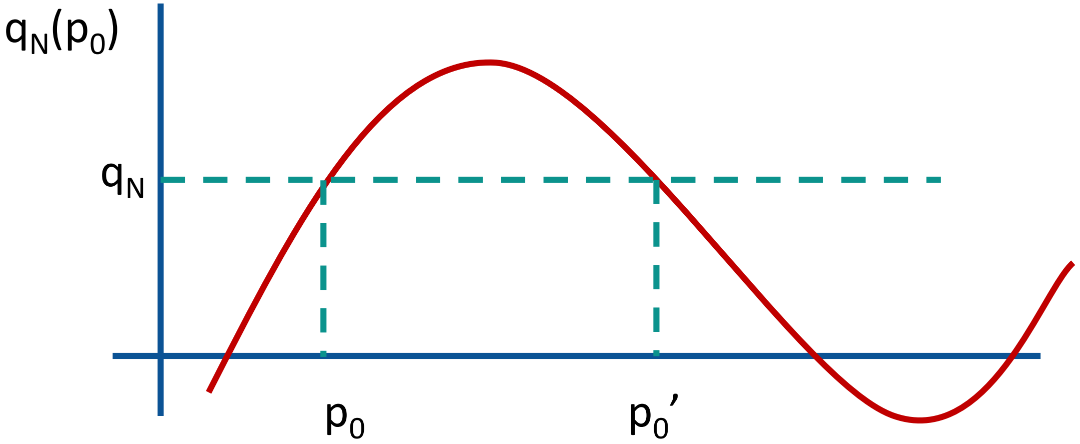
$$\langle q_N | e^{-iHt} | q_0 \rangle \propto \int dq_2 \int dq_3 \ldots \int dq_{N-1} e^{iS(q_0, q_1, \ldots, q_N)}$$

$$\langle q_N | e^{-iHt} | q_0 \rangle = (2\pi i \hbar)^{-N} \sum_j^{classical\ path} \left| \frac{\partial q_N}{\partial p_0} \right|^{-\frac{1}{2}} e^{iS_j(q_N, q_0)/\hbar} e^{-i\pi\nu_j/\hbar}$$

Sum over all possible paths from q_1 to q_N in time ‘t’

Van Vleck, Proc. Natl. Acad. Sci (1928)

INITIAL VALUE REPRESENTATION



$$\sum_{all\ branches} \int dq_N = \int dp_0 \left(\frac{\partial q_N}{\partial p_0}\right)_{q_0}$$

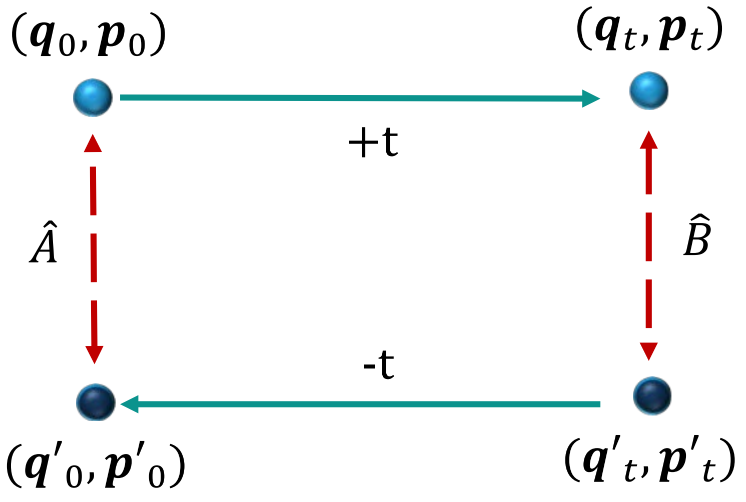
Replace root search problem with an integral over initial phase space conditions.

$$\langle q_N | e^{-iHt} | q_0 \rangle \approx \int dq_0 \int dp_0 \left|\frac{\partial q_N}{\partial p_0}\right|^{\frac{1}{2}} e^{iS_t(q_0,p_0)/\hbar} e^{-i\pi\nu_t/\hbar}$$

W. H. Miller, J. Phys. Chem. A (2001)

APPROXIMATING REAL-TIME CORRELATION FUNCTIONS $C_{AB}(t) = Tr[\hat{A}e^{\frac{i}{\hbar}\hat{H}t}\hat{B}e^{-\frac{i}{\hbar}\hat{H}t}]$

$$C_{AB}(t) \approx (2\pi\hbar)^{-F}\int dp_0 \int dq_0 \int d\Delta p \int d\Delta q \, \langle p_0 q_0|\hat{A}|p_0' q_0'\rangle \, B(p_t, q_t) \, C_{HK}(p_0, q_0, \Delta p, \Delta q) \, e^{\frac{i}{\hbar}(S_t + S_{-t})}$$



\`Jump’ induced by operator B

$$q_t' - q_t = \Delta q$$

$$p_t' - p_t = \Delta p$$

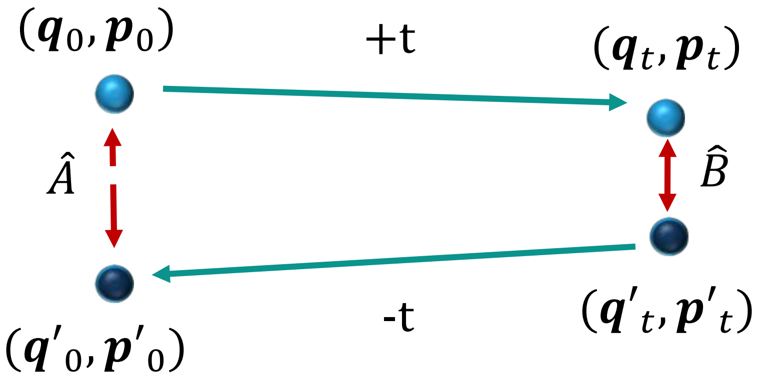
Use two coherent state propagators : Double Herman-Kluk Initial Value Representation (DHK-IVR)

- accurately describes quantum coherence effects, tunneling and ZPE
- computationally expensive, not really feasible for N>5 (semiclassical ‘sign’ problem)

W. H. Miller, J. Phys. Chem. A (2001)

CLASSICAL-LIMIT SEMICLASSICAL METHODS

Take the limit $(\Delta \mathrm{p}, \Delta \mathrm{q}) \rightarrow \delta$: $C_{AB}(t) = \int dp_0 \int dq_0 \, A_W(p_0, q_0) B_W(p_t, q_t)$



\`Jump' induced by operator B

$$q_t' - q_t = \Delta q$$

$$p_t' - p_t = \Delta p$$

e.g. Linearized Semiclassical Initial Value Representation (LSC-IVR)

- captures ZPE and tunneling; mean-field treatment of nonadiabatic dynamics
- computationally feasible for large systems (no sign problem)

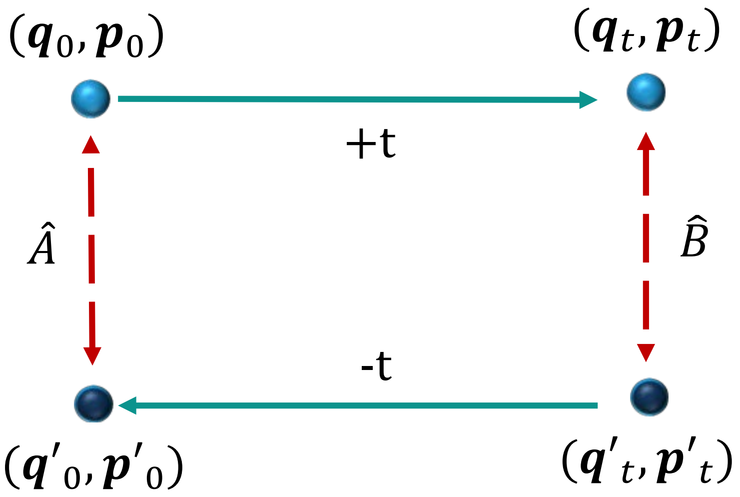
Wang, Sun, and Miller, J. Chem. Phys. (1998)

DERIVING A UNIFORM SC FRAMEWORK: MIXED QUANTUM-CLASSICAL METHODS

Derived using Filinov filtration: a new application of an old filtering trick.

N. Makri and W. H. Miller, J. Chem. Phys. 89, 2170 (1988)

$$\boxed{C_{AB}(t) = (2\pi\hbar)^{-F}\int dp_0\int dq_0\int d\Delta p\int d\Delta q\,\langle p_0 q_0|\hat{A}|p_0' q_0'\rangle\, B(p_t,q_t)\, D_0(p_0,q_0,\Delta p,\Delta q,c_q,c_p)\, e^{\frac{i}{\hbar}(S_t+S_{-t})} \times e^{-\frac{1}{2}\Delta q^T.\boldsymbol{c_q}.\Delta q}\, e^{-\frac{1}{2}\Delta p^T.\boldsymbol{c_p}.\Delta p}}$$



Associate parameter $c^i_{p/q}$ with the i^{th} mode

Quantum Limit: If $c^i \rightarrow 0$, MQC-IVR ≡ DHK-IVR

Classical Limit: If $c^i \rightarrow \infty$, MQC-IVR → ~LSC-IVR

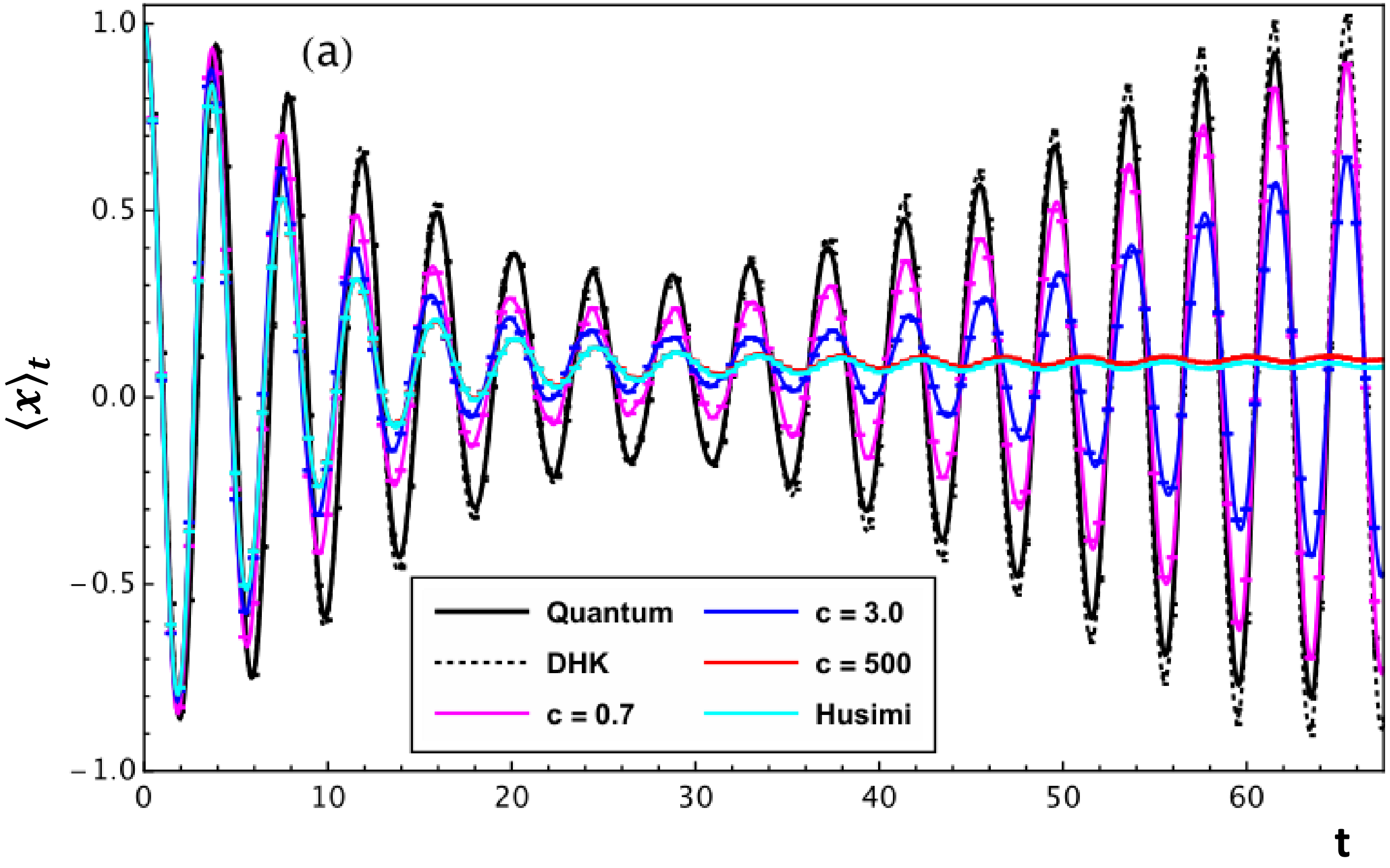
$D_0(p_0, q_0, \Delta p, \Delta q)$: Prefactor involves forward and backward components of Monodromy Matrices

$$\text{e.g. } M^f_{qq} = \frac{\partial q_t}{\partial q_0};\ M^b_{pq} = \frac{\partial p_0'}{\partial q_t'}$$

S. V. Antipov, Z. Ye, and N. Ananth, J. Chem. Phys. (2015)

MIXED QUANTUM-CLASSICAL SC THEORY : 1D MODEL SYSTEM

1-D Anharmonic Oscillator



One tuning parameter for each dof

Large c value = Classical-limit

Long-time oscillation damped

Amplitude recurrences

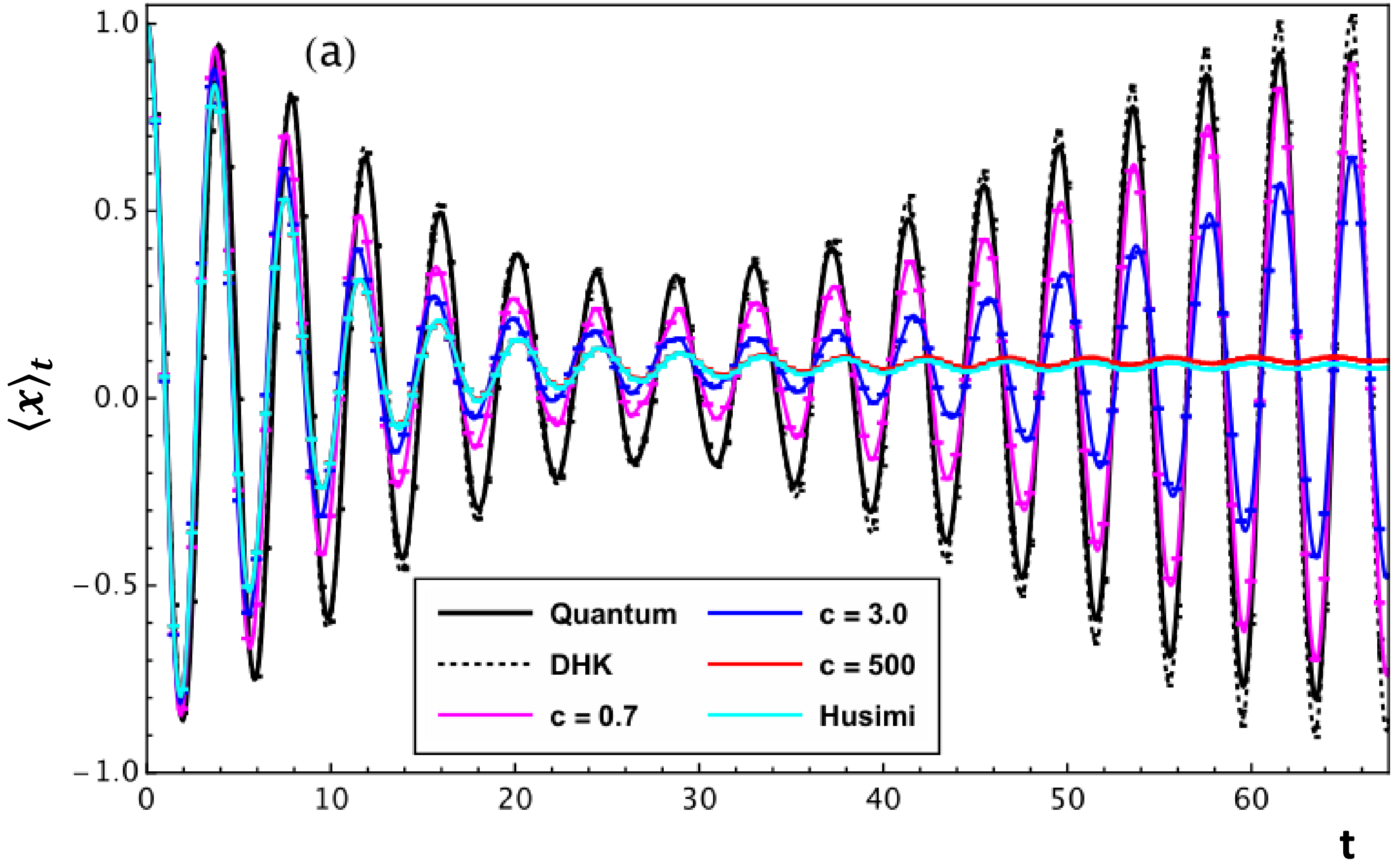
Small c value = Quantum-limit

DHK = Quantum-limit SC
Husimi=Classical-limit SC

S. V. Antipov, Z. Ye, and N. Ananth, J. Chem. Phys. (2015)

Mixed Quantum-Classical SC Theory : 1D Model System

1-D Anharmonic Oscillator



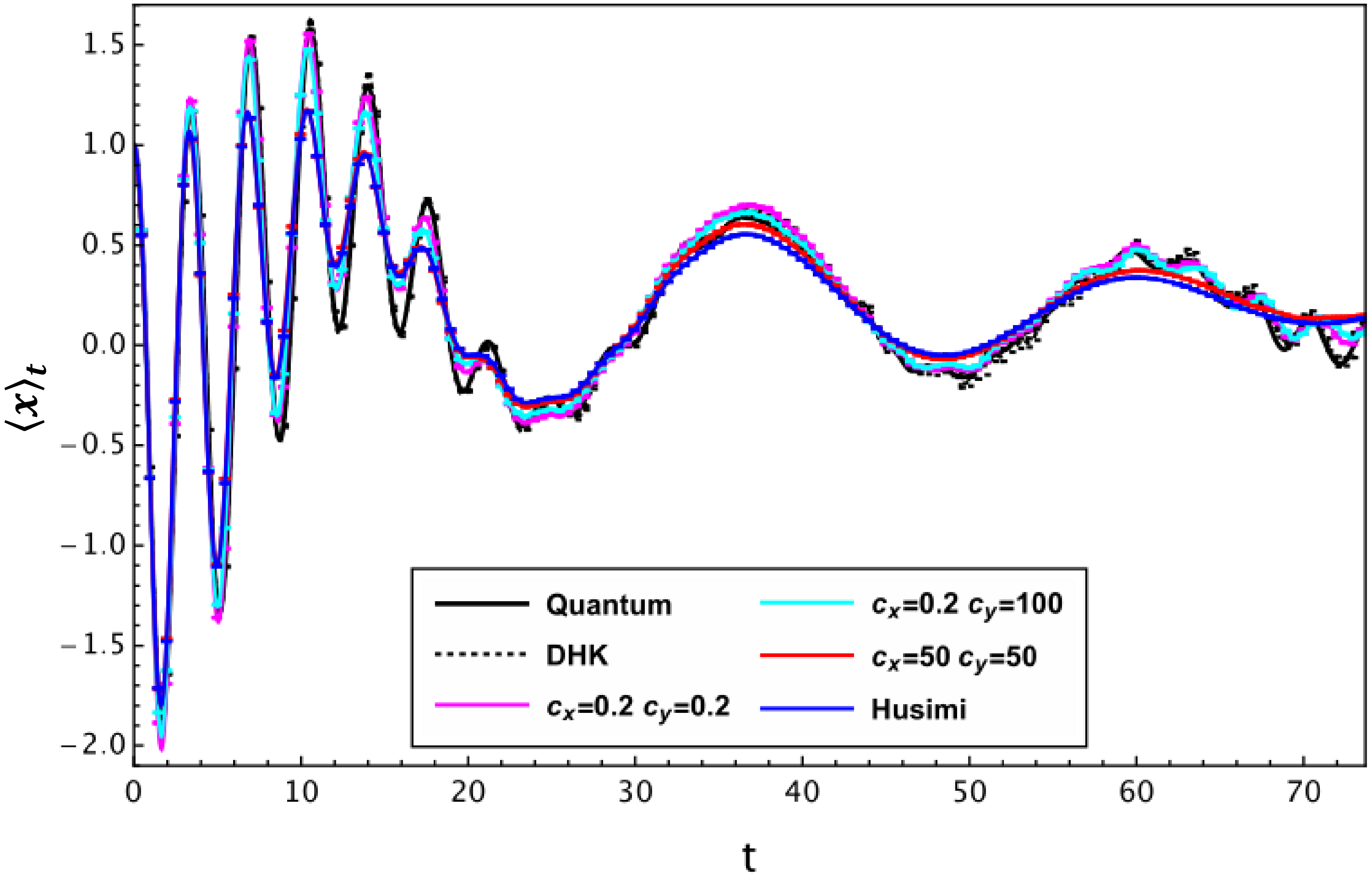
IVR formulation	c	N_{traj}
DHK	0	3.0×10^6
DF-MQC	0.7	2.4×10^4
	3.0	9.6×10^3
	500.0	6.0×10^2
Husimi	∞	2.4×10^2

Small values **c=0.7 :** 100 times fewer trajectories required, almost as accurate

S. V. Antipov, Z. Ye, and N. Ananth, J. Chem. Phys. (2015)

Mixed Limit Semiclassical Simulation : 2-D Model System

1D anharmonic oscillator(x) linearly coupled to heavy harmonic mode (y)



TWO PARAMETERS: c_x and c_y

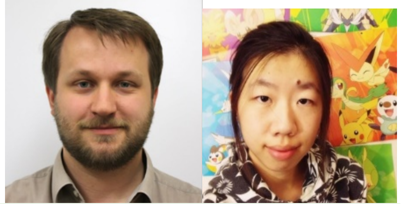
Quantizing x-mode sufficient

To Reproduce Exact, Use:

Large c_y value = Classical-limit y-mode

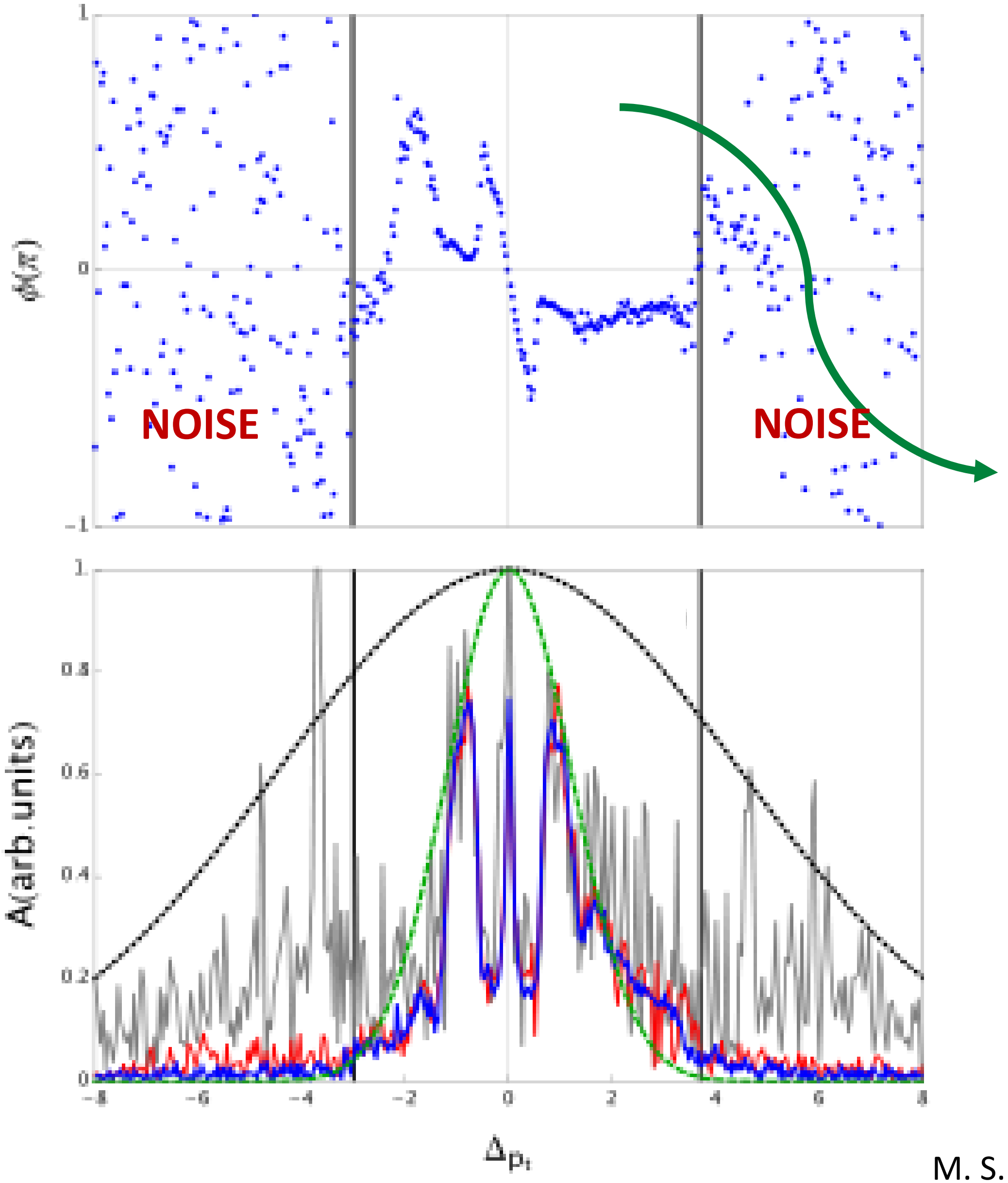
Small c_x value = Quantum-limit x-mode

SC-IVR	c_x	c_y	N_{traj}
DHK	0	0	1.9×10^7
MQC	0.2	0.2	3.8×10^5
	0.2	1.0	1.4×10^5
	0.2	50.0	5.0×10^4
	50.0	50.0	3.0×10^3
Husimi	∞	∞	4.8×10^2



S. V. Antipov, Z. Ye, and N. Ananth, J. Chem. Phys. (2015)

WHY DOES IT WORK?



Filinov filtration is ineffective for SC wavepacket propagation

Single trajectory study: M. Spanner, V. S. Batista, and P. Brumer, J. Chem. Phys. (2005)

Examining the integrand (A) and phase (ϕ) of the semiclassical integrand

Region of stationary phase

As we increase the number of trajectories to 10^6

gray – **red** – **blue** Amplitude in noisy phase regions -> 0

MQC simply filters amplitude at source: envelope for c=0.7 shown in **green**

M. S. Church, S. V. Antipov, and N. Ananth, J. Chem. Phys., *Accepted* (2017)

NONADIABATIC DYNAMICS: CLASSICAL ANALOG VARIABLES FOR DISCRETE ELECTRONIC STATES

$$H = h_0(R,P) + \sum_{n,m=1}^{K} V_{nm}(R)|\psi_n\rangle\langle\psi_m| = h_0(R,P) + \sum_{n,m} V_{nm}(R)a_n^+ a_m$$

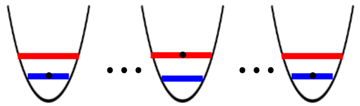
Map K electronic states to singly excited oscillator states via bosonic creation/annihilation operators (Schwinger's theory)

H. D. Meyer and W. H. Miller, J. Chem. Phys. (1979)
G. Stock and M. Thoss, Phys Rev. Lett. (1997)

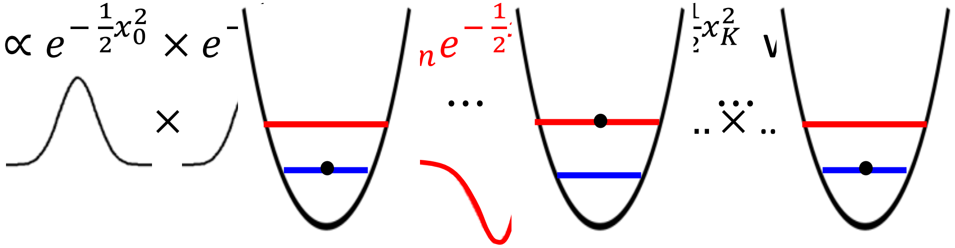
$$|\psi_n\rangle\langle\psi_m| \rightarrow a_n^+ a_m \equiv \frac{1}{2}(x_n - ip_n)(x_m + ip_m) \quad \text{where} \quad [a_n^+, a_m] = \delta_{nm}$$

$$|\psi_n\rangle \rightarrow |0_1 0_2 \cdots 1_n \cdots 0_K\rangle \equiv |n\rangle$$

Electronic wavefunction in the Singly Excited Oscillator (SEO) basis



$\langle \boldsymbol{x}|n\rangle \propto e^{-\frac{1}{2}x_0^2} \times e^{-}$ … $n e^{-\frac{1}{2}}$ … x_K^2 w… a K-dimensional vector



Miller, Meyer, McCurdy, Stock, Thoss, Geva, Coker, Kapral,….

THE MAPPING VARIABLE HAMILTONIAN AND A MODEL SYSTEM

Map discrete electronic states to Cartesian coordinates

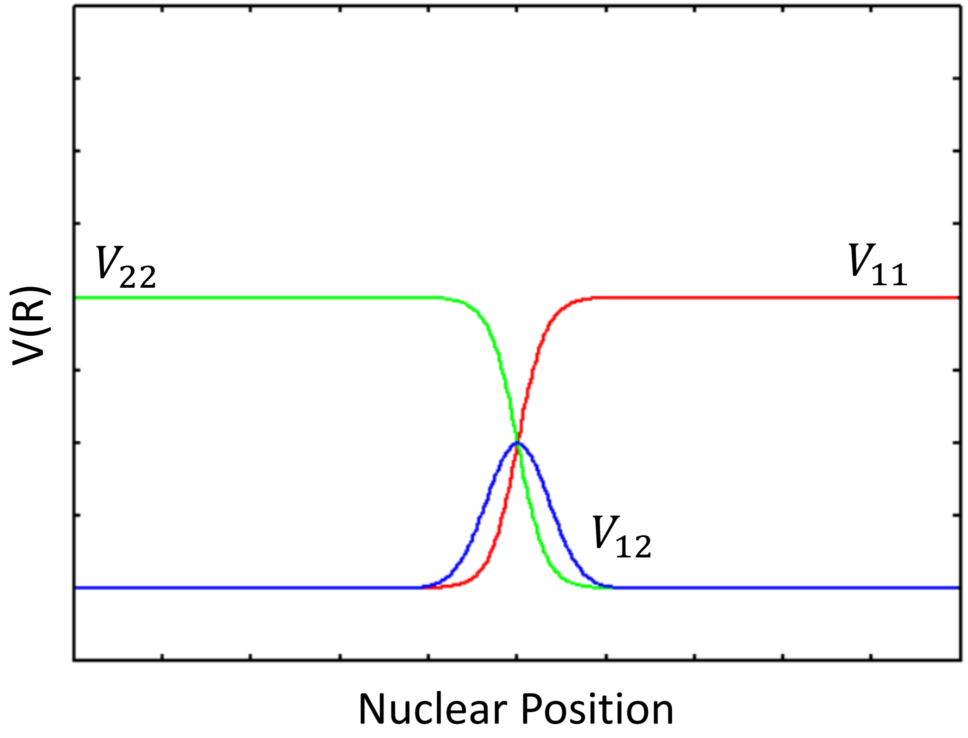
$$H = h_0(R,P) + \sum_{n,m=1}^{N} V_{nm}(R)|\psi_n\rangle\langle\psi_m| \longrightarrow H = h_0(R,P) + \frac{1}{2}\sum_{n,m=1}^{N} V_{nm}(R)(x_n x_m + p_n p_m - \delta_{nm})$$

H. D. Meyer and W. H. Miller, J. Chem. Phys. (1979)

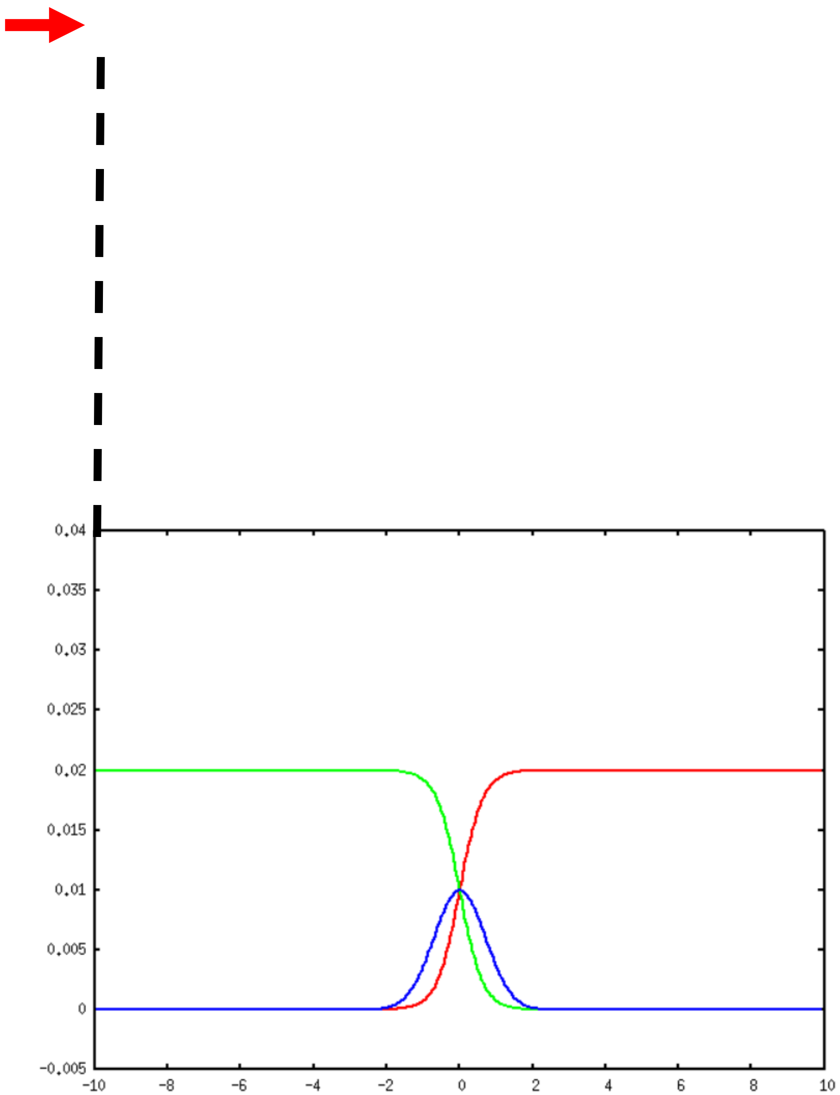
Compute the Correlation function

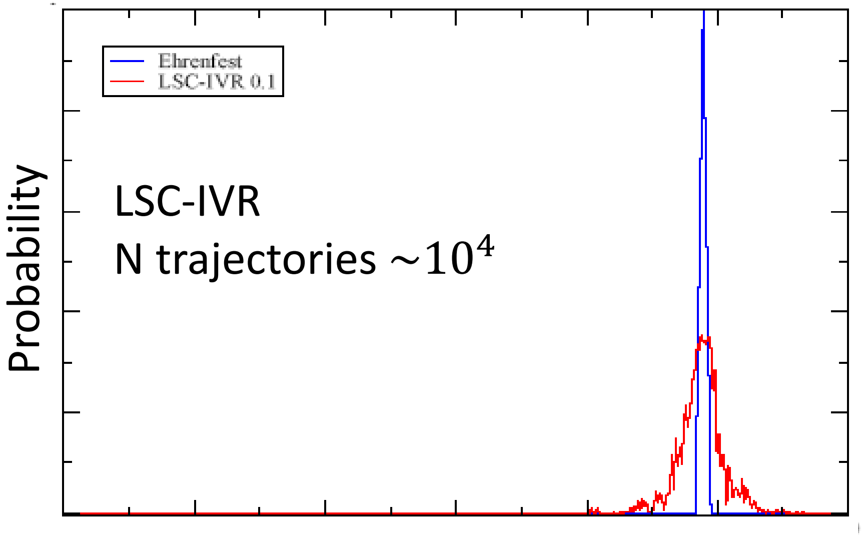
$$\hat{A} = |\psi_i\rangle\langle\psi_i|$$

$$\hat{B} = \delta(P_f - \hat{P})$$



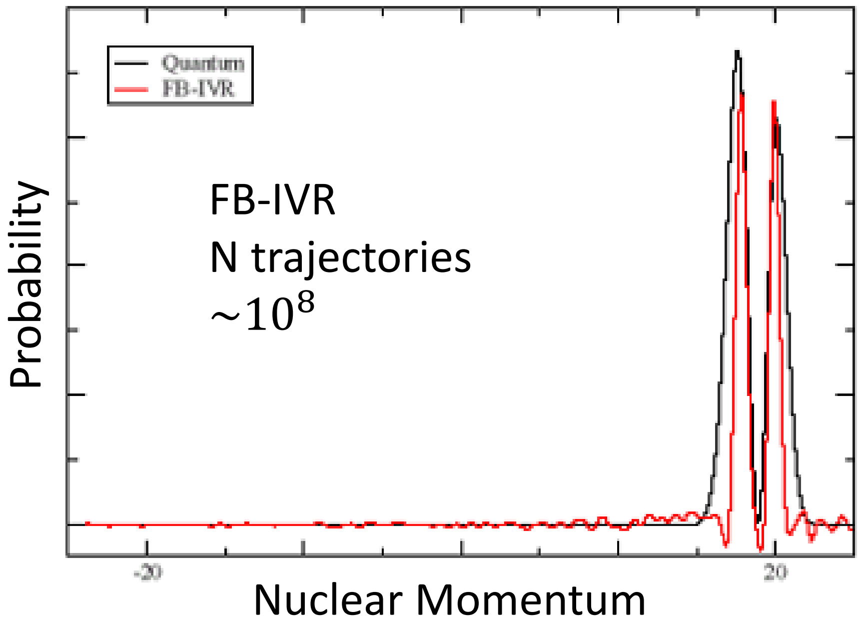
HEIRARCHY OF SEMICLASSICS FOR NONADIABATIC DYNAMICS





LSC-IVR

N trajectories $\sim 10^4$

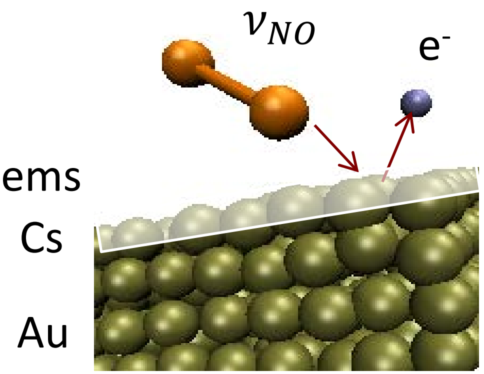


FB-IVR

N trajectories $\sim 10^8$

N. Ananth, C. Venkataraman, and W. H. Miller, J. Chem. Phys. (2007)

SUMMARY OF SC-IVR METHODOLOGY



Quantum-limit methods accurate for adiabatic and nonadiabatic dynamics

Computationally efficient in low-dimensions; prefactor remains a challenge for large systems

Applications to systems where nuclear coherence effects play an important role

OPEN-SOURCE SOFTWARE: SC-CORR

Open Source Software created to calculate Semiclassical Correlation Functions

Code written in Fortran 90, modular structure to allow for easy code modification. Full Documentation.

Linked on group website: http://ananth.chem.cornell.edu/software.html

Download open-source: https://github.com/AnanthGroup/SC-IVR-Code-Package

Semiclassical methods included:

- Double Herman Kluk (Quantum-Limit)
- Linearized SC (Classical-limit)
- Mixed Quantum Classical with new double-forward Implementation (2 orders of magnitude saving in time)

CONDENSED PHASE CHARGE AND ENERGY TRANSFER

A Uniform Dynamic Framework for Electronic and Nuclear Motion

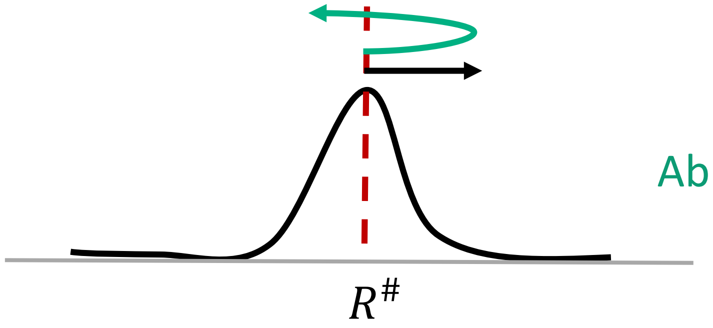
- Exact quantum dynamics
- Approximate Path Integral and Semiclassical based approaches

Dynamics that preserve detailed balance

- obtain rates independent of choice of ‘transition state’

Computational efficiency

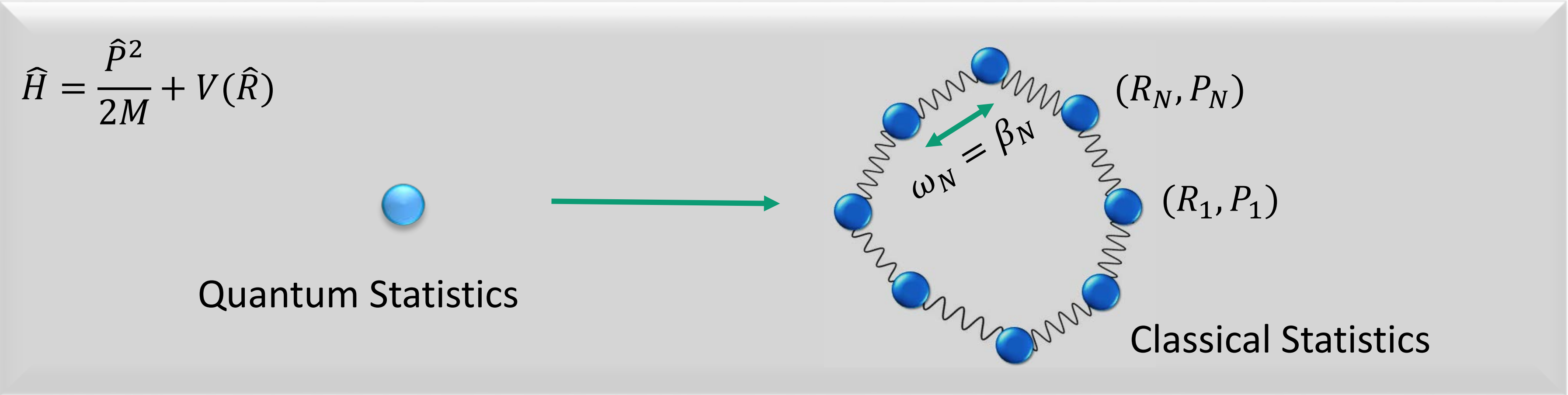
– employs classical molecular dynamics trajectories



Ability to incorporate important quantum effects

- Zero-point energy
- Tunneling
- Nuclear/Electronic Coherence (?)

IMAGINARY TIME PATH INTEGRALS


$$\hat{H} = \frac{\hat{P}^2}{2M} + V(\hat{R})$$

R. P. Feynman

$1 = \int dR|R\rangle\langle R|$ Insert multiple copies of the identity operator

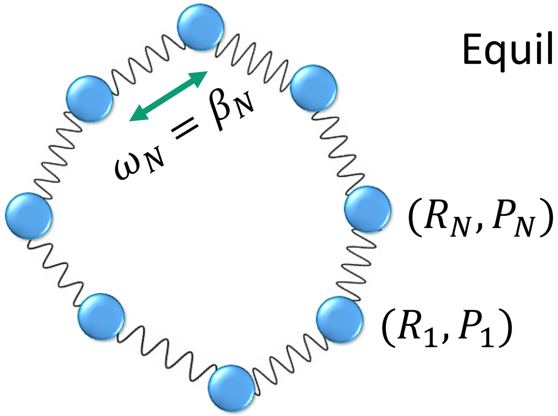
$$Z = Tr\left[e^{-\beta\hat{H}}\right] =\rangle \mathrm{Tr}\left[\left(e^{-\beta_N\hat{H}}\right)^N\right] \qquad = \int dR_1 \int dR_2 \cdots \int dR_N \prod_{\alpha=1}^{N} \langle \boldsymbol{R}_\alpha|\, e^{-\beta_N\hat{H}} |\boldsymbol{R}_{\alpha+1}\rangle$$

Employ high temperature approximation $\beta_N = \frac{1}{k_B(NT)}$; Insert normalized momentum integrals (for PIMD)

$$\mathrm{Z} = \lim_{N\to\infty} \Omega \int dR_1 \int dR_2 \cdots \int dR_N \int dP_1 \int dP_2 \cdots \int dP_N e^{-\beta_N H_N(\boldsymbol{R},\boldsymbol{P})}$$

where $H_N = \sum_i \frac{P_i^2}{2M'} + \frac{M\omega_N^2}{2}(R_i - R_{i+1})^2 + V(R_i)$

PATH INTEGRAL MOLECULAR DYNAMICS



Equilibrium configurations of a quantum system sampled using classical molecular dynamics

$$\dot{P}_i = -\frac{\partial H_N}{\partial R_i} \quad \text{and} \quad \dot{R}_i = \frac{\partial H_N}{\partial P_i}$$

Parrinello and Rahman, J. Chem. Phys. (1984)

RING POLYMER MOLECULAR DYNAMICS

Can we obtain approximate quantum dynamics from the classical time evolution of the Ring Polymer?

Choose $M' = M$. Approximation to the Kubo-transform real-time thermal correlation function

$$C_{AB}^{RPMD}(t) \approx Z^{-1} \int dR_1 \int dP_1 \cdots \int dR_N \int dP_N \, e^{-\beta_N H_N(\mathbf{R},\mathbf{P})} \, \overline{A}(R_0) \, \overline{B}(R_t),$$

where $\bar{A} = \frac{1}{N}\sum_{j=1}^{N} A(R_j(0))$ and $\bar{B} = \frac{1}{N}\sum_{j=1}^{N} B(R_j(t))$

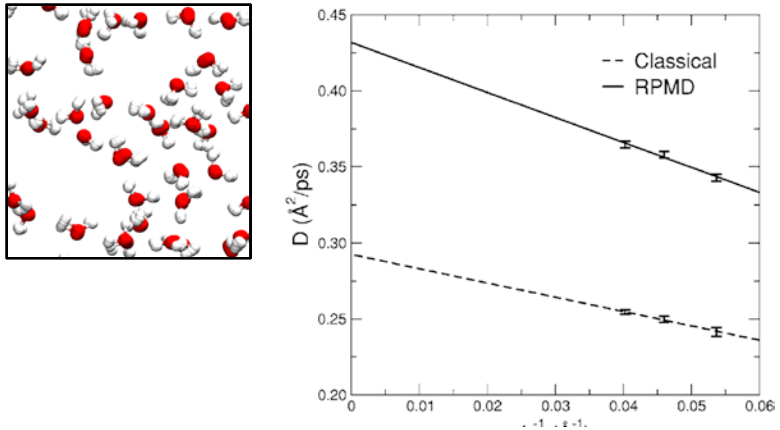
D. E. Manolopoulos, I. R. Craig, S. Althorpe, T. F. Miller III, S. Habershon, T. E. Markland, ...

Related Methods:

Centroid Molecular Dynamics	G. A. Voth, J. Cao, S. Jang, ...
Linearized Semiclassical	W. H. Miller, E. Geva, X.Sun, H. Wang, ...

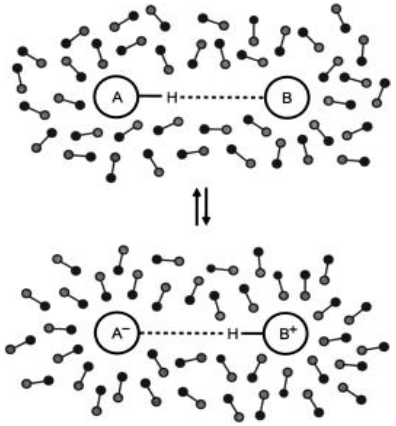
RPMD: THE GOOD

Trajectories preserve the quantum Boltzmann distribution (detailed balance)

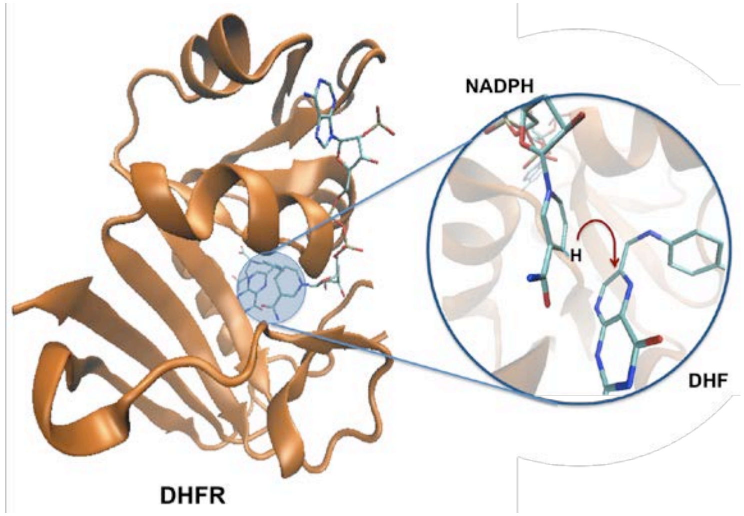


T. F. Miller III and D. E Manolopoulos, (2005)

Reaction rates independent of mechanistic assumptions



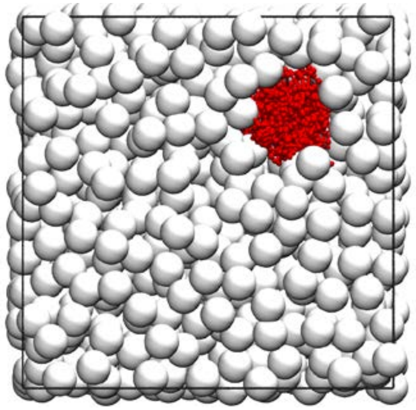
R. C. Guevara, I. R. Craig and D. E. Manolopoulos, J. Chem. Phys. (2008)

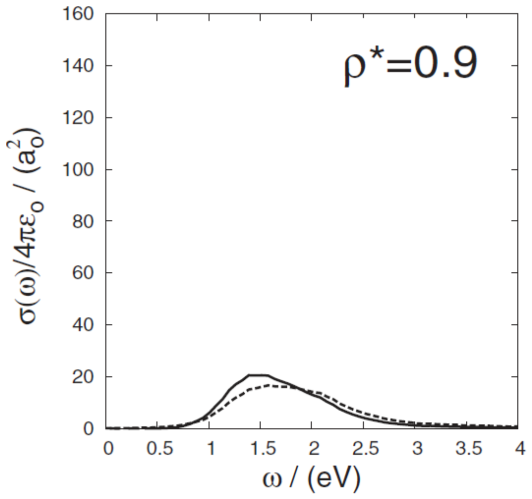


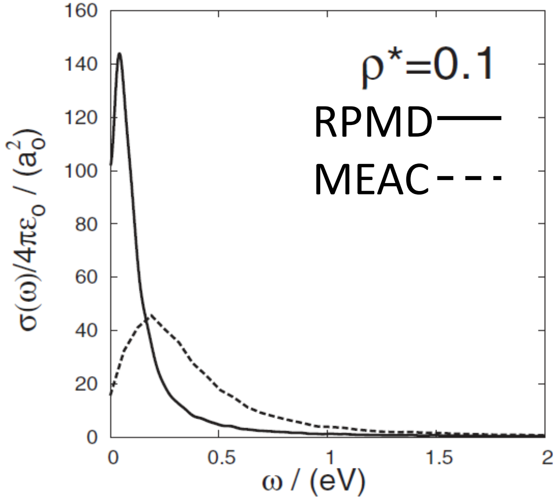
RPMD employs classical trajectories, captures tunneling and zero-point energy effects

N. Boekelheide, R. Salomon-Ferrer, and T. F. Miller III, Proc. Natl. Acad. Soc. (2011)

RPMD LIMITATIONS



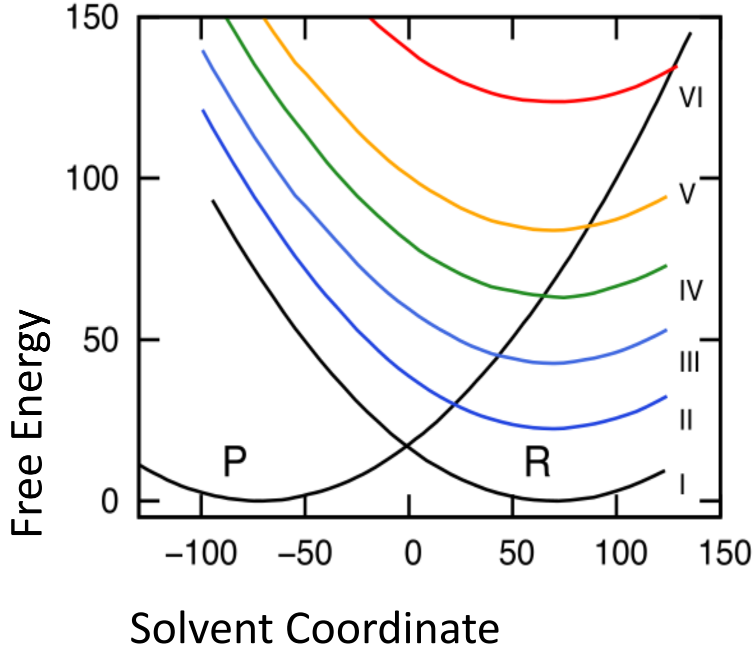


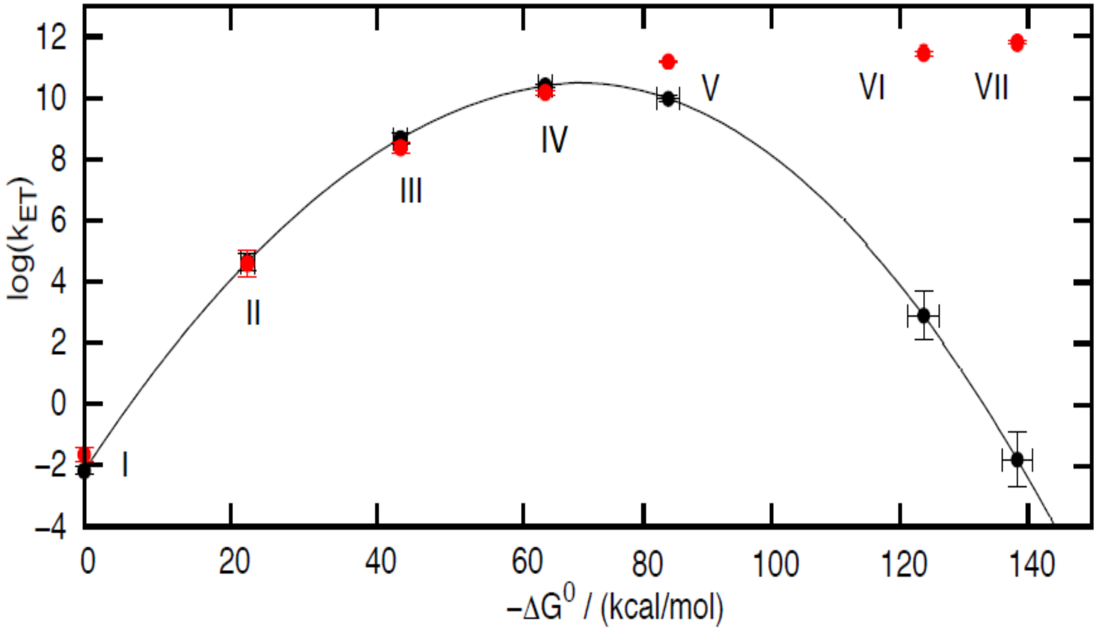


Good for nonadiabatic dynamics

Bad for scattering problems
(no coherence effects)

T. F. Miller III, J. Chem. Phys. (2008)

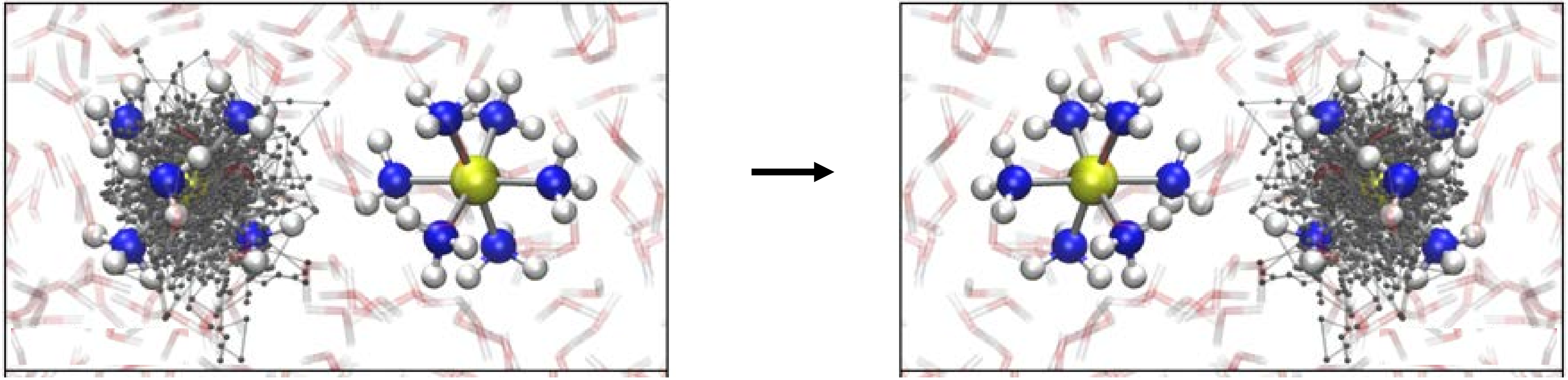




A. R. Menzeleev, N. Ananth, T. F. Miller, III, J. Chem. Phys. (2010)

THE COBALT HEXAMMINE SELF-EXCHANGE REACTION: AN RPMD APPLICATION

$$Co(NH_3)_6^{2+} + Co(NH_3)_6^{3+} \rightarrow Co(NH_3)_6^{3+} + Co(NH_3)_6^{2+}$$



2 $Co(NH_3)_6^{3+}$ complexes, 430 SPC water molecules, 1024 bead ring polymer for transferring electron

Force Field Parameters: CHARMM22, Co - Co distance fixed at $7A^o$

Each RP electron bead

- interacts electrostatically with solvent/complex atom
- has a harmonic bond with two neighbor beads

Reaction coordinate: "bead count" – count number of RP beads on donor vs acceptor complex

Kenion and Ananth, Phys. Chem. Chem. Phys. (2016)

OUTER SPHERE (SOLVENT) FREE ENERGY BARRIER

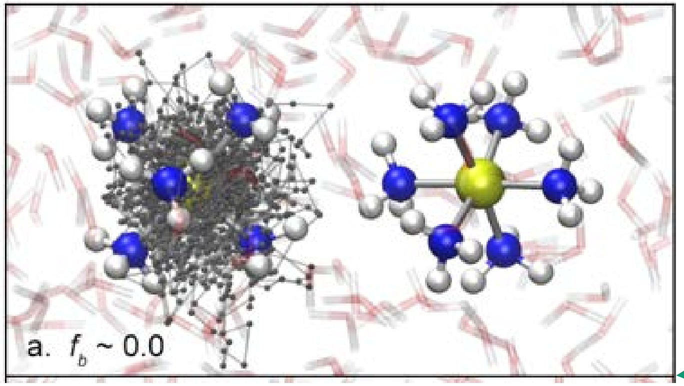
- Assume separability of inner and outer sphere free energy barriers

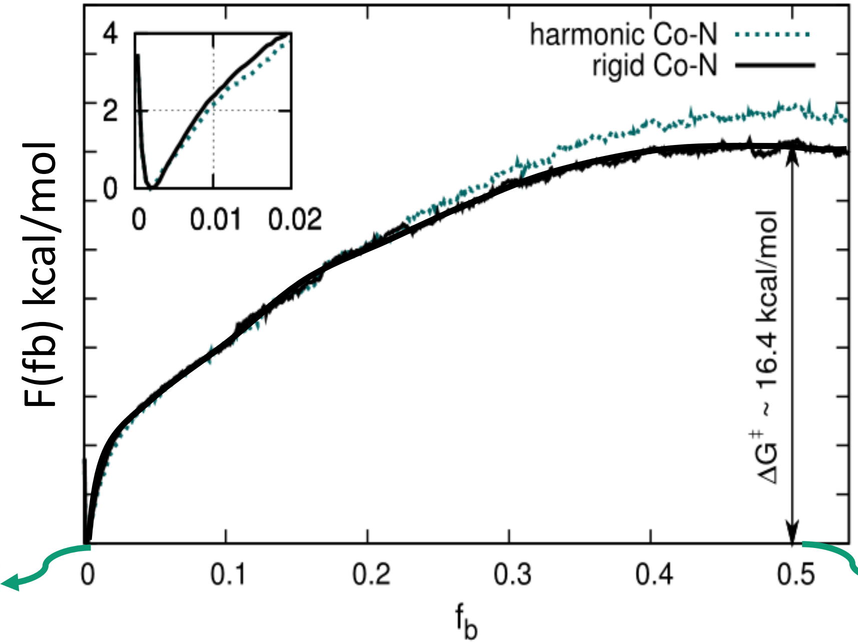
Brunschwig and Sutin, Coord. Chem. Rev. (1999)

  - No re-parameterization of force field as the electron transfer reaction progresses

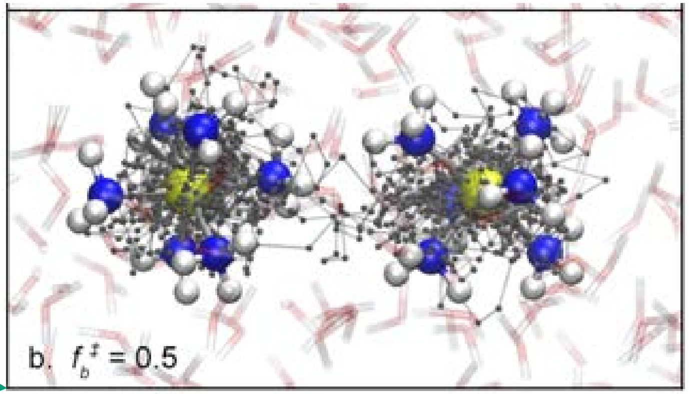
Path Integral Molecular Dynamics: Free energy barrier along the ET reaction coordinate

Reactant State configuration



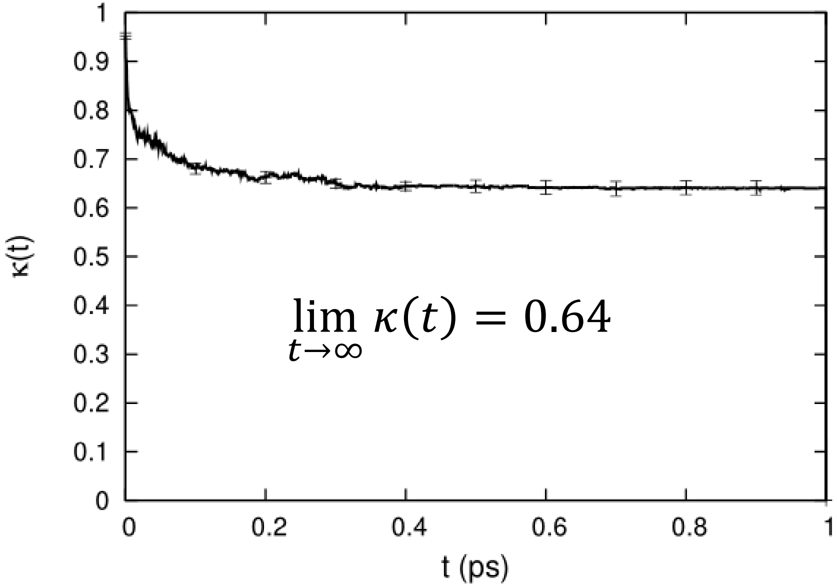


Transition State configuration



Kenion and Ananth, Phys. Chem. Chem. Phys. (2016)

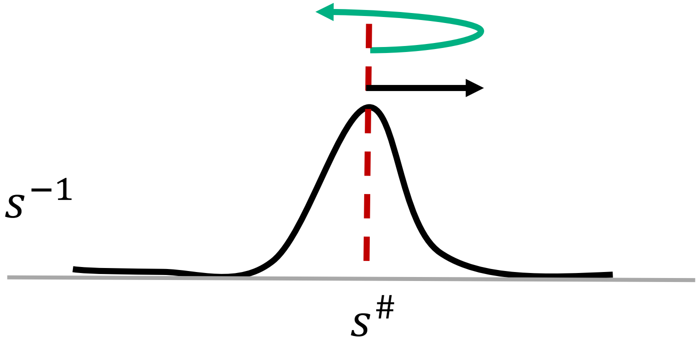
REACTION RATE



$$\lim_{t\to\infty} \kappa(t) = 0.64$$

$$k_{RPMD} = K_{bi} \times \lim_{t\to\infty} \kappa(t)\ k_{TST}$$
$$= 0.9 \times 10^{-8} - 2 \times 10^{-7}\ M^{-1}s^{-1}$$

$$k_{expt} \approx 10^{-7}\ M^{-1}s^{-1}$$



Hammershoi, Geselowitz, Taube, Inorg. Chem. (1984)

R. L. Kenion and N. Ananth, Phys. Chem. Chem. Phys. (2016)

EXTENDING RPMD TO MULTI-STATE SYSTEMS

Dynamics that preserve detailed balance

Uniform Dynamic Framework

Incorporate tunneling and zero-point energy

Multi-electron systems and the inverted regime

Simulating excited electronic state dynamics

Linear scaling with system size

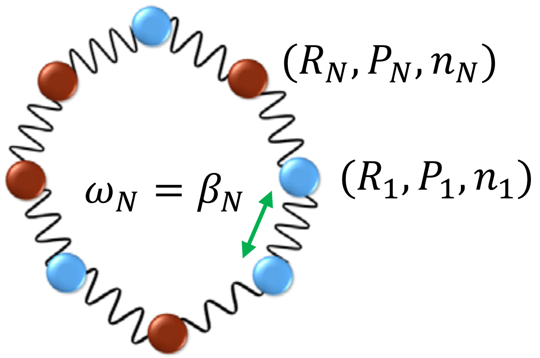
Multi-State Systems

Canonical partition function for a quantum, K-state system Hamiltonian $H = \frac{P^2}{2M} + \sum_{n,m=1}^{K} |n\rangle\langle m| V(R)$

$$Z = Tr\left[e^{-\beta H}\right] = \int dR_1 \int dR_2 \cdots \int dR_N \sum_{n_1=1}^{K} \sum_{n_2=1}^{K} .. \sum_{n_N=1}^{K} \prod_{\alpha=1}^{N} \langle \boldsymbol{R}_\alpha n_\alpha |\, e^{-\beta_N H_N(\boldsymbol{R})} | n_{\alpha+1}, \boldsymbol{R}_{\alpha+1} \rangle$$

$$= \lim_{N\to\infty} F \int d\{\boldsymbol{R}_\alpha\} \int d\{\boldsymbol{P}_\alpha\} e^{-\beta_N H_{MF}} \mathrm{sgn}(\Gamma)$$

= Canonical Partition Function for a classical system with $H_N = \sum_i \frac{P_i^2}{2M} + \frac{M\omega_N^2}{2}(R_i - R_{i+1})^2 - \frac{1}{\beta_N} \ln \boldsymbol{\Gamma}_{\mathbf{MF}}$



where $\boldsymbol{\Gamma}_{\mathbf{MF}} = \mathrm{Tr}[\prod_{\alpha=1}^{P} M(\boldsymbol{R}_\alpha)]$ and the matrix

$$M_{nm}(\boldsymbol{R}_\alpha) = \begin{cases} e^{-\beta_N V_{nn}(\boldsymbol{R}_\alpha)}, & n = m \\ -\beta_N V_{nm}(\boldsymbol{R}_\alpha) e^{-\beta_N V_{nn}(\boldsymbol{R}_\alpha)}, & n \neq m \end{cases}$$

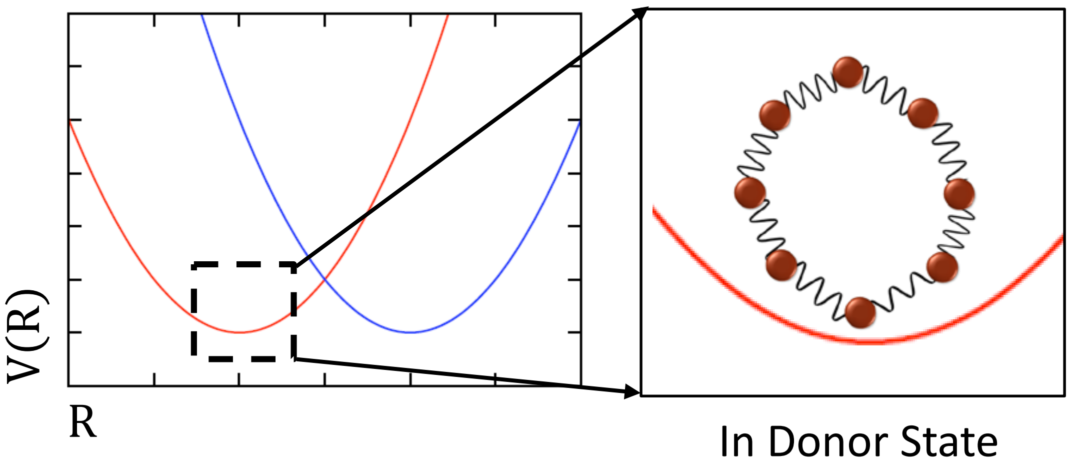
Γ averages over all RP state space configurations

Feynman, Chandler, Wolynes,...

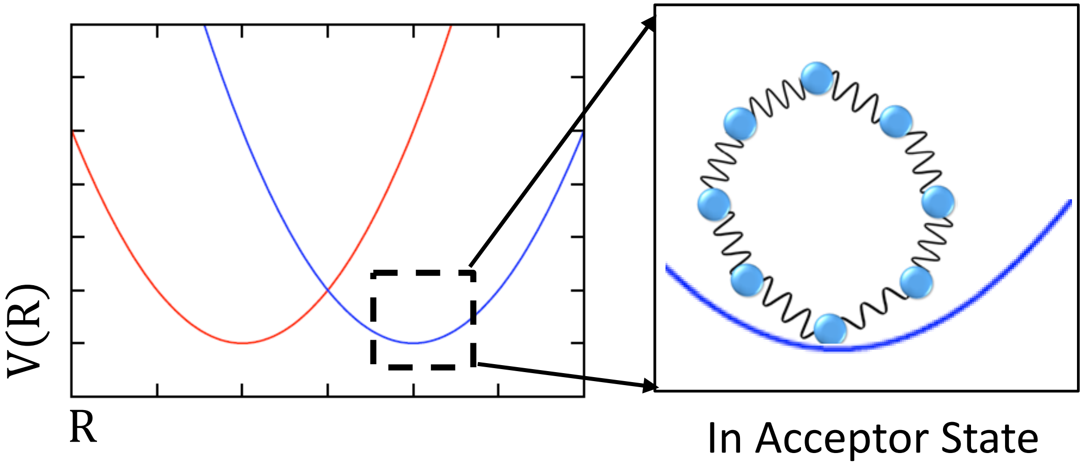
MF-RPMD: Real-time correlation functions from classical trajectories with dynamics generated by H_N

Manolopoulos, Miller, Ananth, ….

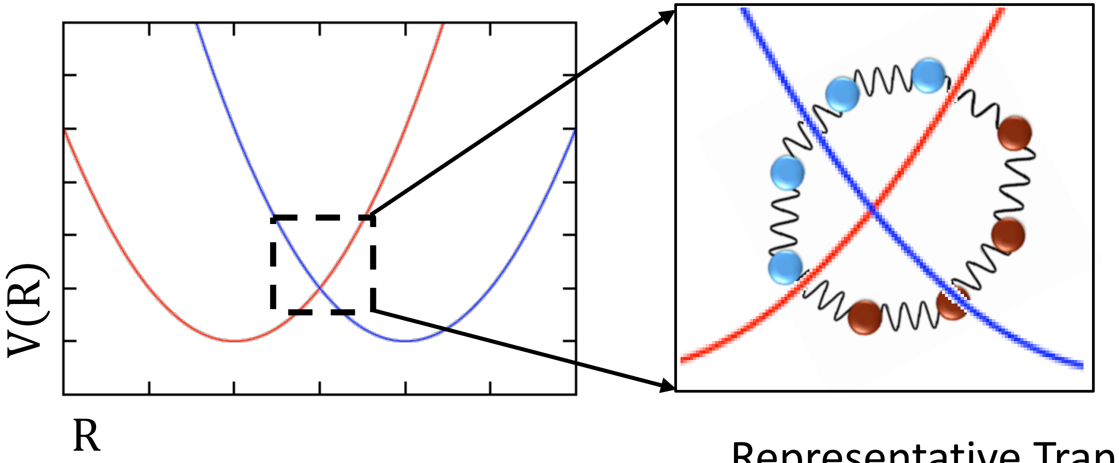
STATE SPACE RING POLYMERS FOR ELECTRON TRANSFER



In Donor State



In Acceptor State



Representative Transition State

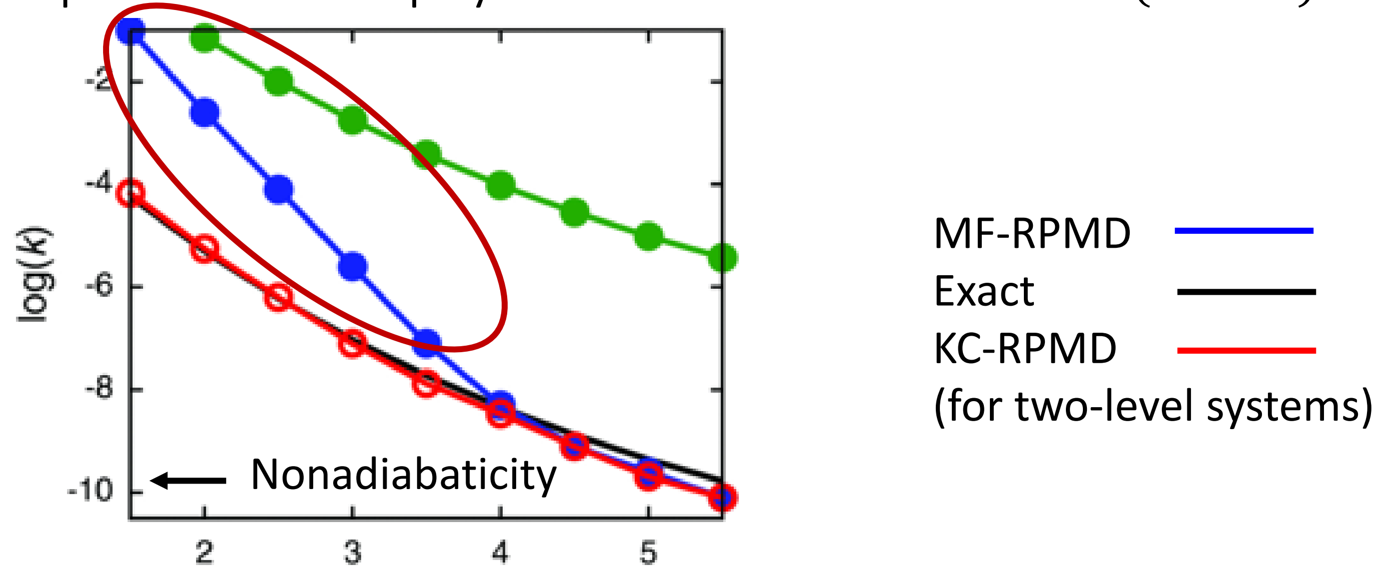
MEAN-FIELD RPMD AND REACTION RATES

Properties of Mean-Field

- Exact for equilibrium properties of an N-level system
- Simple implementation
- Trajectory ensemble preserves the quantum Boltzmann distribution

Can Mean-Field capture dynamics in the weak-coupling (nonadiabatic regime)?

Traditional MF-RPMD rate implementation: Employs a solvent reaction coordinate $P(R = R^{\#})$



(for two-level systems)

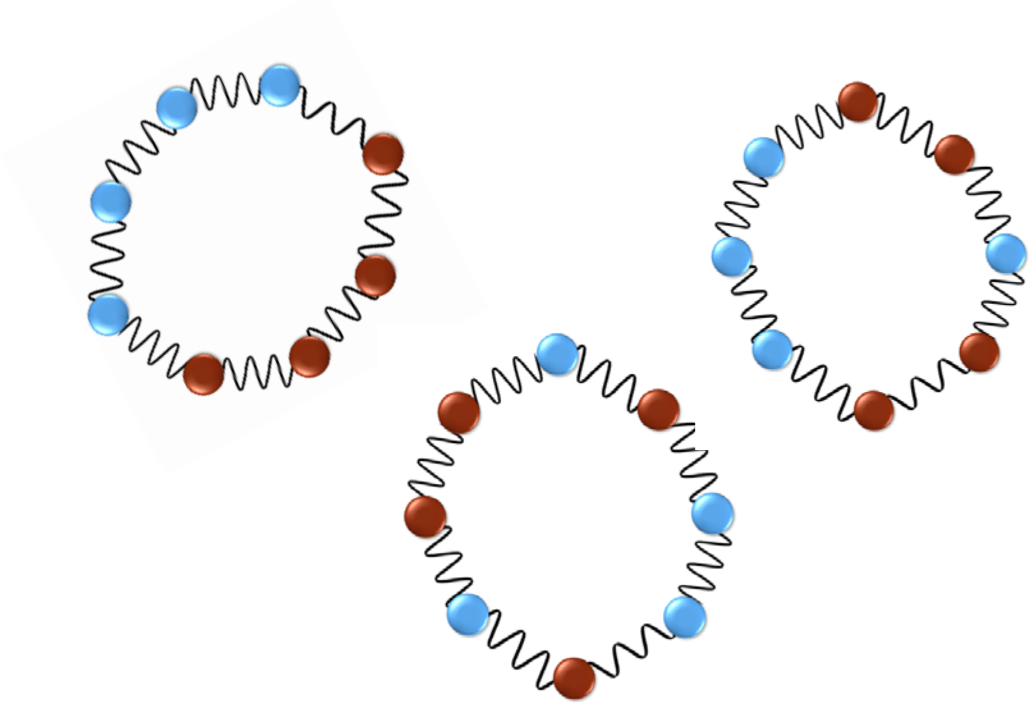
Figure adapted from paper on “Kinetically Constrained RPMD” - A.R. Menzeleev, F. Bell, and T. F. Miller III, J. Chem. Phys. 140, 6 (2014)

TRANSITION STATE CONFIGURATIONS AND THEIR ASSOCIATED PROBABILITY

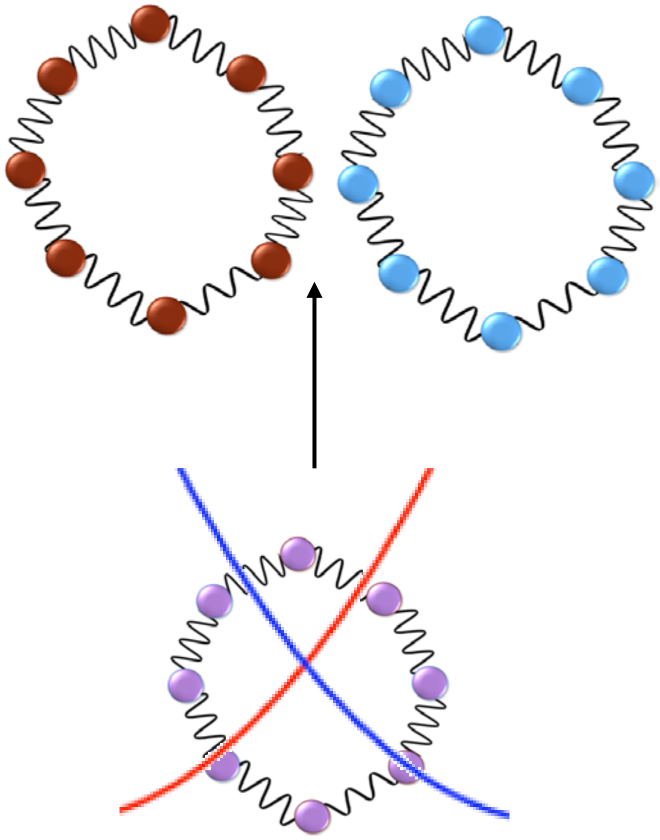
$\boldsymbol{\Gamma_{\mathrm{MF}}}$ includes transition-state RP configurations: classify by number of kink-pairs and number of beads in each state

Kinked configurations: Neighboring beads in different states

Free energy of Kink-pair formation $\propto |V_{12}|^2$



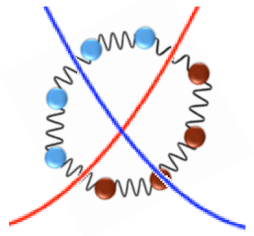
In the weak-coupling (nonadiabatic) limit



P. G. Wolynes and D. Chandler, J. Chem. Phys. (1981)

A SIMPLE FIX: ENFORCE KINK-PAIR FORMATION

Solvent Transition State defined by: $P(R = R^{\#} | \, kink \; formation)$



Probability of reaching solvent configurations where donor/acceptor states are degenerate

x Probability of kink formation at $R^{\#}$

$$k_{TST} = P(R = R^{\#}) \times P(kink \; formation \; at \; R^{\#}) \times forward \; velocity \; at \; TS$$

- Free Energy profile obtained from PIMD + Umbrella Sampling + WHAM

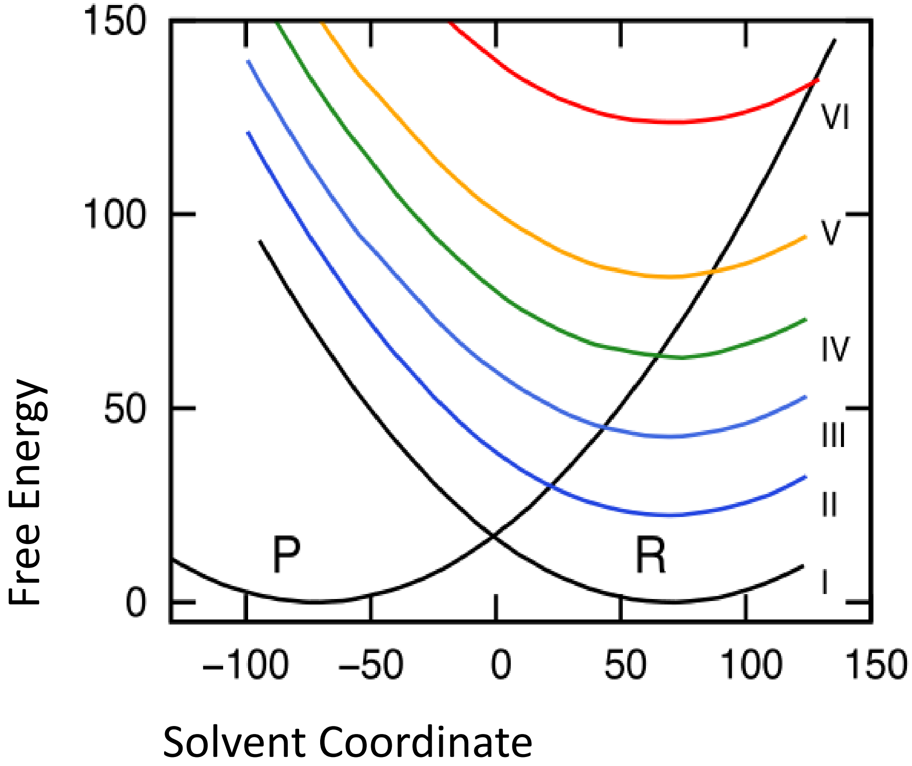
Dynamic Recrossing Factor: $\kappa(t)$ = Real-time MF-RPMD thermal correlation function

Flux associated with dividing surface obtained from finite difference

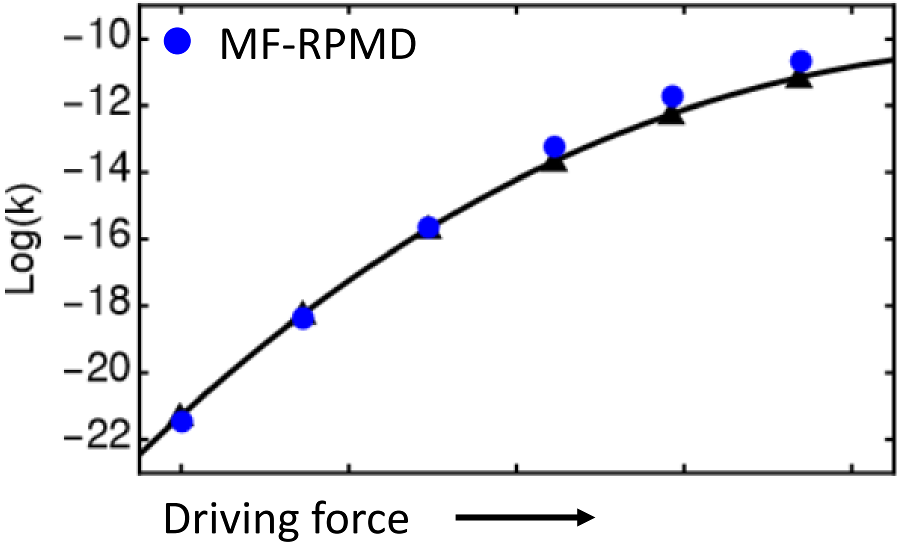
J. R. Duke and N. Ananth, Faraday Discuss. on Reaction Rate Theory (2016)

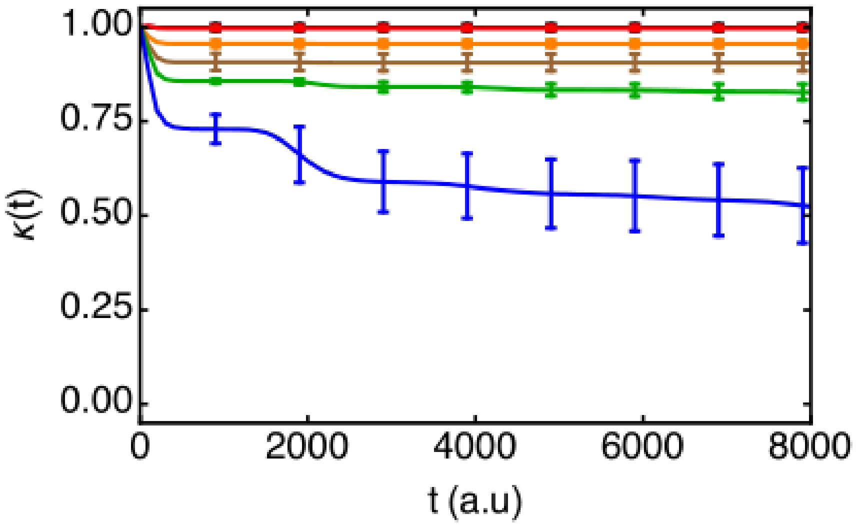
REACTION RATES IN THE NORMAL-ACTIVATIONLESS REGIMES

Electron Transfer Models: Exploring Marcus Regimes



Rates for different driving forces vs Golden rule rates

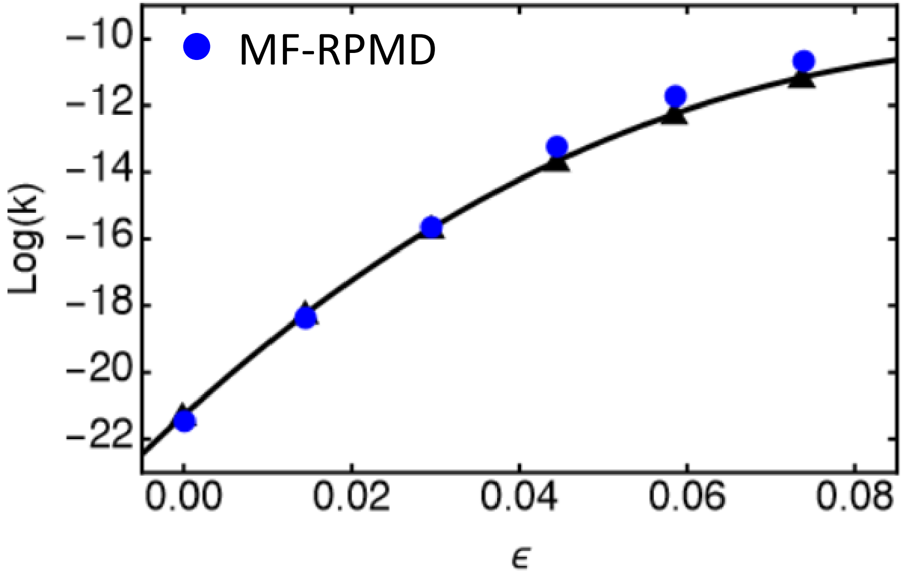


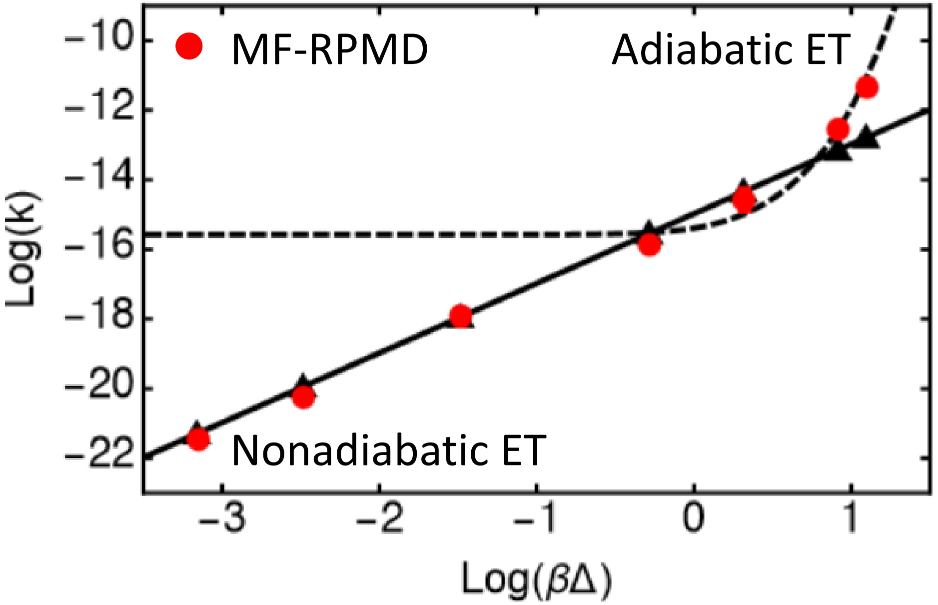


REACTION RATES IN THE NORMAL-ACTIVATIONLESS REGIMES

Rates for different driving forces vs Golden rule rates

Rates over a range of coupling strenths (V_{12})





A pleasant surprise: Mean-field dynamics sufficiently accurate in the weak-coupling nonadiabatic reactions

All the features of RPMD extended to general multi-state, multi-electron processes

Alternative strategy for two-state systems see ‘KC-RPMD’ A. R. Menzeleev, F. Bell, and T. F. Miller III, J. Chem. Phys. (2014)

Inverted regime?

J. R. Duke and N. Ananth, Faraday Discuss. on Reaction Rate Theory (2016)

MEAN-FIELD RPMD AND THE INVERTED REGIME

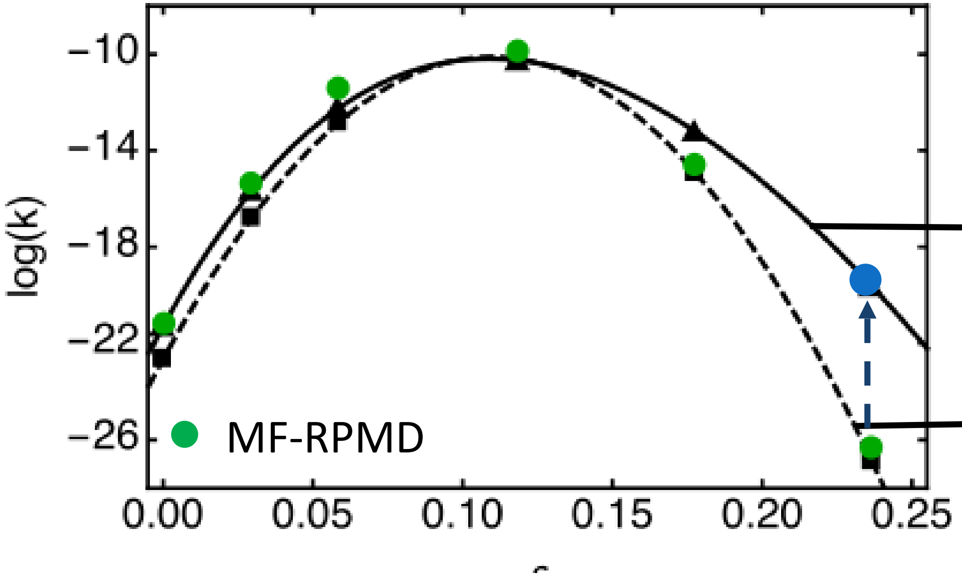
Population Coordinate: $\Delta P = P_2 - P_1$

Transition State: $\Delta P = 0$

First Implementation: $\Delta P\left(R^{\#}\right) = 0$

Include quantum solvent tunneling:

Replace $\delta\left(R - R^{\#}\right)$ by $e^{-\alpha\left(\left(R-R^{\#}\right)^2\right.}$



Golden Rule rate

Marcus Theory rate

MF-RPMD for electron transfer:

- accurate for normal-activationless, captures Marcus turnover in the inverted regime
- comparable to KC-RPMD for two-level systems, but MF-RPMD is general for N-level systems
- easy implementation

Not applicable to photoinduced processes: need explicit electronic state variables

J. R. Duke and N. Ananth, Invited Faraday Discussion on Reaction Rate Theory (2016)

NONADIABATIC DYNAMICS: CLASSICAL ANALOG VARIABLES FOR DISCRETE ELECTRONIC STATES

$$H = h_0(R,P) + \sum_{n,m=1}^{K} V_{nm}(R)|\psi_n\rangle\langle\psi_m| = h_0(R,P) + \sum_{n,m} V_{nm}(R) a_n^+ a_m$$

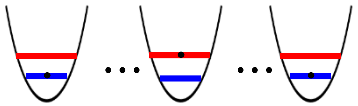
Map K electronic states to singly excited oscillator states via bosonic creation/annihilation operators (Schwinger's theory)

H. D. Meyer and W. H. Miller, J. Chem. Phys. (1979)
G. Stock and M. Thoss, Phys Rev. Lett. (1997)

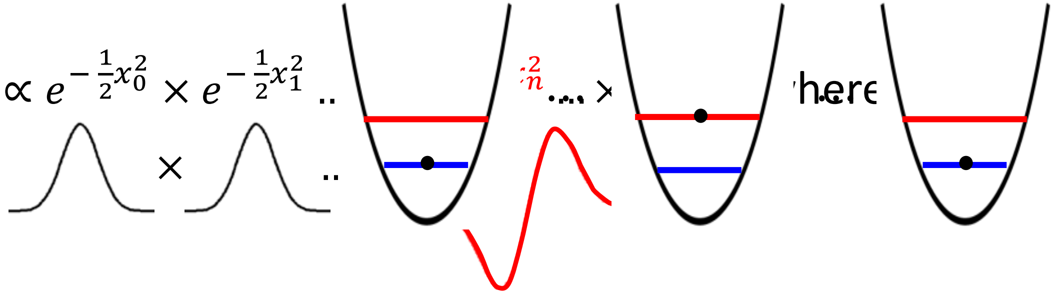
$$|\psi_n\rangle\langle\psi_m| \rightarrow a_n^+ a_m \equiv \frac{1}{2}(x_n - ip_n)(x_m + ip_m) \quad \text{where} \quad [a_n^+, a_m] = \delta_{nm}$$

$$|\psi_n\rangle \rightarrow |0_1 0_2 \cdots 1_n \cdots 0_D\rangle \equiv |n\rangle$$

Electronic wavefunction in the Singly Excited Oscillator (SEO) basis



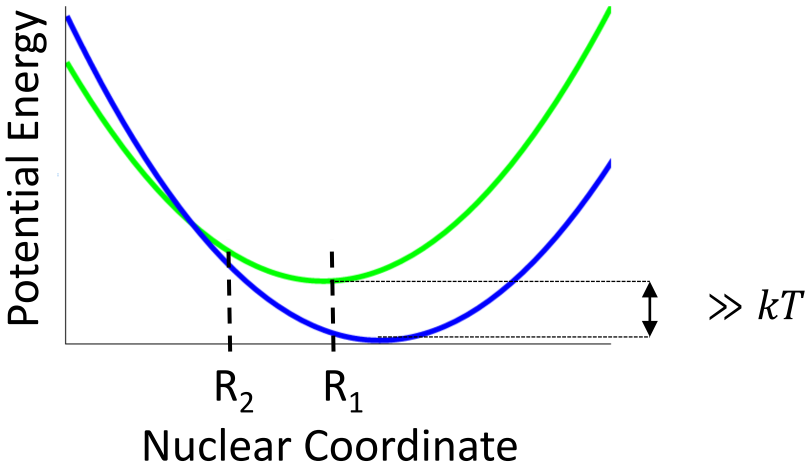
$\langle \boldsymbol{x}|n\rangle \propto e^{-\frac{1}{2}x_0^2} \times e^{-\frac{1}{2}x_1^2}$ ..



dimensional vector

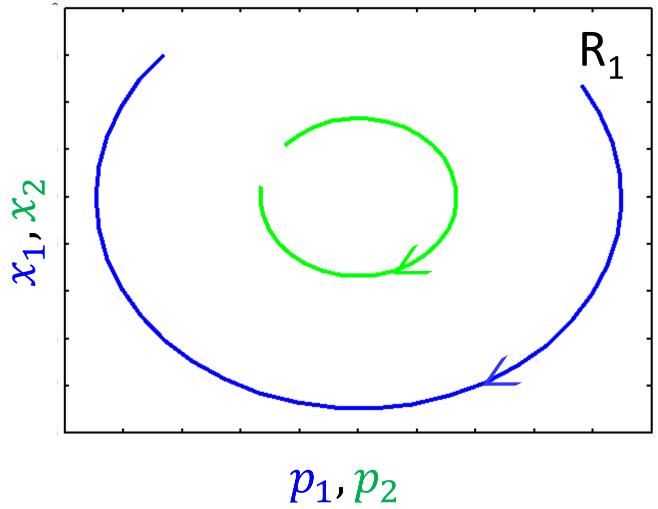
Miller, Meyer, McCurdy, Stock, Thoss, Geva, Coker, Kapral,….

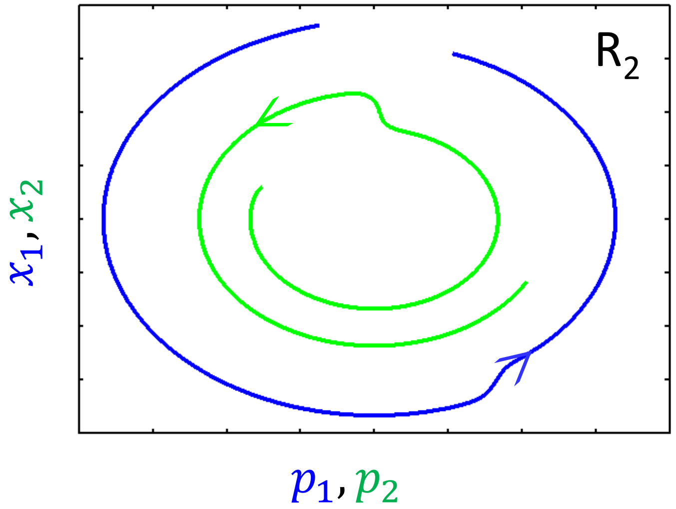
DYNAMICS IN THE MAPPING VARIABLE FRAMEWORK



The 2 SEO states are
$|1_1 0_2\rangle$ and $|0_1 1_2\rangle$

Plot electronic phase space distribution at R value indicated by the dashed line – only state 1 $|1_1 0_2\rangle$ occupied

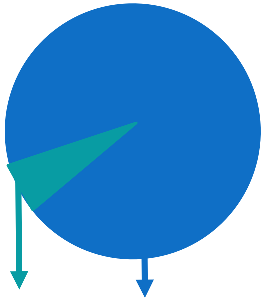




PATH INTEGRAL DISCRETIZATION IN THE MAPPING FRAMEWORK

$$Z = \lim_{N\to\infty} \Phi \int d\{\boldsymbol{R}_\alpha, \boldsymbol{P}_\alpha\}\, e^{-\beta_N H_R(\boldsymbol{R}_\alpha,\boldsymbol{P}_\alpha)} \sum_{\{n_\alpha\}=1}^{D} \prod_{\alpha=1}^{N} \left\langle n_\alpha \middle| e^{-\frac{\beta}{N}\hat{V}(\boldsymbol{R}_\alpha,\boldsymbol{R}_{\alpha+1})} \middle| n_{\alpha+1}\right\rangle$$

Identifying the Identity :



All space

Position space: $\hat{I} = \int dx\, |x\rangle\langle x|$

Oscilator space: $\hat{I} = \prod_{i=1}^{D} \sum_{j_i=0}^{\infty} |j_i\rangle = \hat{\mathrm{P}}_{\mathrm{SEO}} + \hat{\mathrm{P}}_{\mathrm{other}}$

Mapping subspace

SEO subspace: $\hat{I} = \sum_n |n\rangle\langle n| = \hat{\mathrm{P}}_{\mathrm{SEO}}$

Position subspace: $\boxed{\hat{I} = \int dx\, |x\rangle\langle x|\hat{\mathrm{P}}_{\mathrm{SEO}}}$

N. Ananth and T. F. Miller III, J. Chem. Phys. 2010

Constructing the Mapping Variable RPMD Hamiltonian:

Insert identity N times

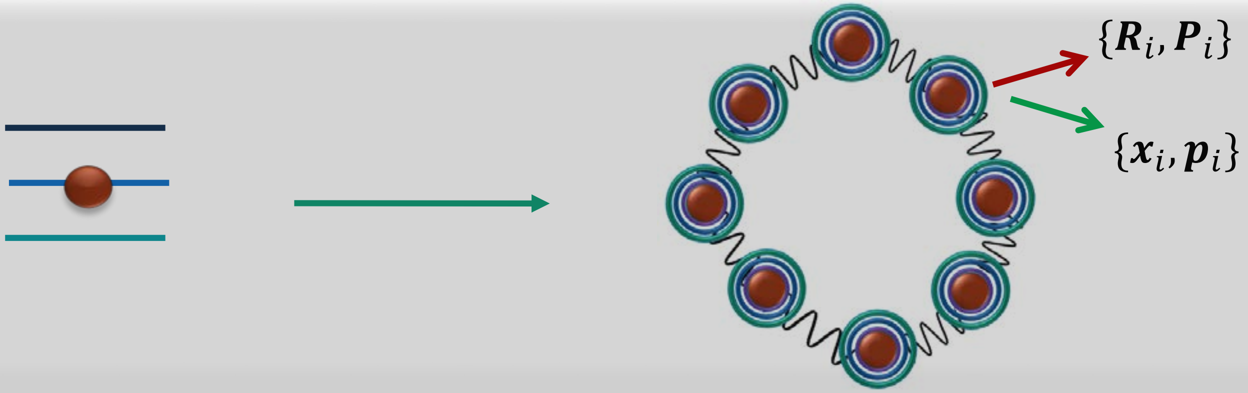
Wigner transform trace over electronic states to obtain expression in mapping variable phase-space

$$Tr\left[\hat{O}\right] = \int d\boldsymbol{x} \int d\boldsymbol{p}\, O(\boldsymbol{x},\boldsymbol{p}) \text{ where } O(\boldsymbol{x},\boldsymbol{p}) = \frac{1}{(2\pi\hbar)^D} \int d\Delta\boldsymbol{x} \left\langle \boldsymbol{x} - \frac{\Delta\boldsymbol{x}}{2} \middle| \hat{\boldsymbol{P}}_{\boldsymbol{SEO}} \hat{O} \hat{\boldsymbol{P}}_{\boldsymbol{SEO}} \middle| \boldsymbol{x} + \frac{\Delta\boldsymbol{x}}{2} \right\rangle e^{i\boldsymbol{p}^T.\Delta\boldsymbol{x}}$$

N. Ananth, J. Chem. Phys. 2013

MAPPING VARIABLE PIMD: AN EXACT MAPPING AT EQUILIBRIUM

$$\hat{H} = \frac{\hat{P}^2}{2M} + \boldsymbol{V}(\hat{R})$$



N. Ananth, J. Chem. Phys. (2013)

$$\boxed{Z = \lim_{N\to\infty} F \int d\{\boldsymbol{x}_\alpha\} \int d\{\boldsymbol{R}_\alpha\} \int d\{\boldsymbol{p}_\alpha\} \int d\{\boldsymbol{P}_\alpha\} e^{-\beta_N H_{MV}} \,\mathrm{sgn}(\boldsymbol{\Gamma})}$$

$$\{\,.\,, H_{MV}\} = 0$$

$$H_{MV} = \sum_\alpha \underline{\frac{\boldsymbol{P}_\alpha^T.\boldsymbol{P}_\alpha}{2M} + \frac{MN^2}{2\beta^2\hbar^2}(\boldsymbol{R}_\alpha - \boldsymbol{R}_{\alpha+1})^T.(\boldsymbol{R}_\alpha - \boldsymbol{R}_{\alpha+1}) + V_0(\boldsymbol{R}_\alpha)} + \frac{N}{\beta}\underline{(\boldsymbol{x}_\alpha^T.\boldsymbol{x}_\alpha + \boldsymbol{p}_\alpha^T.\boldsymbol{p}_\alpha)} - \frac{N}{\beta}\underline{\ln|\boldsymbol{\Gamma}|}$$

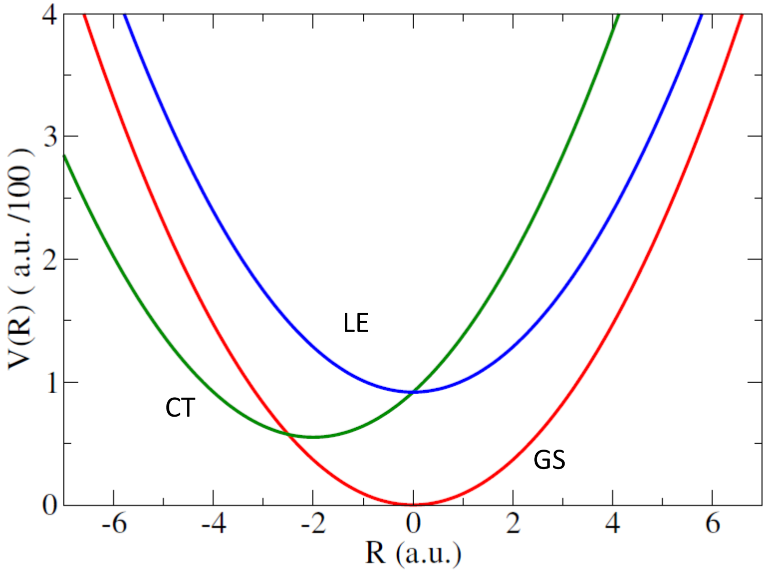
$$\boldsymbol{\Gamma} = \mathrm{Re}\left[\prod_{\alpha=1}^{P}(\boldsymbol{C}_\alpha - \frac{1}{2}\mathbb{1})\, M^I(\boldsymbol{R}_\alpha)\right]$$

$$\boldsymbol{C}_\alpha = (\boldsymbol{x}_\alpha + i\boldsymbol{p}_\alpha)\otimes(\boldsymbol{x}_\alpha - i\boldsymbol{p}_\alpha)^{\boldsymbol{T}}$$

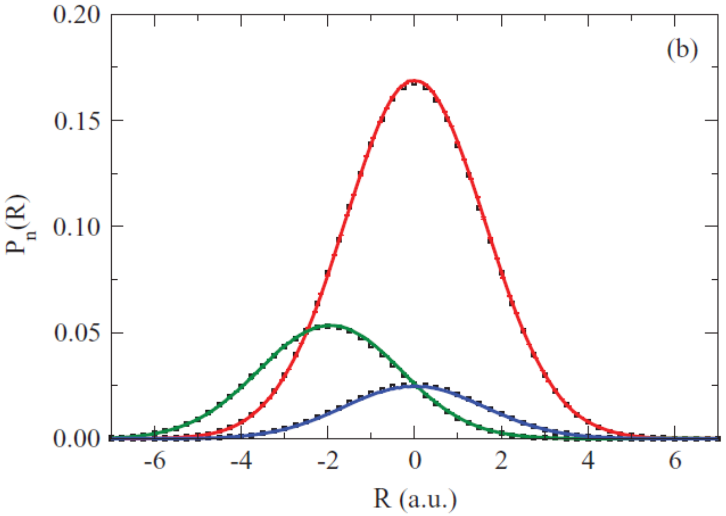
$$M^I_{nm}(\boldsymbol{R}_\alpha) = \begin{cases} e^{-\beta_N V_{nn}(\boldsymbol{R}_\alpha)}, & n = m \\ -\beta_N V_{nm}(\boldsymbol{R}_\alpha) e^{-\beta_N V_{nn}(\boldsymbol{R}_\alpha)}, & n \neq m \end{cases}$$

EXACT EQUILIBRIUM PROPERTIES

Three-level system: model for ultrafast electron transfer



No: of beads	Average Energy $(\times 10^{-3}\ \mathrm{a.u.})$
1	5.54
2	6.63
4	6.69
Exact	6.69



GS: ground state

CT: charge-transfer state

LE: locally excited state

MV-RPMD: APPROXIMATE DYNAMICS

$$H_{MV} = \sum_\alpha \frac{\boldsymbol{P}_\alpha^T.\boldsymbol{P}_\alpha}{2M} + \frac{MN^2}{2\beta^2\hbar^2}(\boldsymbol{R}_\alpha - \boldsymbol{R}_{\alpha+1})^T.(\boldsymbol{R}_\alpha - \boldsymbol{R}_{\alpha+1}) + V_0(\boldsymbol{R}_\alpha) + \frac{N}{\beta}(\boldsymbol{x}_\alpha^T.\boldsymbol{x}_\alpha + \boldsymbol{p}_\alpha^T.\boldsymbol{p}_\alpha) - \frac{N}{\beta}\ln|\boldsymbol{\Gamma}|$$

Equations of Motion for Nuclear variables $\dot{R}_i = \frac{\partial H_{MV}}{\partial P_i}$ $\dot{P}_i = -\frac{\partial H_{MV}}{\partial R_i}$

Equations of Motion for n^th^ Electronic state variables $\dot{x}_i{}^{(n)} = \frac{\partial H_{MV}}{\partial p_i^{(n)}}$ $\dot{p}_i{}^{(n)} = -\frac{\partial H_{MV}}{\partial x_i^{(n)}}$

Real-time MV-RPMD correlation function $C_{AB}^{MV}(t) = Z^{-1}\int d\boldsymbol{y}_1 \cdots \int d\boldsymbol{y}_N \, e^{-\beta_N H_{MV}(\boldsymbol{y})} \, \overline{A}(\boldsymbol{y}_0) \, \overline{B}(\boldsymbol{y}_t)\mathrm{sgn}(\boldsymbol{\Gamma})$

$\boldsymbol{y} = \{\boldsymbol{x}, \boldsymbol{p}, \boldsymbol{R}, \boldsymbol{P}\}$

N. Ananth, J. Chem. Phys. (2013)

Properties:

Dynamics conserve detailed balance

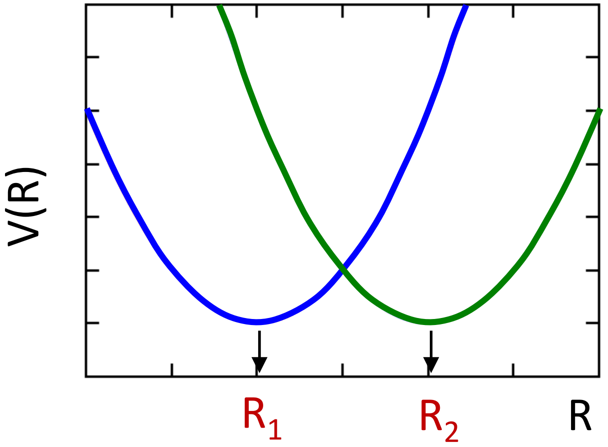
Reduces to RPMD for single surface dynamics and in the zero-coupling limit (1-electronic bead limit)

Alternate Strategies:

Combine MV initial distribution with semiclassical dynamics – but dynamics do not obey detailed balance

N. Ananth and T. F. Miller III, J. Chem. Phys. (2010); J. O. Richardson and M. Thoss, J. Chem. Phys. Comm. (2012)

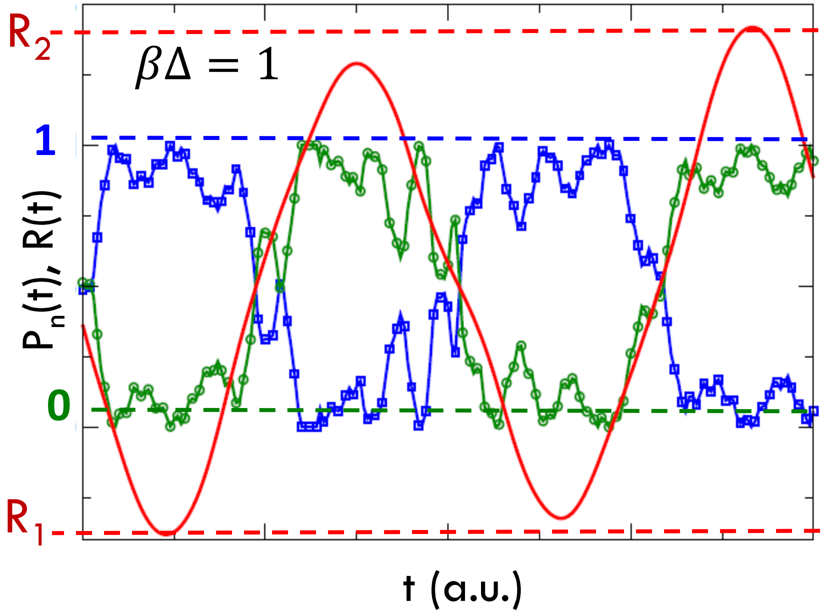
MV-RPMD AND ELECTRONIC STATE POPULATIONS: SINGLE TRAJECTORY ANALYSIS

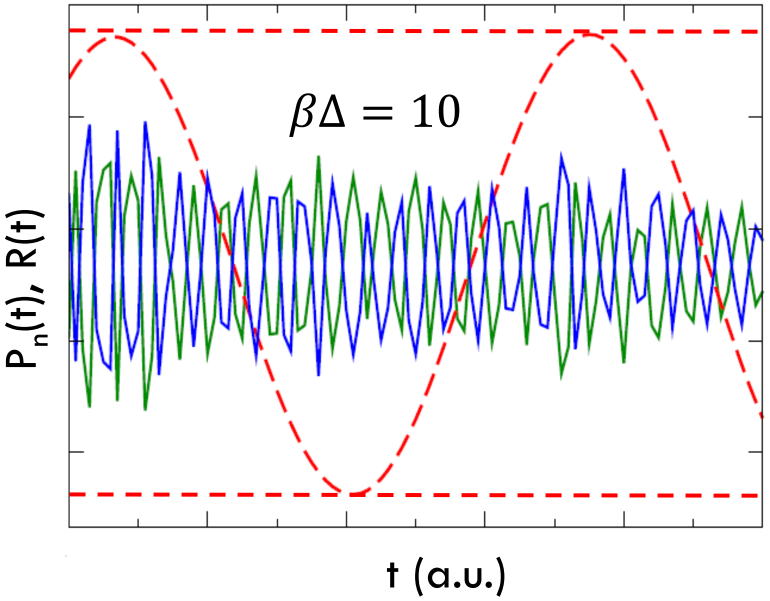


$$V_{11}(R) = -R + \frac{1}{2}R^2$$

$$V_{22}(R) = R + \frac{1}{2}R^2$$

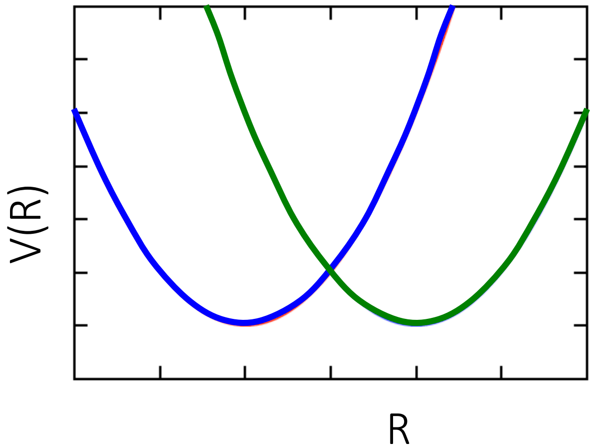
$$V_{12} = \Delta$$





N. Ananth, J. Chem. Phys. 2013

ELECTRON TRANSFER MODEL: POSITION AUTO-CORRELATION FUNCTION



$$V_{11}(R) = -R + \frac{1}{2}R^2$$

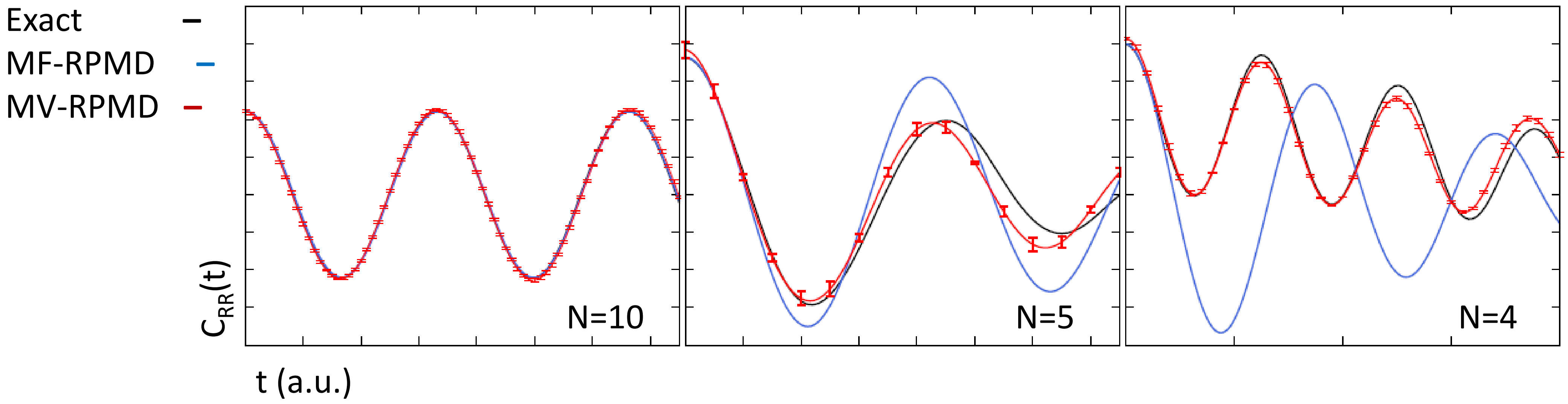
$$V_{22}(R) = R + \frac{1}{2}R^2$$

$$V_{12} = \Delta$$

Strong coupling
$\beta V_{12} = 10$

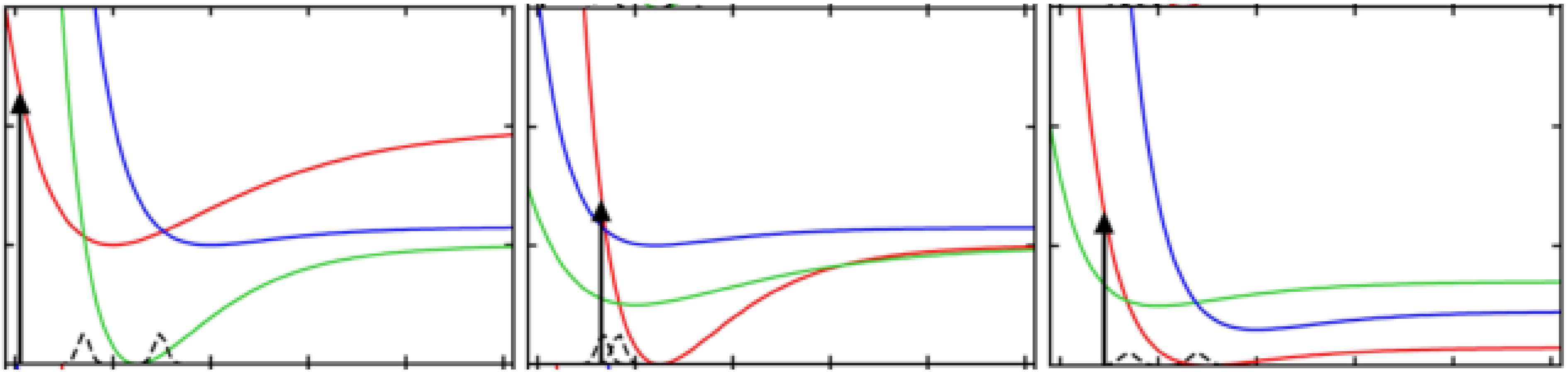
Moderate coupling
$\beta V_{12} = 1$

Weak coupling
$\beta V_{12} = 0.1$



N. Ananth, J. Chem. Phys. (2013)

MV-RPMD APPLICATION: ULTRAFAST PHOTO-INDUCED DISSOCIATION



E. Coronado, J. Xing, and W. H. Miller, Chem. Phys. Lett. (2001)

Potential Energy Surfaces

$$V_i = De_i\left(1 - e^{-\beta_i(R-Re_i)}\right)^2 + c_i$$

Coupling between surfaces:

$$V_{ij} = A_{ij}e^{-a_{ij}\left(R-R_{ij}\right)^2}$$

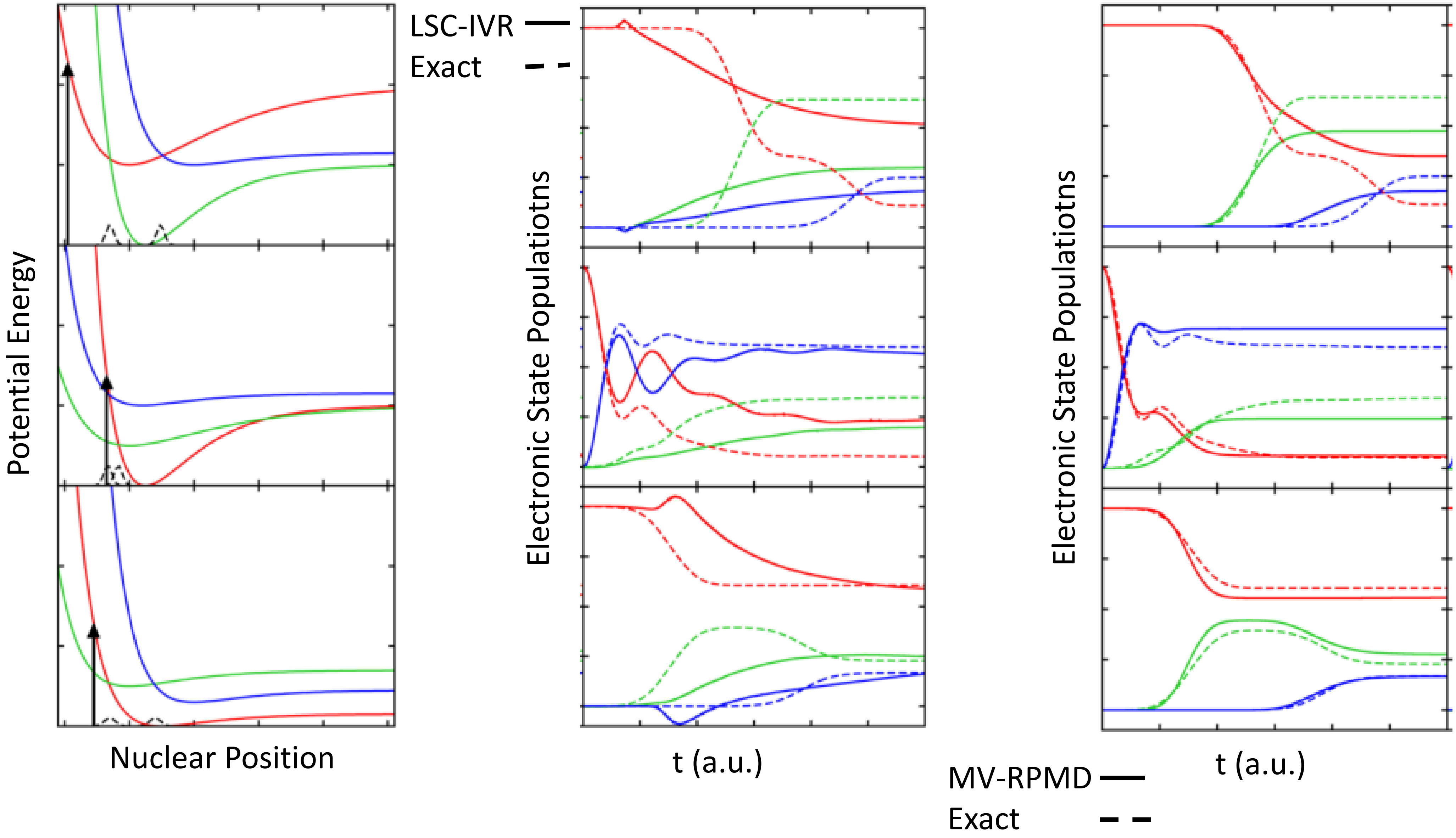
Deriving State Population Estimators

$P_n^{\mathrm{SC}} = \frac{1}{2N}\sum_\alpha([x_\alpha]_n^2 + [p_\alpha]_n^2 - 1)$ or $P_n^{\mathrm{W}} = \frac{1}{N}\sum_\alpha([x_\alpha]_n^2 + [p_\alpha]_n^2 - \frac{1}{2})\, e^{-\boldsymbol{x}_\alpha^T\cdot\boldsymbol{x}_\alpha + \boldsymbol{p}_\alpha^T\cdot\boldsymbol{p}_\alpha}$ or $P_n^{\beta} = \frac{[\boldsymbol{\Gamma}]_{11}}{\mathrm{Tr}[\boldsymbol{\Gamma}]}$

Initial non-equilibrium conditions: constrain $P_{\mathbf{1}}^{\mathrm{W}} = 1$ and nuclear RP = ground state wavepacket (Franck-Condon)

Dynamics employ a fictitious temperature in the MV-RPMD Hamiltonian: $kT = \Delta E$

GAS-PHASE EXCITED STATE DYNAMICS

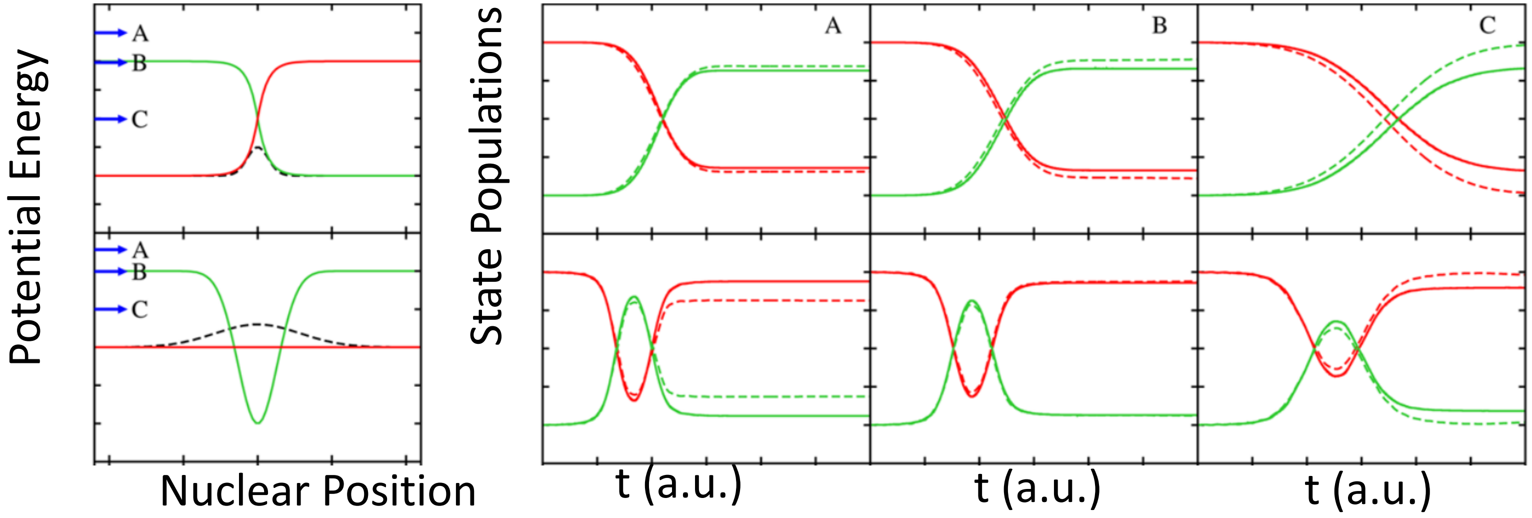


LSC-IVR's detailed balance problems = zero-point energy leakage

J. R. Duke and N. Ananth, J. Phys. Chem. Lett. (2015).

MV-RPMD APPLICATIONS

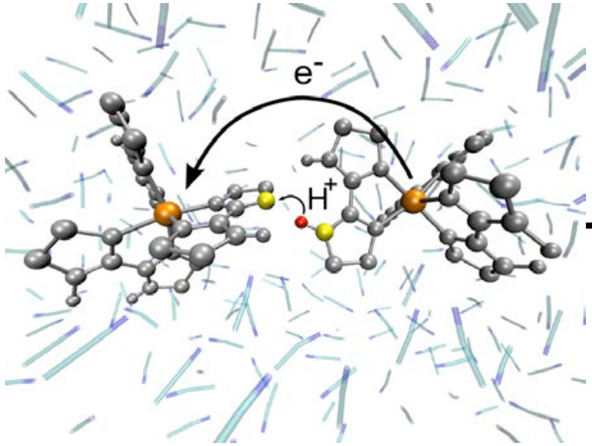
Gas phase scattering models (Tully) exploring different regimes of coupled electron-nuclear dynamics



Duke and Ananth, J. Phys. Chem. Lett. (2015)

Jessica R. Duke

Condensed Phase Proton Coupled Electron Transfer:



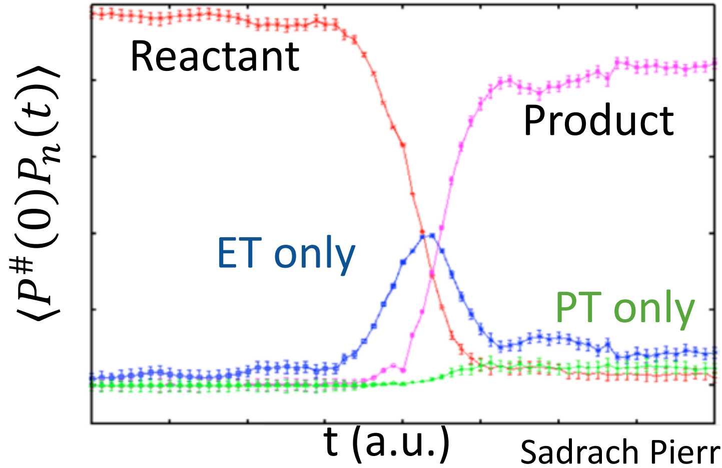
4 Electron/Proton States

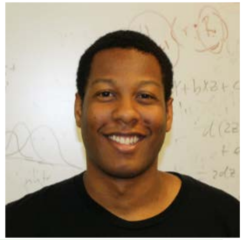
1 Solvent Coordinate

Thermal bath (24 modes)

N=10 beads

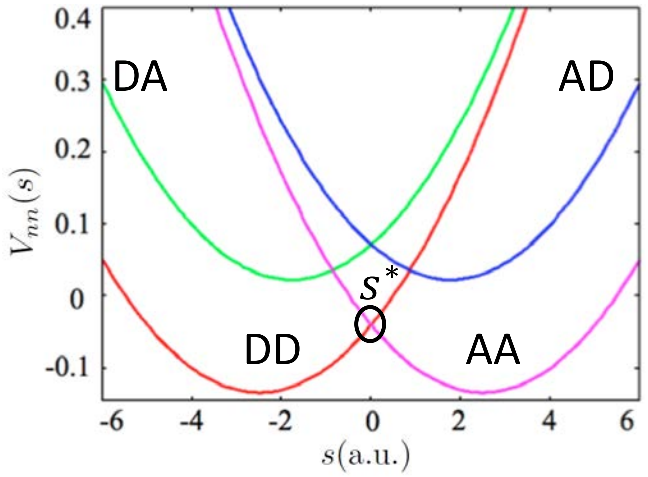
$\beta = 300\text{K}$





Sadrach Pierre

INVESTIGATING THE MECHANISMS OF PCET: AN MV-RPMD APPLICATION



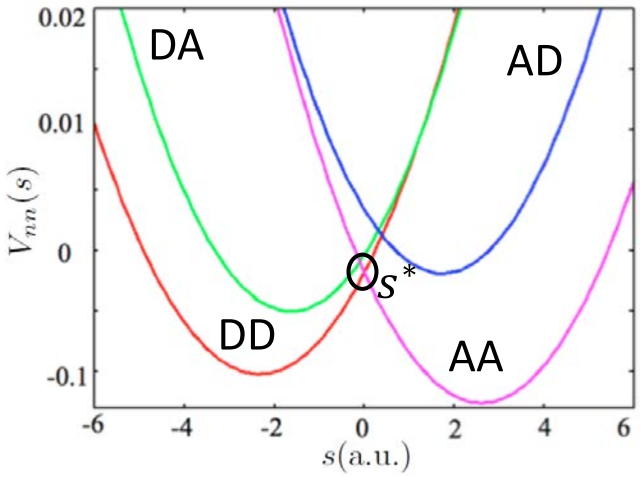
Initial Non-Equilibrium Conditions

System constrained such that $V_{DD} = V_{AA}$

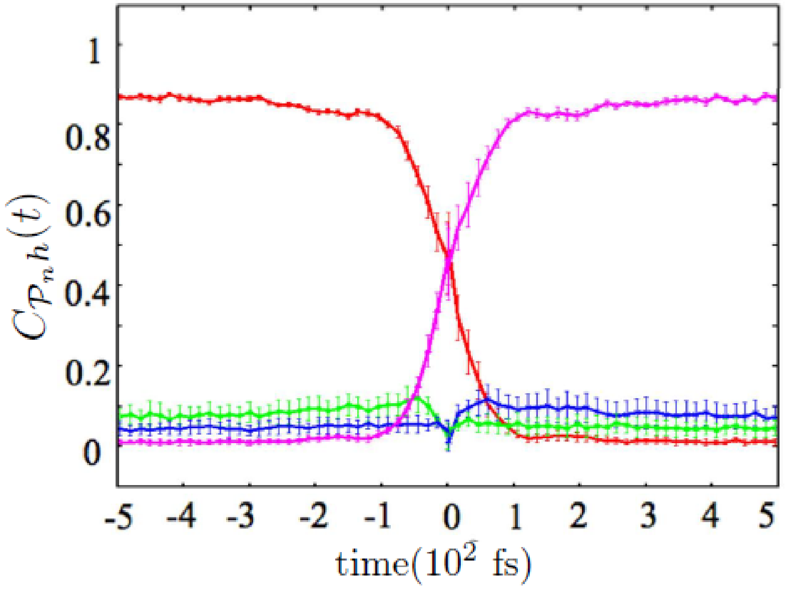
$\Rightarrow$ solvent centroid $\bar{s} = s^*$

and state populations

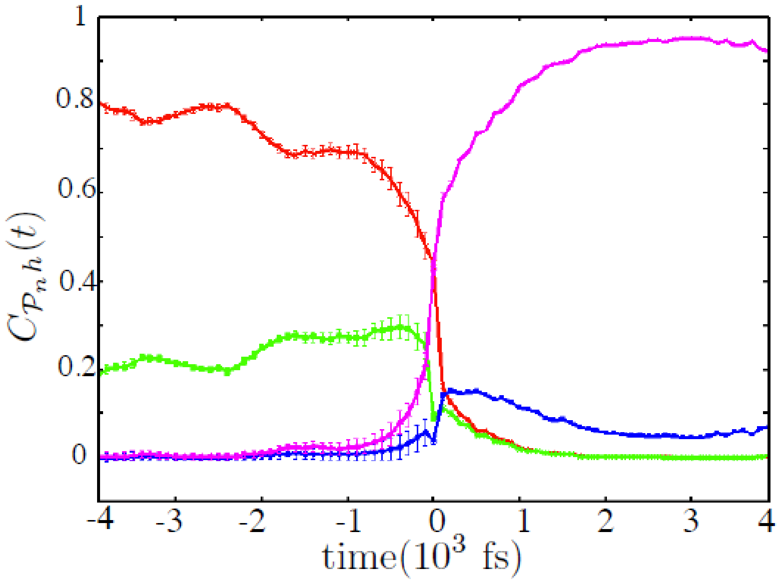
$$P_{AA} = P_{DD} = 0.5, \quad P_{AD} = P_{DA} = 0$$



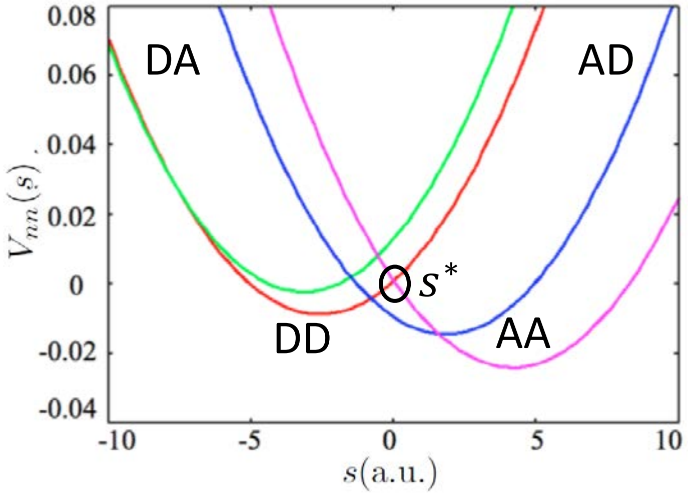
Concerted PCET



Sequential PCET – PT followed by ET



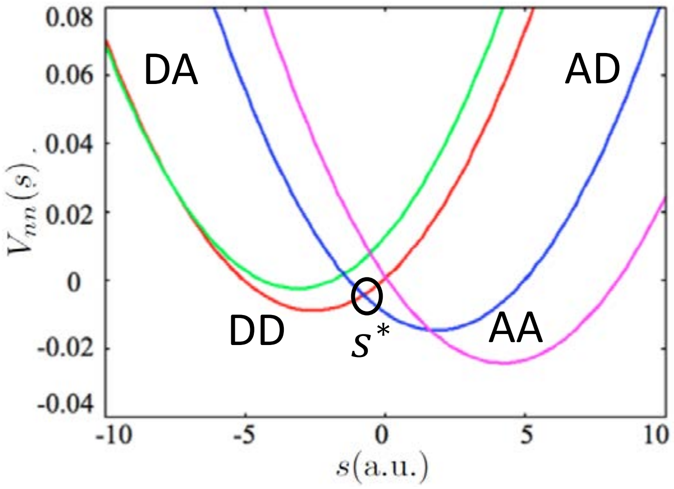
INVESTIGATING THE MECHANISMS OF PCET: AN MV-RPMD APPLICATION



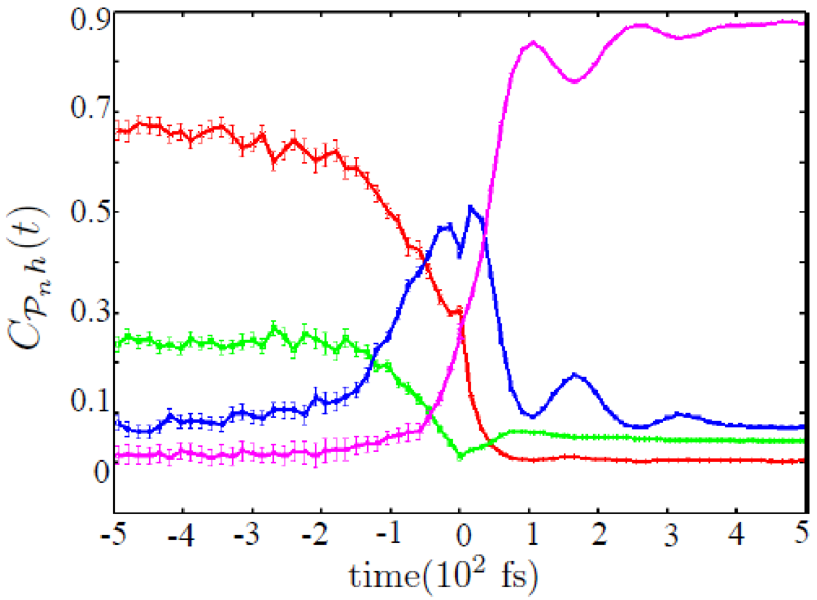
Initialized such that $V_{DD} = V_{AA}$

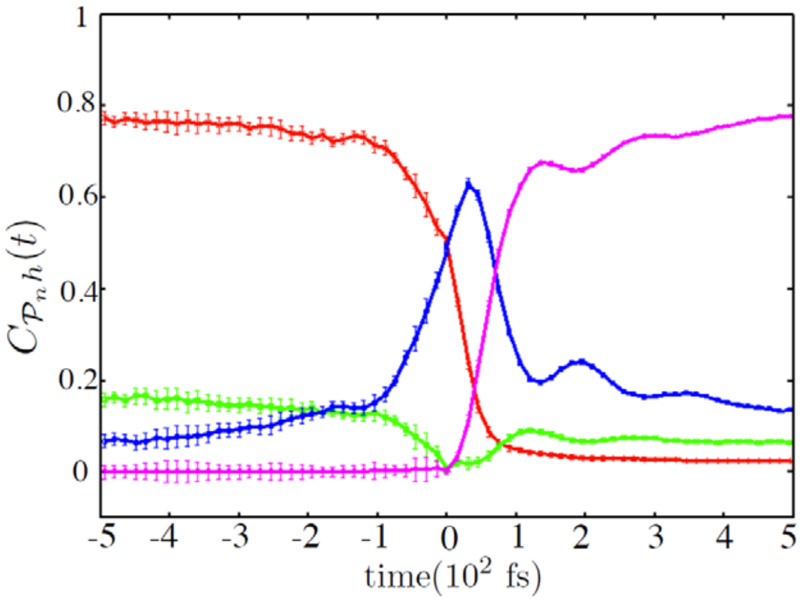
Sequential PCET

ET followed by PT



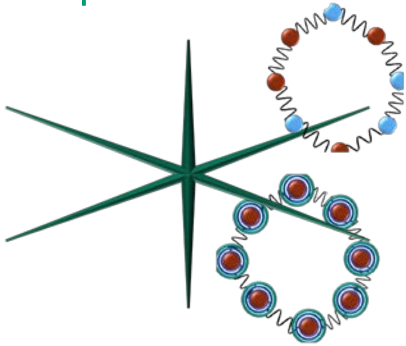
Initialized such that $V_{DD} = V_{AD}$





SUMMARY

We have a general path-integral based framework to simulate condensed phase charge and energy transfer



Dynamics that preserve detailed balance

Uniform Dynamic Framework

Multi-electron, multi-state processes + inverted regime

Incorporate tunneling and zero-point energy

Simulating excited electronic state dynamics

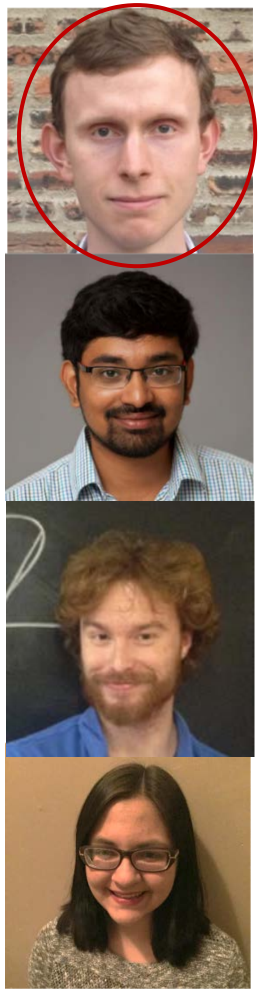
Computationally efficient: employs classical MD trajectories

Moving Forward:

- Exact quantum propagator in Mapping Variables — Hele and Ananth, Faraday Discussion on Reaction Rate Theory (2016)
- Establish a derivation for MV-RPMD from first principles
- Interfacing with MD Software for Atomistic Simulations

Cornell University
Chemistry and Chemical Biology

ACKNOWLEDGEMENTS



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DEPARTMENT OF ENERGY UNITED STATES OF AMERICA

DEPARTMENT OF DEFENSE UNITED STATES OF AMERICA

ALFRED P. SLOAN FOUNDATION 1934

RESEARCH CORPORATION for SCIENCE ADVANCEMENT

Collaborators: Luis Campos and Xiaoyang Zhu (Columbia University), Matt Sfeir (Brookhaven National Lab), Roald Hoffmann (Cornell University)