Charge Transfer and Charge Transport in Photoactivated Systems

Developing Electron-Correlated Methods for Excited State Structure and Dynamics in the NWChem Software Suite

SciDAC Report – Truhlar group, Feb. 10, 2016

Slides 2 and 3: highlight slides

Slides 4–17: presentation slides:

> Slides 4–14: electronically excited states, photochemical simulation, diabatization and diabatic potential energy surfaces

> Slides 15–17: work to make ANT a top-of-the line code with new methods for electronically nonadiabatic dynamics that can be included in *NWChem*

Potential Energy Surfaces for Photodissociation of Thioanisole
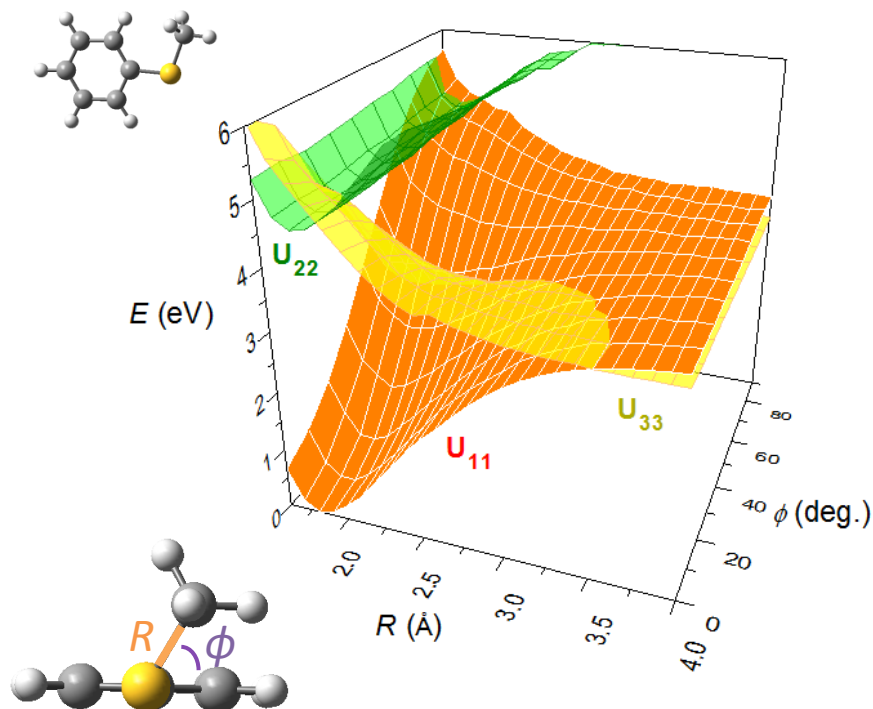
Diabatic potential energy surfaces along the two reactive coordinates, R (S-CH$_3$ bond stretch) and ϕ (C-C-S-C torsion) with other coordinates fixed at their values for the ground-state equilibrium geometry.

S. L. Li, X. Xu, C. E. Hoyer, D. G. Truhlar,
    J. Phys. Chem. Lett. 6, 3352 (2015).
S. Li, D. G. Truhlar, to be published.

Scientific achievement

We developed a 3x3 coupled diabatic potential energy surface matrix in 42 dimensions for the $C_6H_5SCH_3 \rightarrow C_6H_5S\cdot + \cdot CH_3$ photodissociation reaction.

Significance and Impact

Non-adiabatic molecular dynamics simulations are now feasible for studying the detailed mechanism of the photoreaction.

Research Details

– Analytic diabatic potential and coupling functions were fitted to ab initio data with dynamic electron correlation. (XMC-QDPT)

– A multi-level scheme, called Anchor Points Reactive Potential, enabled the construction of potential functions and couplings for high-dimensional systems by treating reactive coordinates globally and other coordinates by system-specific, reaction-coordinate-specific MM.

U.S. DEPARTMENT OF ENERGY | Office of Science

ANT (Adiabatic and Nonadiabatic Trajectories) Program

Major Capabilities include:

Treatment of electronically nonadiabatic processes
- Coherent switches with decay of mixing (CSDM)
- Improved surface hopping methods
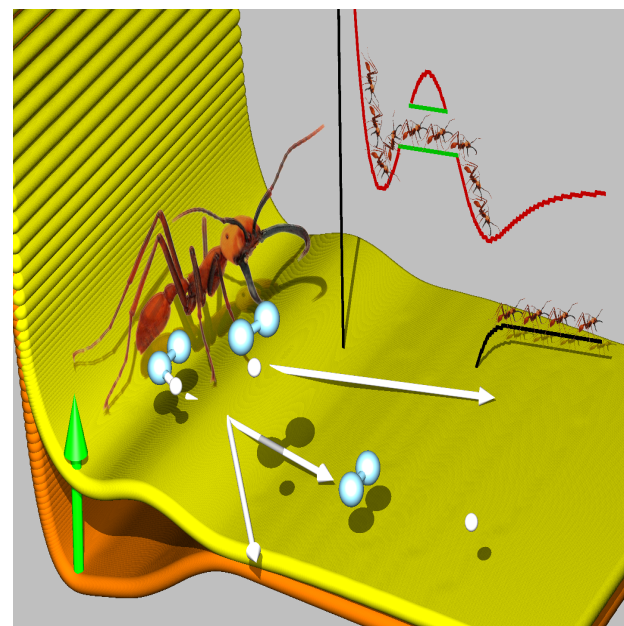- Semiclassical Ehrenfest method

Army Ants Tunneling methods
- Treats unimolecular tunneling – electronically adiabatic or nonadiabatic
- Tunneling paths defined by a valence internal coordinate or a combination of two stretch coordinates

Direct dynamics
- Interfaces to *Gaussian09*, *Molpro*, *MOPAC-mn*

Benchmarking Multiconfiguration Pair-Density Functional Theory on Excited States

Time-dependent Kohn-Sham DFT is the most practical method for excitation energies of complex systems, but with conventional functionals, TD-KS-DFT *performs poorly on Rydberg and charge-transfer excitation energies.*

Multiconfiguration pair-density functional theory (MC-PDFT):

- based the density, kinetic energy, and on-top pair density of a multiconfiguration self-consistent field (MCSCF) calculation.
- treats open-shell systems and bond breaking with right spatial and spin symmetry.

Rydberg Excitations

Mean unsigned error (in eV)
of 8 atomic Rydberg excitation energies
with d-aug-cc-pVQZ basis

TD-KS-DFT/PBE	2.5
/PBE0	1.5
MC-PDFT/tPBE	0.4

Charge-Transfer Excitations

Lowest charge-transfer at
excitation energy (eV)
of $NH_3 \bullet \bullet \bullet F_2$ at a separation of 6 Å

|	
TD-KS-DFT/PBE	0.1
/PBE0	2.8
MC-PDFT/tPBE	8.3
average of CASPT2 and SAC-CI	8.6

References on next slide.

Benchmarking Multiconfiguration Pair-Density Functional Theory on Excited States

To treat charge transfer excitations in dynamical processes, one usually needs a consistent treatment of valence, Rydberg, and charge transfer excitations.
The performance of MC-PDFT with first-generation functionals for spectroscopy is already competitive in performance with a frequently used, more expensive method (CASPT2).

## 23 Electronic Excitations

- *Valence*
- *Rydberg*
- *Charge Transfer (CT)*

	CASPT2	tPBE
Average Mean Unsigned Error	0.21 eV	0.20 eV
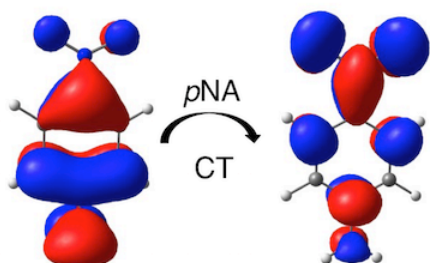
a first generational on-top functional obtained from the PBE exchange-correlation functional by a simple translation

G. Li Manni, R. K. Carlson, S. Luo, D. Ma, J. Olsen, D. G. Truhlar, L. Gagliardi, J. Chem. Theory Comput. 10, 3669 (2014).
F. Aquilante et al., J. Comp. Chem. 37, 506 (2015).
C. E. Hoyer, L. Gagliardi, D. G. Truhlar, J. Phys. Chem. Lett. 6, 4184 (2015).
C. E. Hoyer, S. Ghosh, D. G. Truhlar, L. Gagliardi, J. Phys. Chem. Lett. **7**, 586 (2016).

A strategic choice in electronically nonadiabatic dynamics

- Direct dynamics:
  - High cost usually means
    - reduced dimensionality
    - insufficient sampling
    - lack of dynamic correlation

- Dynamics with fitted surfaces in adiabatic representation:
  - adiabatic surfaces have cuspidal ridges
    ⇒ essentially impossible to fit
 - couplings in adiabatic representation are singular
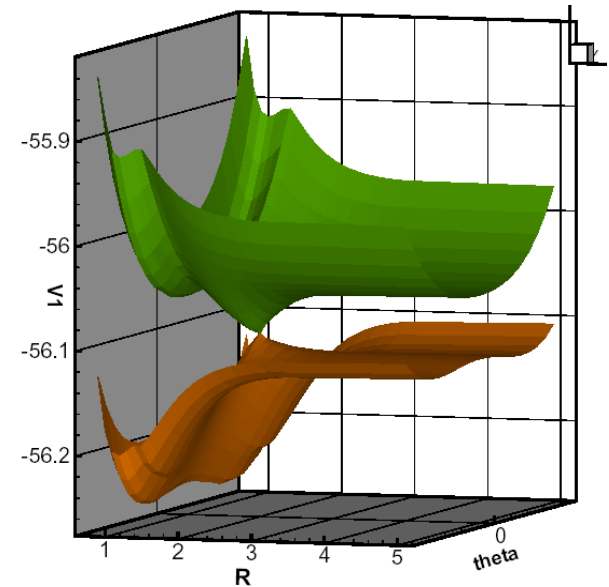
Solution to these problems:
use fitted surfaces and couplings in a diabatic representation
  - surfaces are smooth: can be fit ⇒ full dimensionality possible
  - couplings are scalar ⇒ easier to work with
  - can be used with the state-of-the-art electronic structure methods including dynamic correlation
  - affordable ⇒ sufficient sampling

C. Hoyer, K. Parker, G. Song, S. Mielke, O. Tishchenko, R. Mean-Pañeda, L. Gagliardi, D. G. Truhlar, work in progress at University of Minnesota

Photodissociation of Phenol: Full-Dimensional Multi-State Simulations including Tunneling
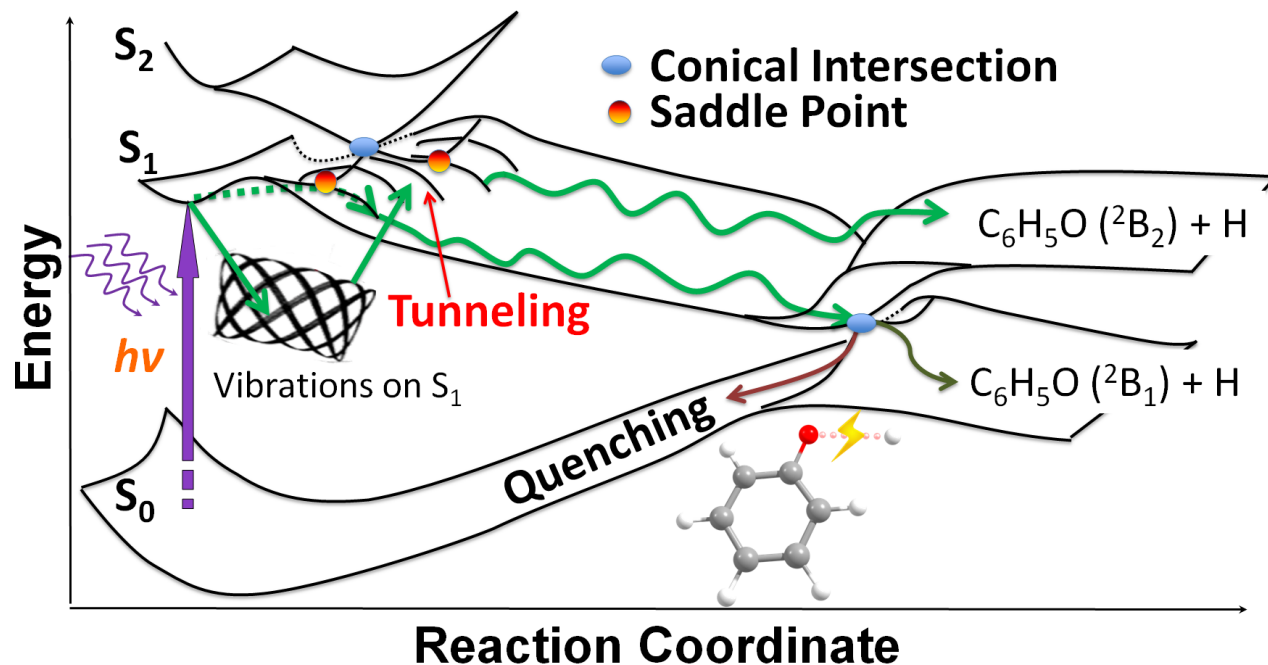
Work combines four state-of-the-art methods in a complementary way:
- fourfold way diabatization based on MC-QDPT
- anchor points reactive potentials for fitting surfaces of complex systems
- coherent switches with decay of mixing for multi-state trajectories
- army ants tunneling

# *Full-dimensional coupled potential energy surfaces for thioanisole photodissociation*

- Analytic potential energy surfaces (PESs) and state couplings of the ground and two lowest-lying singlet excited states are constructed, including all 42 internal degrees of freedom.

- Wide range of geometries from the Franck-Condon region to the breaking of the S-CH$_3$ bond is covered.
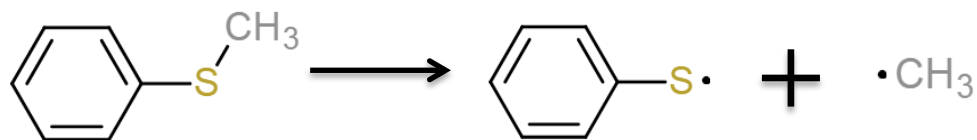
- It is the largest-ever photochemical system treated with full-dimensional PESs based on electronic structure calculations including dynamic electron correlation.

- Fourfold-way diabatization is nonintuitive in this case but produces smooth, cusp-free diabatic potentials and couplings that are easy to fit

- The PESs and couplings are suitable for study of topography of the potential energy landscape and of non-adiabatic molecular dynamics simulations.

Full-dimensional coupled potential energy surfaces for thioanisole photodissociation

- *Internal coordinates:* $R + \phi + \mathbf{Q}$

  reactive coordinates — other 40 degrees of freedom
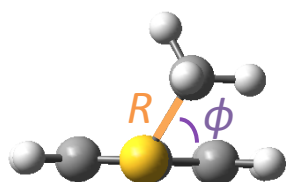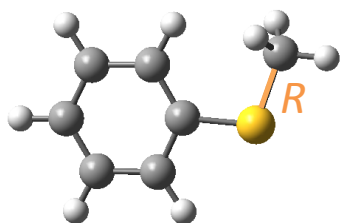
- *Full-dimensional diabatic PESs and couplings (XMC-QDPT and 4-fold way/model space diabatization except TD-KS-DFT for* $U_{ii}^{[3]}$ *)*

$$U_{ij}(R,\phi,\mathbf{Q}) = U_{ij}^{[1]}(R,\phi \,|\, \mathbf{Q}_{\mathrm{ref}}) + U_{ij}^{[3]}(\mathbf{Q} \,|\, R,\phi)$$

Fitted with general analytic function

Fitted with MM-like analytic function to local expansion about anchor points [TD-KS-DFT for *i=j*]

weighted average of nearby anchor points at geometries between anchor points
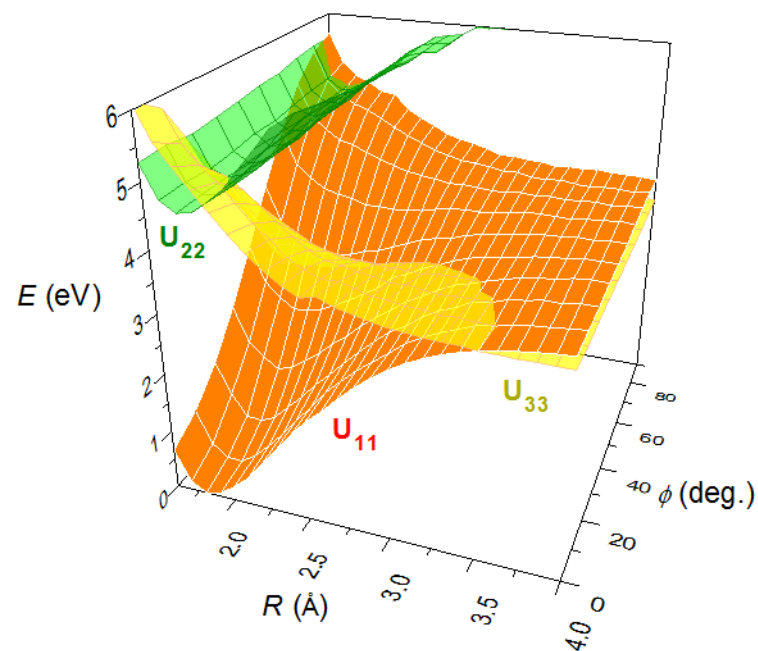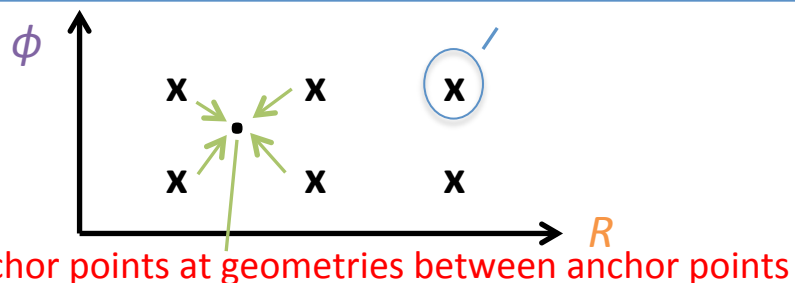
S. L. Li, D. G. Truhlar, M. W. Schmidt, M. S. Gordon, J. Chem.l Phys. 142, 064106 (2015).
S. L. Li, X. Xu, C. E. Hoyer, D. G. Truhlar, J. Phys. Chem. Lett. 6, 3352-3359 (2015).
S. L. Li, D. G. Truhlar, work in progress at University of Minnesota

- **1st step:** Diabatic representation obtained by fourfold way from electronic structure calculations by MC-QDPT.

- **2nd step:** The full-dimensional representation of the three diabatic states U_{11}, U_{22}, and U_{33} are fit using a permutationally invariant polynomial basis.

- **Challenging 3rd step:** The full-dimensional global representation of the diabatic coupling terms U_{12}, U_{13}, and U_{23} is more challenging because their signs depend on permutations and inversions.
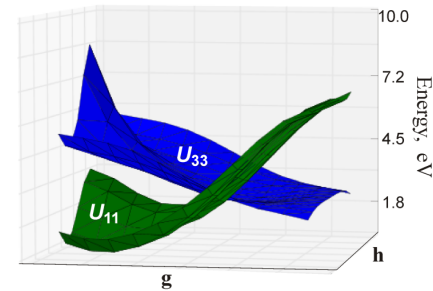
  We are developing a strategy for fitting the diabatic potential energy matrix elements as functions of internal geometry in a basis with definite symmetry under the permutation–inversion group.

H. Nakamura, D. G. Truhlar, J. Chem. Phys. **117**, 5576 (2002).
I. Kryven, A. Oliveira Filho, G. Song, S. L. Mielke, R. Meana-Pañeda, B. Fu, J. Bowman, D. G. Truhlar, work in progress at University of Minnesota in collaboration with Emory University and Universidade de São Paolo

Property-Based Diabatization: A New Method and Software

Property-based diabatization is a promising alternative to the orbital-based fourfold way since it is more automatable.

We developed two methods:

DQ method computes diabatic states by maximizing:

$$f_{DQ} = \sum_{A=1}^{N} \left(|\langle \phi_A | \boldsymbol{\mu} | \phi_A \rangle|^2 + \sum_{j=1}^{N_Q} \alpha_j |\langle \phi_A | Q^{(j)} | \phi_A \rangle|^2 \right)$$

- ϕ_A — diabatic state
- $\boldsymbol{\mu}$ — dipole operator
- Q — quadrupole operator
- α — parameter
- j — choice of origin

DQΦ method computes diabatic states by maximizing:

$$f_{DQ\Phi} = f_{DQ} + \sum_{A=1}^{N} \left(\sum_{k=1}^{N_\Phi} \beta_k |\langle \phi_A | \Phi^{(k)} | \phi_A \rangle|^2 \right)$$

- ϕ_A — diabatic state
- Φ — electrostatic potential operator
- β — parameter
- k — choice of origin

DQ and DQΦ can be used with any electronic structure method and are path independent.

Software: DQΦpac performs DQ and DQΦ using Q-Chem or Molpro properties.
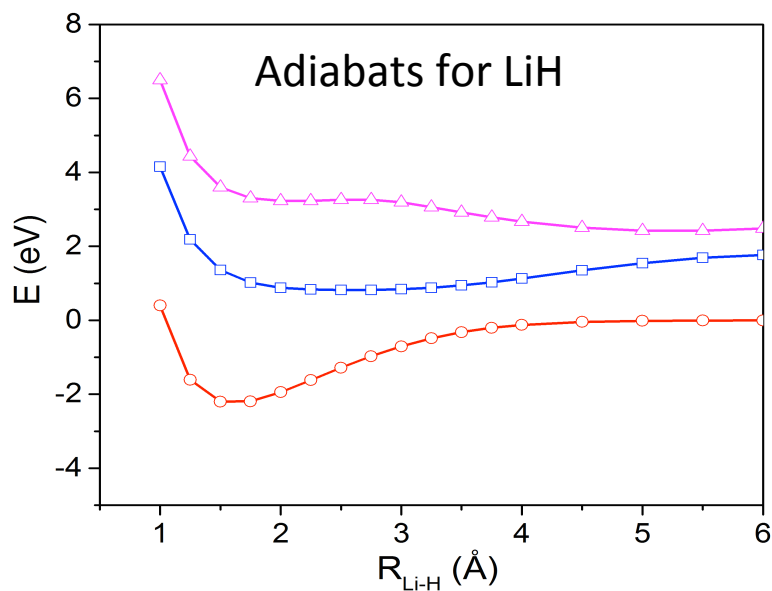
C. Hoyer, X. Xu, D. Ma, L. Gagliardi, D. G. Truhlar, J. Chem. Phys. 141, 114104 (2014).
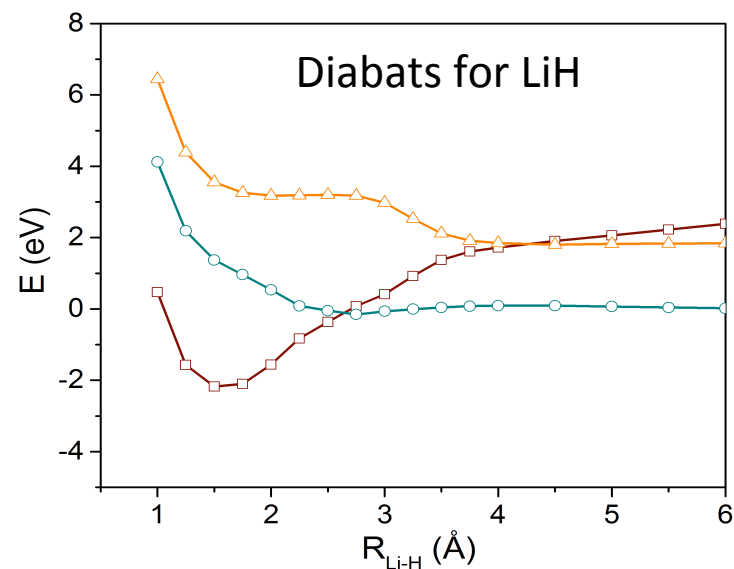C. Hoyer, K. Parker, L. Gagliardi, and D. G. Truhlar, J. Chem. Phys., submitted.
C. Hoyer, L. Gagliardi, D. G. Truhlar, DQΦpac, v. 1.0. comp.chem.umn.edu/DQPhipac

Property-Based Diabatization: Illustration

Other successful applications: phenol, HCl, H_2 dimer, and two more on next slide: ozone and the reaction Li + HF $\rightarrow$ LiF + H.

C. Hoyer, X. Xu, D. Ma, L. Gagliardi, D. G. Truhlar, J. Chem. Phys. 141, 114104 (2014).

Property-Based Diabatization: More examples and Challenge

Li + HF ➡ LiF + H

Asymmetrical stretch of O_3
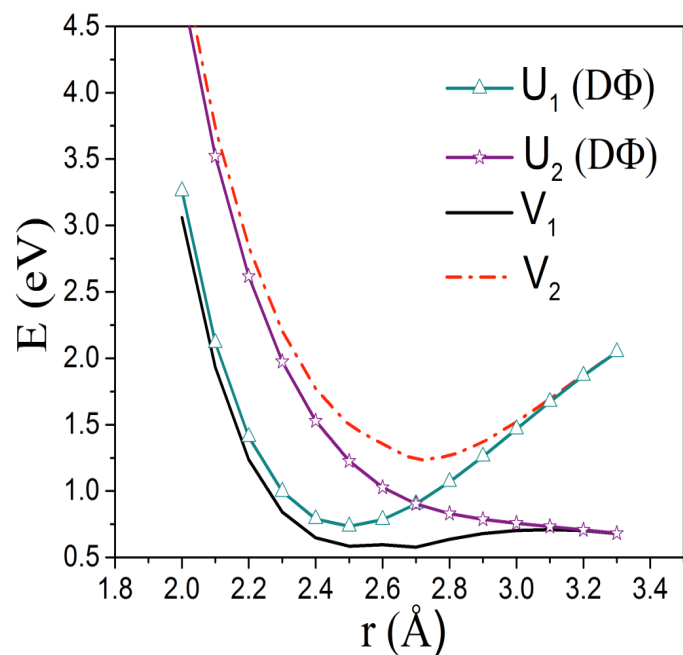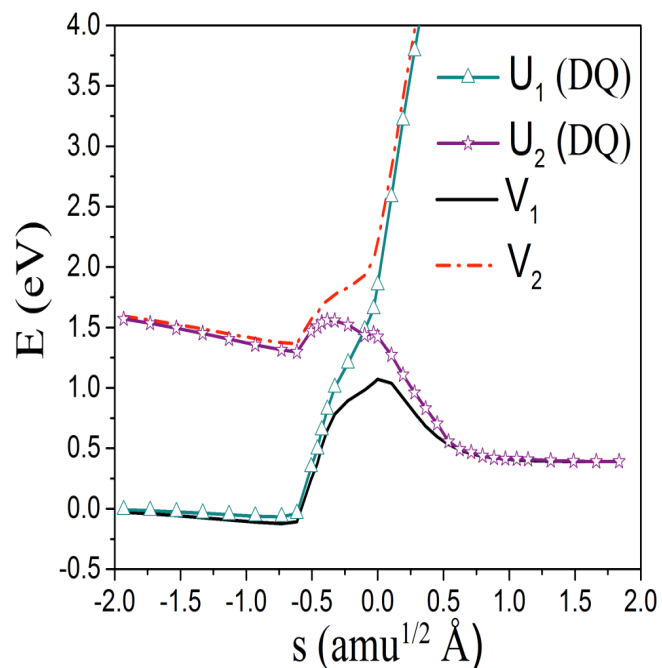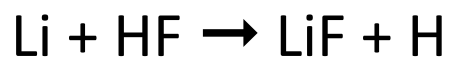
- The diabats are smooth and approach the adiabatic curves away from the crossing.

C. Hoyer, K. Parker, L. Gagliardi, D. G. Truhlar, J. Chem. Phys., submitted.

Current computational challenge:
Interfacing DQΦpac with *NWChem* and other electronic structure packages

Adiabatic and Nonadiabatic Trajectories: ANT Program

ANT version 2016 will be released in mid-Feb. 2016.

ANT version 2016–2 is under development.

http://comp.chem.umn.edu/ant/

Major Development Goal of ANT project:

Incorporation of new capabilities in NWChem

Specifics planned for version 2016-2 or later:

More efficient rare event sampling

More efficient tunneling treatment

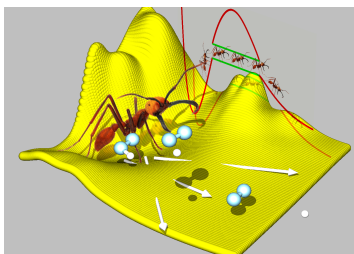Improved treatment of zero point energy

Improved options for initial conditions

Parallelization

Direct dynamics interface with *NWChem*

S. L. Mielke, R. Meana-Pañeda, N. Govind, and D. G. Truhlar, work in progress.

Work is a collaboration of University of Minnesota and PNNL.

Including Tunneling in Semiclassical Simulations

The army ants tunneling method has been developed to include tunneling in classical trajectories for molecular dynamics simulations.

- It uses internal coordinates to define the tunneling path.


Stretching   Bending   Torsion
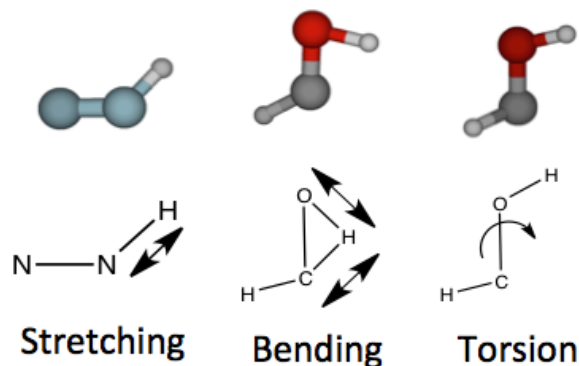
- The method allows one to explore regions of the phase space reached only by tunneling.

- It is very efficient, the full calculations on an ensemble can even be less computationally expensive than calculating the reaction rate without tunneling.

Including Tunneling in Semiclassical Simulations (continued)

- The tunneling events are followed about half the time, but they are weighted to ensure that the result converges to the same result as if paths were followed according to their probability.

- The method has been extended to electronically nonadiabatic dynamics, where the trajectory is propagated by the semiclassical Ehrenfest method during tunneling and by coherent switches with decay of mixing between tunneling events.

tunneling through
adiabatic potential

tunneling through
self-consistent potential
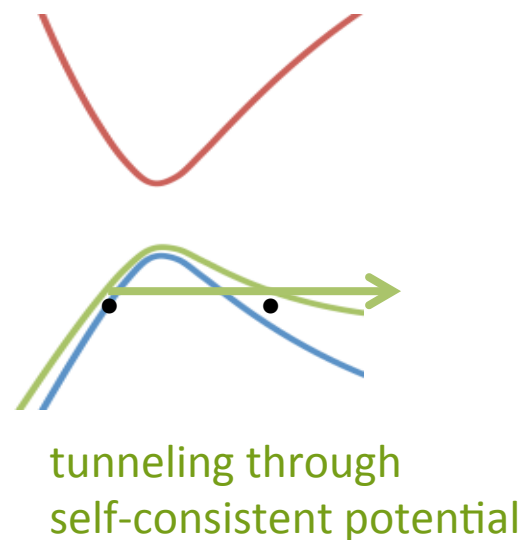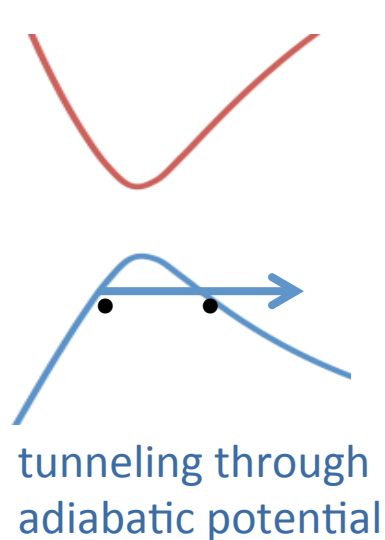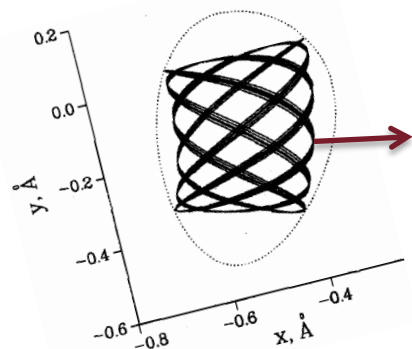
J. Zheng, R. Meana-Pañeda, and D. G. Truhlar, J. Phys. Chem. Lett. **5**, 2039-2043 (2014).
S. L. Mielke, R. Meana-Pañeda, and D. G. Truhlar, work in progress.

Work at the University of Minnesota.