

Developing Advanced Methods for Excited State Chemistry in the NWChem Software Suite

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SciDAC Team

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Don Truhlar
Today's talk will be limited to this work, some of which is in collaboration with Cramer or Gagliardi.

Bert DeJong

Niri Govind



Our work has two aspects.

In the second year we made progress in these areas:

New and improved methods

Best procedures for spin-flip

TDDFT

CIC-TDA for excited states at
conical intersections

Multi-Configuration Pair-Density
Functional Theory

Simultaneous tunneling and
nonadiabatic transitions in
molecular simulations of
photochemistry

Testing and improving methods
for diabatic representations
with applications to OH₃,
phenol, and thiosanisole

Anchor Points Reactive Potential

Implementation in user-friendly software

CM5PAC for G09

Solvation in Q-Chem

VEMGAUSS for G09

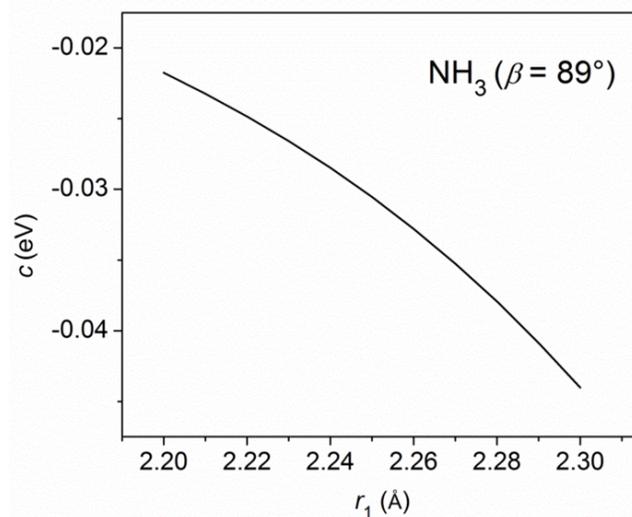
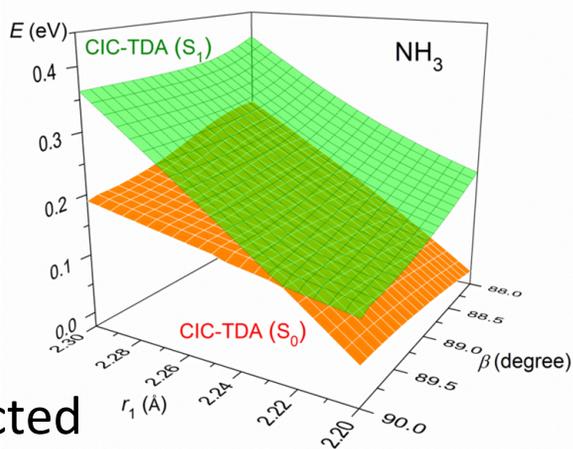
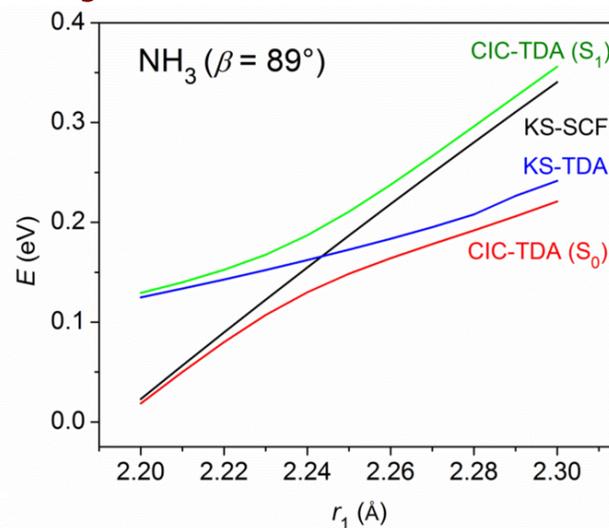
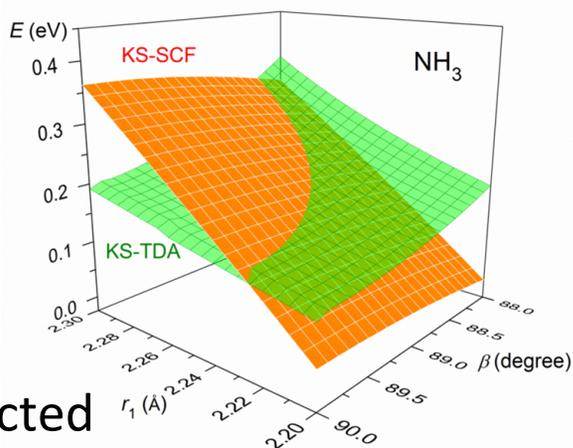
CIC-TDA in GAMESS

SMD in NWChem

TDDFT Methodology

Configuration-Interaction-Corrected
Tamm–Dancoff Approximation
(CIC-TDA)

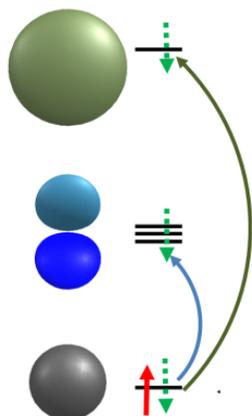
Configuration Interaction-Corrected Tamm–Dancoff Approximation: A Time-Dependent Density Functional Method with the Correct Dimensionality of Conical Intersections



S. L. Li, A. V. Marenich, X. Xu, and D. G. Truhlar,
J. Phys. Chem. Lett. **2014**, *5*, 322.

Best procedures for
spin-flip time-dependent density functional theory
(SF-TDDFT)

Optimizing TDDFT methods by predicting electronic excitation energies of closed-shell atoms



Conventional TDDFT and TDA; WFT
Collinear and noncollinear spin-flip TDDFT

- 9 schemes
 - Ex.: calculate S_2 with SF unprojected with T_1 as reference
- 3 assignment methods (by energy, occupation, or spin)

functionals:

GVWN5, PBE, B3PW91, B97-1, LRC- ω PBE, LRC- ω PBEh, ω B97X, M06-L, M06, M06-2X

3360 TDDFT spectra assigned



Mean errors (in eV) for
120 valence and 240 Rydberg excitations

	MUE	MUEV	MUER
EOM -CCSD	0.09	0.04	0.12
CASPT2	0.24	0.12	0.30
CIS	0.77	0.72	0.79
SF-CIS-best	0.89	0.78	0.95
TDHF	1.11	1.73	0.80
noncollinear spin-flip N-OA-S22:10 func'ls	0.78	1.40	0.46
collinear spin-flip C-EA-S11:10 func'ls	1.42	1.56	1.35
conventional KS-TDA:10 func'ls	0.99	0.25	1.36
KS-LR:10 func'ls	1.06	0.43	1.37

X. Xu, K. R. Yang, and D. G. Truhlar
J. Chem. Theory Comp. **2014**, *10*, 2070

Multi-Configuration
Pair-Density Functional theory
(MC-PDFT)

Multiconfigurational Pair-Density Functional Theory

Open-shell and multireference systems are an unmet challenge for KS-DFT, which often gives incorrect spatial and spin symmetries.

An MCSCF type wave function gets the correct state symmetries, but combining MCSCF with DFT has led to

double counting of dynamic correlation.

How to avoid this problem?

Calculate kinetic and Coulomb contribution to total energy from a CASSCF wave function and the exchange and correlation contribution from DFT.

$$E = V_{\text{nn}} + 2 \sum_i h_{ii} + 2 \sum_{ij} g_{ijij} + \sum_{vw} h_{vw} D_{vw} + 2 \sum_{ivw} g_{iivw} D_{vw} + \frac{1}{2} \sum_{vwxy} g_{vwxy} D_{vw} D_{xy} + E_{\text{ot}}[\rho, \Pi]$$

where we have written the functional in terms of density ρ and on-top pair density Π .

Collaboration of Gagliardi and Truhlar groups

Averaged mean absolute errors (eV)

Quantity	CASSCF	CASPT2	MC-PDFT	KS-DFT
			tGGA ^a	GGA ^b
main group atomic excitation energies	0.29	0.07	0.48	1.01
transition metal atomic excitation energies	0.41	0.26	0.23	0.21
singlet-to-singlet molecular excitation energies	1.39	0.26	0.55	0.33
bond dissociation energies	0.89	0.32	0.33	0.51
average	0.75	0.23	0.40	0.52

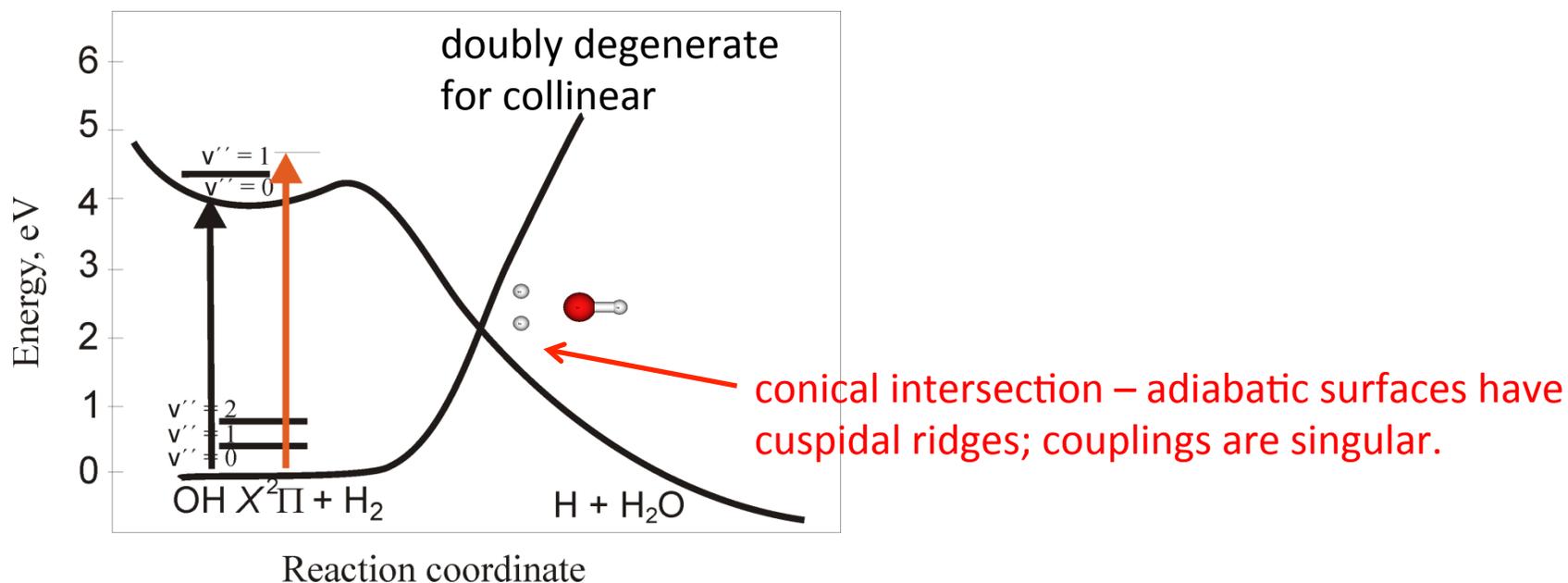
^atGGA averaged over tPBE and tBLYP

^bGGA averaged over PBE and BLYP

Photochemistry



Direct Diabatization and Fitting of Coupled Potential Energy Surfaces for the Reactive Quenching of the Excited $^2\Sigma^+$ state of OH by Molecular Hydrogen



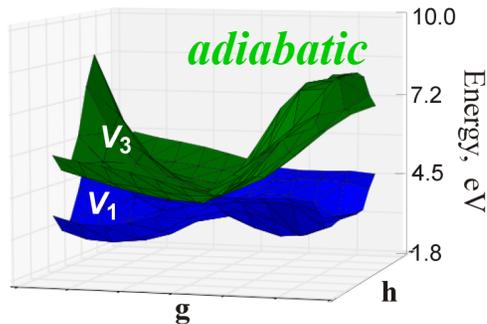
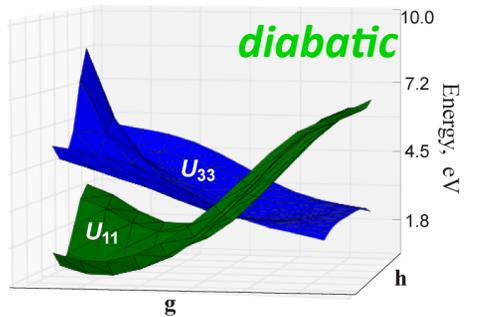
OBJECTIVE:

Use fourfold way to develop a set of three coupled full-dimensional analytic potential energy surfaces for dynamics simulations

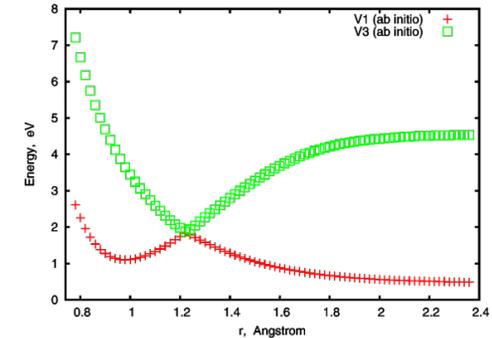
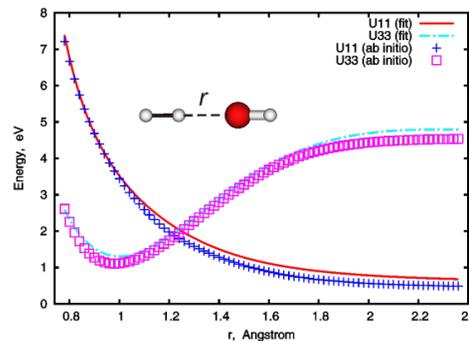
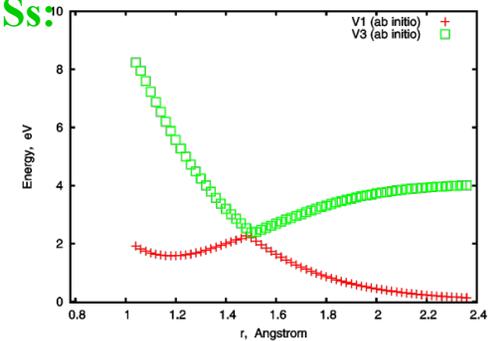
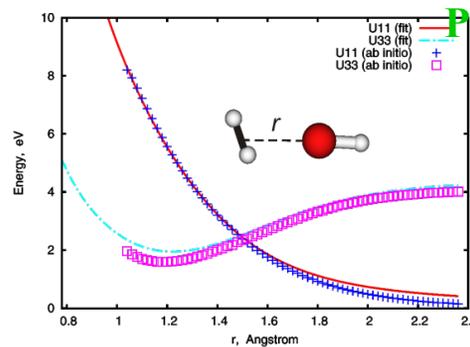
Direct Diabatization and Fitting of Coupled Potential Energy Surfaces for the Reactive Quenching of the Excited $^2\Sigma^+$ state of OH by Molecular Hydrogen

Fourfold way diabatization Nakamura, Truhlar, JCP (2001-3) , Xu, Yang, Truhlar, JCTC (2013).

- I. Determine (smooth) diabatic MOs (DMOs) by fourfold way (threefold density matrix functional + reference orbital term)
- II. Construct lists of dominant configurations of diabatic many-electron states
- III. Apply configurational uniformity to get diabatic state functions by maximizing the dominance of prototypes in them



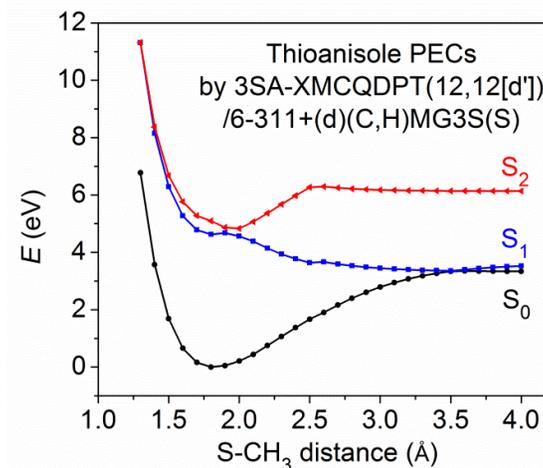
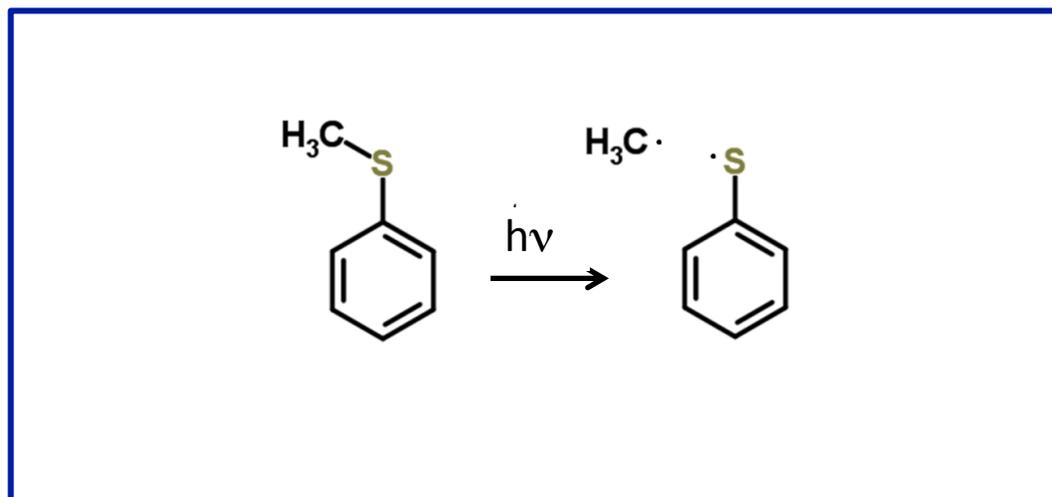
REPRESENTATIVE CUTS THROUGH FITTED



Photochemistry

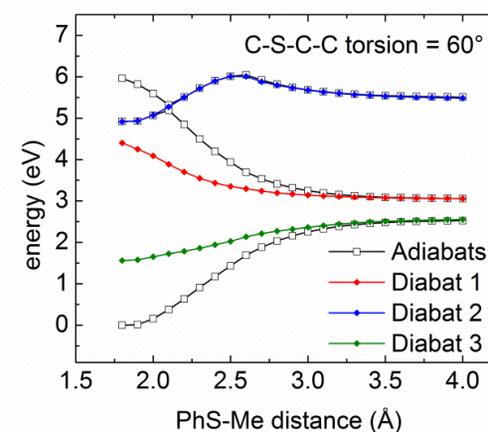
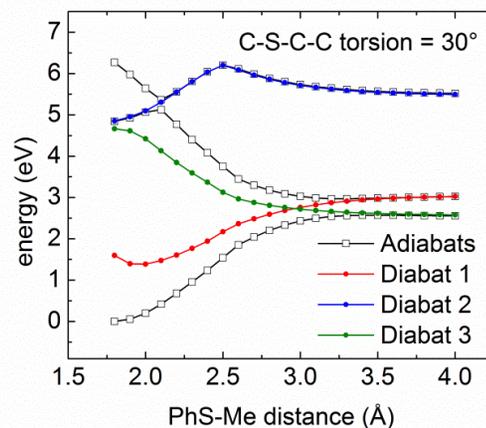
Thioanisole photodissociation

Ground and excited potential energy surfaces (PESs) of thioanisole as functions of S-CH₃ distance and C-S-C-C torsion



Adiabatic potentials vs. S-CH₃ distance (other coordinates at equilibrium values)

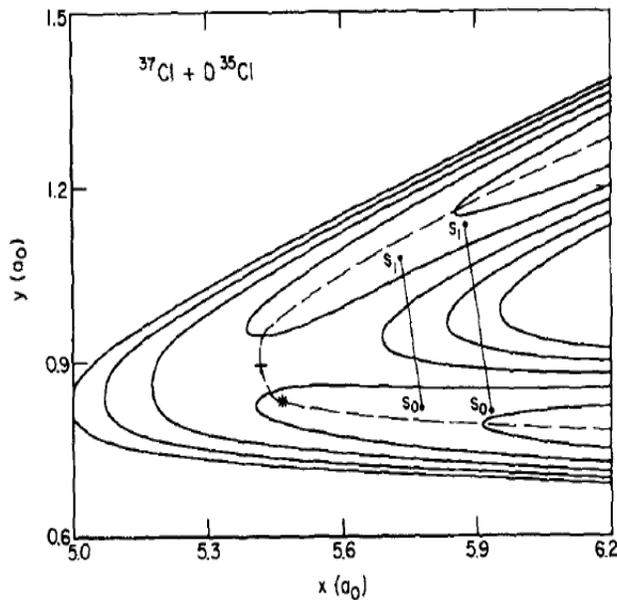
Generate CASSCF diabatic MOs by fourfold way and XMC-QDPT diabatic states by configurational uniformity.



Putting tunneling in molecular dynamics simulations

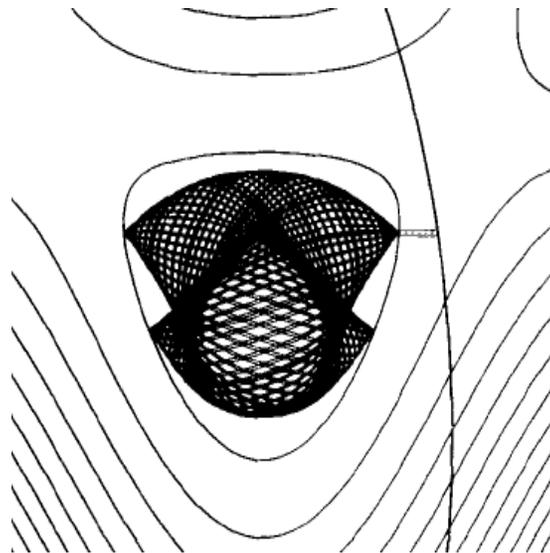
What about tunneling in molecular dynamics simulations?

Tunneling paths between caustics – background theory



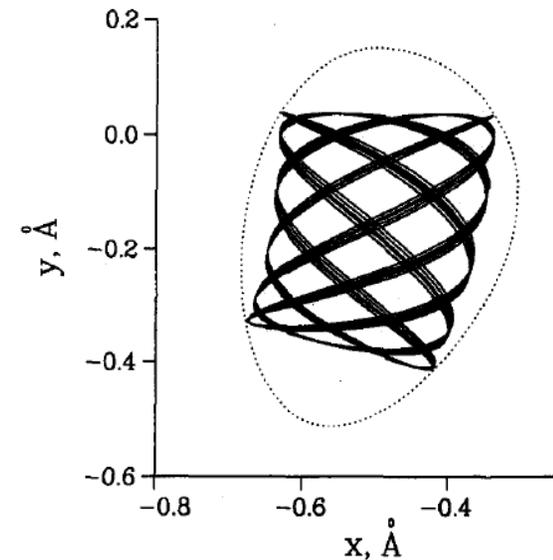
“...Tunneling for a Heavy-Light-Heavy Reaction ...,” Garrett, Truhlar, Wagner, Dunning, JCP (1983).

straight-line tunneling from one caustic to another – large-curvature tunneling



“Radiationless Transitions in a New Light,” Heller, Brown, JCP (1983).

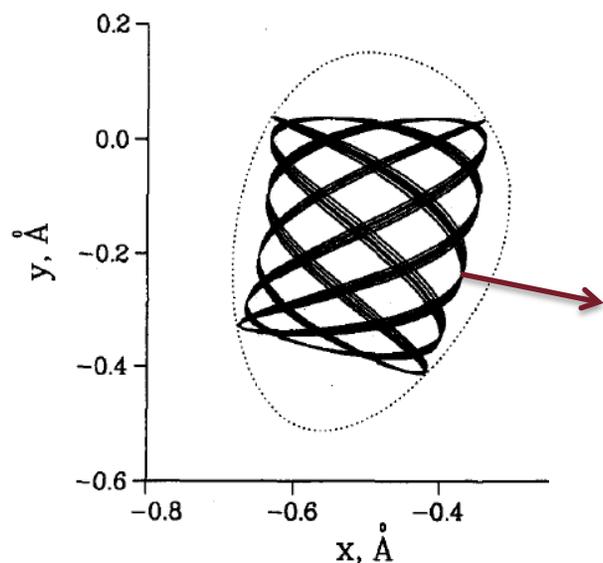
similar ideas for photochemistry



“A Semiclassical Tunneling Model for Use in Classical Trajectory Simulations,” Makri, Miller, JCP (1989).

tunneling branching for molecular dynamics

Tunneling paths added to trajectories: Why not more widely used?



Makri-Miller tunneling algorithm is based on the “anteater” algorithm.

When system reaches a turning point, tunnel along **rectilinear** mode \perp caustic with probability

$$P = \exp \left[-\frac{2}{\hbar} \int_{\text{next classically allowed region}} \mathbf{p} \cdot d\mathbf{q} \right]$$

If P is 10^{-3} , tunneling paths will rarely be selected.
Also, normal-mode tunneling path is not usually good.

Solution:

The “**army ants**” algorithm for rare events.

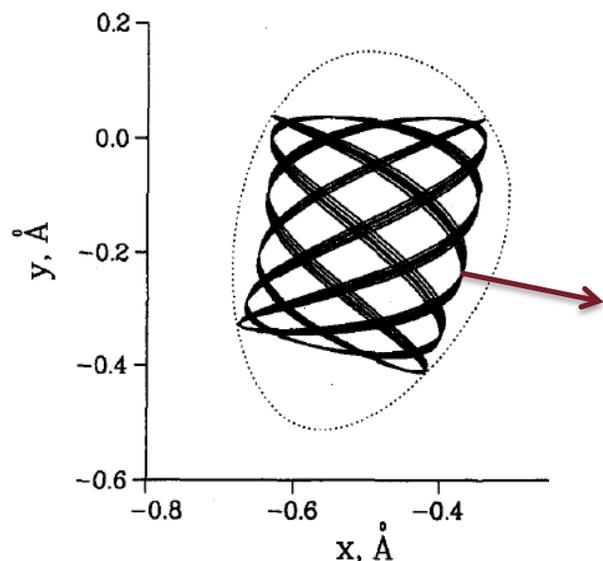
Nangia, Jasper, Miller, Truhlar, JCP (2004)

has now been extended to tunneling using **curvilinear tunneling paths**.

Zheng, Xu, Meana-Pañeda, Truhlar, Chem. Sci. (2014)

Army ants tunneling for trajectories

Zheng, Xu, Meana-Pañeda, Truhlar, Chem. Sci. (2014)



When system reaches a turning point,
*calculate tunneling for
curvilinear internal-coordinate paths.*

The trajectories have weights. Based on two random numbers, we follow successful tunneling events half the time, but give them appropriate weight.

- We can get good good statistics **even if prob. tun. $\ll 0.000001$.**
- We can explore regions of space reached only by tunneling.

We have combined this with the coherent switches with the decay of mixing algorithm (based on a *time-dependent self-consistent-field potential*) to treat **simultaneous tunneling and coherent surface switching** (more accurate than surface hopping).

Army Ants Reactive Potential

Anchor Points Reactive Potential (APRP)

K. Yang, X. Xu, and D. G. Truhlar, JCTC **10**, 924 (2014).

K. Yang, X. Xu, J. Zheng, D. Truhlar, Chem. Sci., submitted 7/1/14.

APRP : global fitting of potentials

::

QM/MM : QM



actually system-specific-MM

Next slide:

33-dim. potential surfaces for of phenol $\xrightarrow{h\nu}$ phenoxyl + H.

(fit in diabatic representation)

Anchor points reactive potential

Partition internal coordinates into three groups:

Reactive coordinates: \mathbf{q} ← OH stretch

Secondary coordinates: \mathbf{s} ← C-O-H and C-O-O-H angles

Tertiary coordinates: \mathbf{Q} ← all others

$$V = V^{[1]}(\mathbf{q}) + V^{[2]}(\mathbf{s} | \mathbf{q}) + V^{[3]}(\mathbf{Q} | \mathbf{q})$$

General functional form
to describe coordinates
that are active during
bond dissociations.

MM-like terms for spectator
degrees of freedom,
*but molecule-specific MM,
in fact, anchor-point-specific MM*

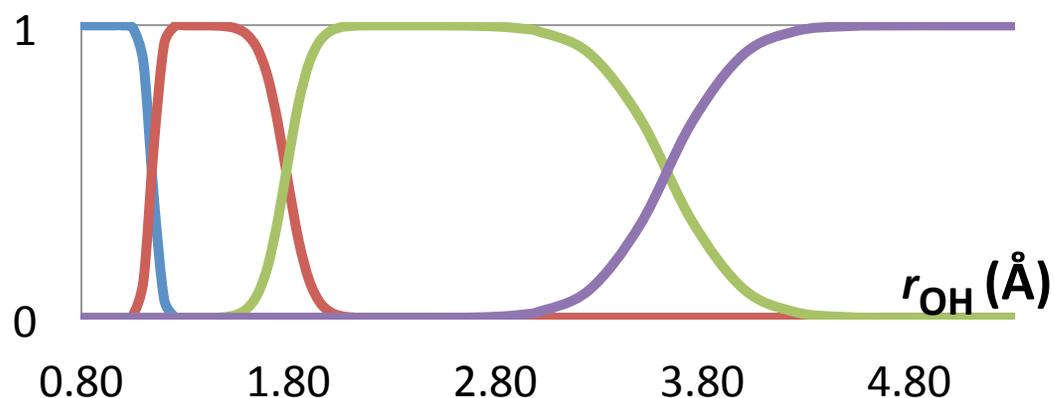
Anchor points reactive potential

$$U_i^{[3]} = \sum_{\substack{\text{anchor points} \\ a=1}}^5 U_i^{[a]}(\mathbf{Q}^{[a]}) T_i^{[a]}(r)$$

Quadratic functions of internal coordinates with good global behavior:

$$(r - r_e)/r$$
$$\cos \theta - \cos \theta_e$$
$$\sin(n/m)(\varphi - \varphi_e)$$

tent functions.
For example:



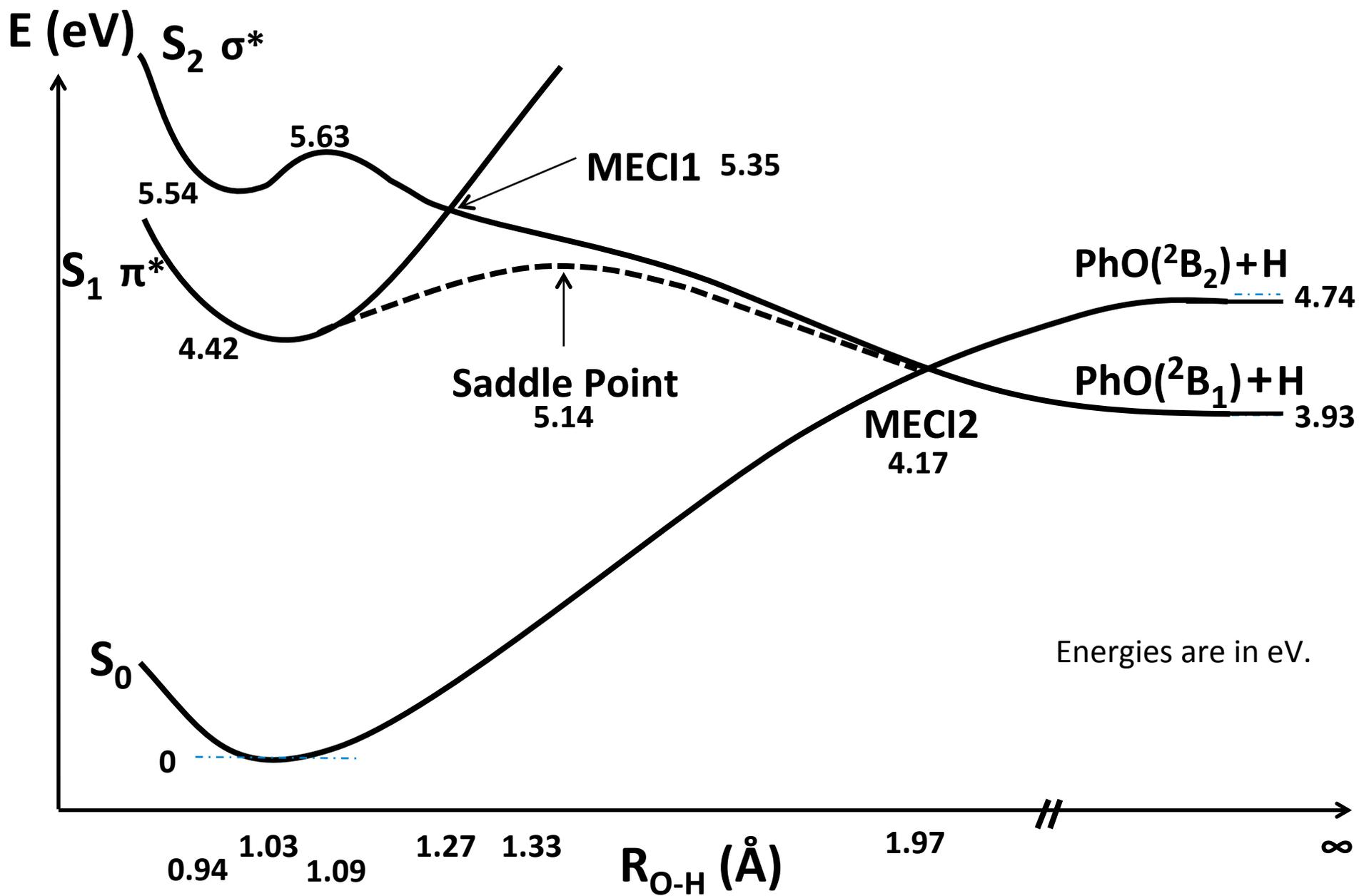
APRP is

- analytic
- system specific
- semiglobal – valid over a wide enough domain to include
 - bond breaking
 - high kinetic energy
- can use high-level electronic structure

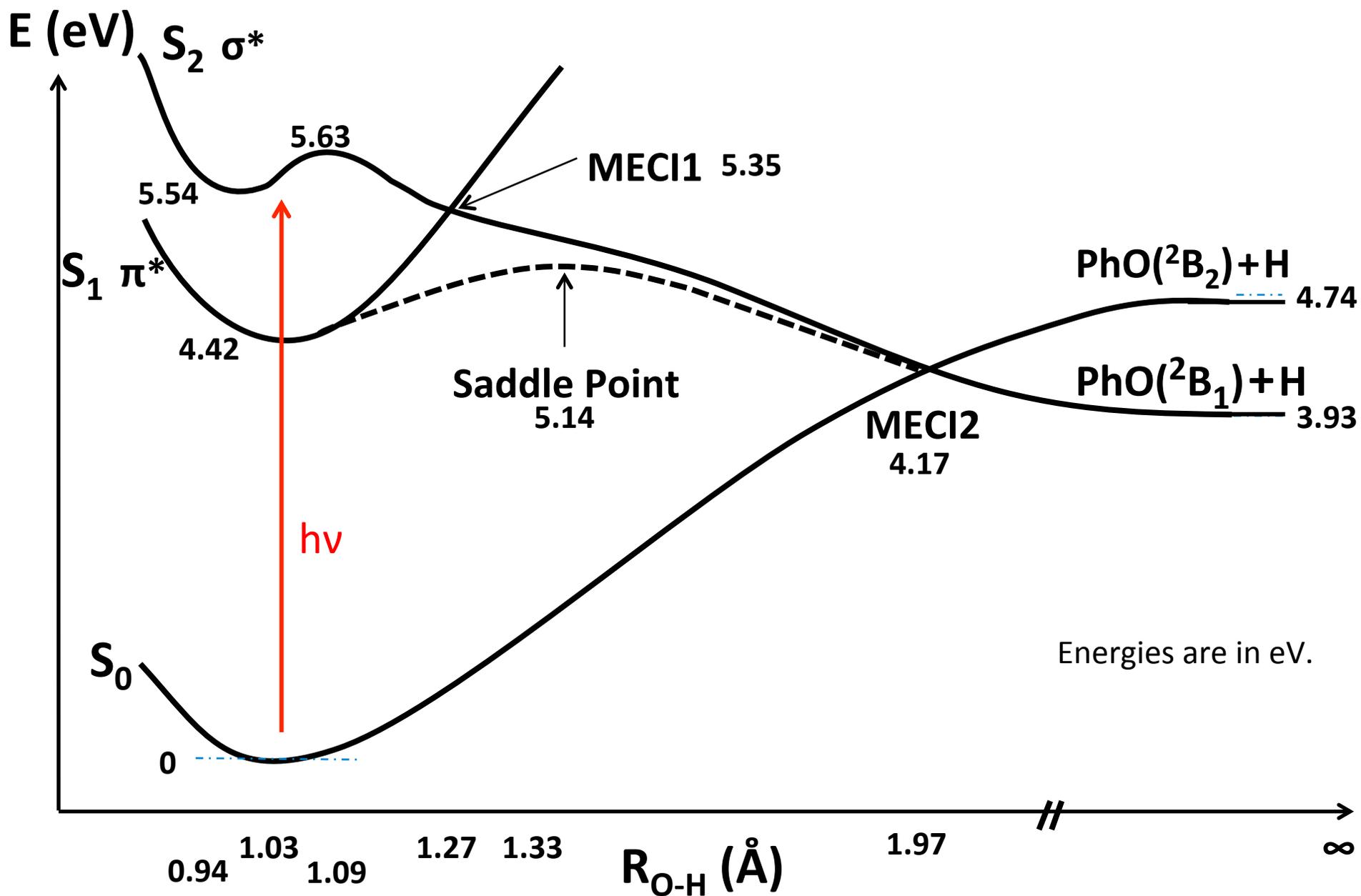
Photochemistry

Phenol photodissociation
with electronically nonadiabatic tunneling

Stationary points and MECIs on phenols PESs

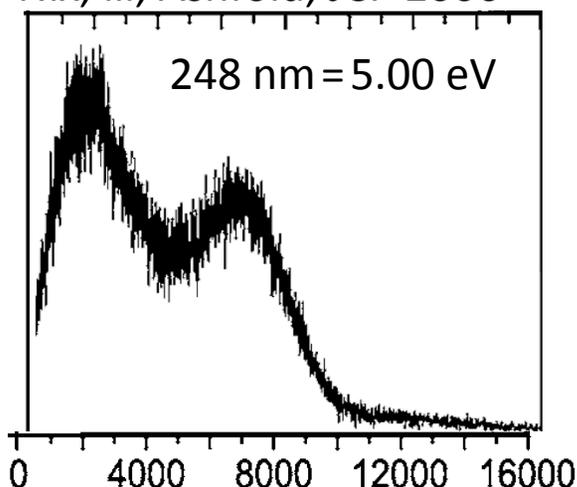


Stationary points and MECIs on phenols PESs

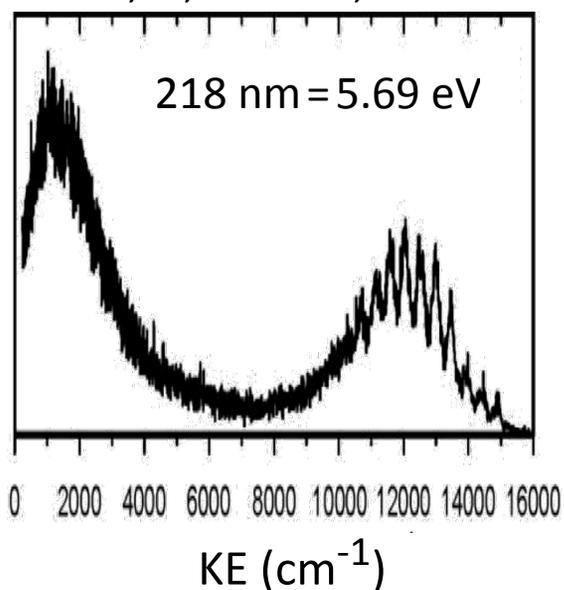


Kinetic energy distribution in phenol photodissociation

Nix, ..., Ashfold, JCP 2006



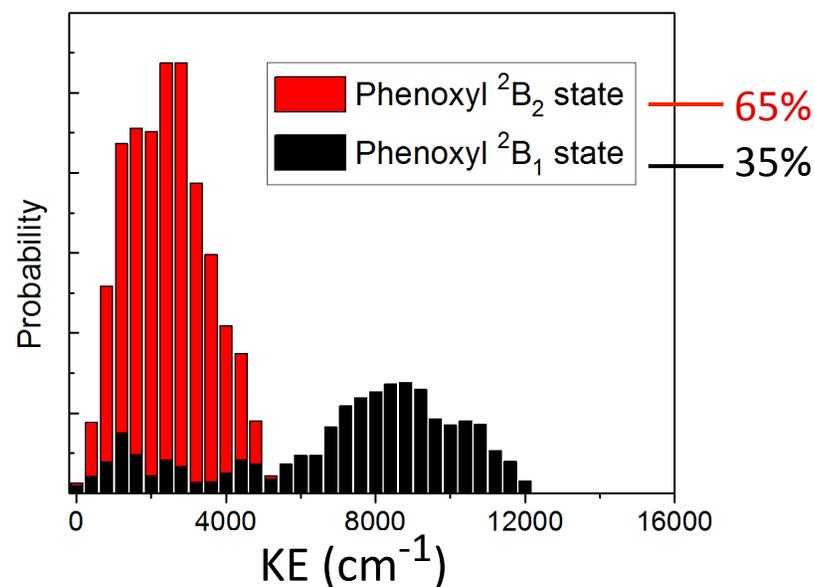
Dixon, ..., Ashfold, JCP 2011



13-atom, 3-state coherent switches with decay of mixing and electronically nonadiabatic quasiclassical simulation with tunneling

OH: $n=1$; a'' : max of ZPE or 0.013 eV; a' : 0.013 eV

Total Energy (eV)	5.61
Time (ps)	10
Number of trajectories	16003
Number of reactive trajectories	5095
Reactive trajectories w/o tunneling	8



Xu, Zheng, Yang, Truhlar, unpublished.

Implementation in user-friendly software – Part 1

VEMGAUSS for G09

vertical excitation or emission from TDDFT or CIS
two-response-time electrostatics plus dispersion

SMD and VMD in NWChem

Modules containing the SMD solvation model and the VEM model have been interfaced with the NWChem program. As in VEMGAUSS, the VEM model in NWChem is augmented with a new efficient treatment of the solute–solvent dispersion contribution to solvatochromic shifts based on state-specific polarizability.

The models will be released in the future official version of NWChem in due course.

Collaboration of Cramer and Truhlar groups

Implementation in user-friendly software – Part 2

CM5PAC for G09

Hirshfeld charges → class IV charges

Solvation in Q-Chem

SMD, CM5, and SM12

CIC-TDA in GAMESS

correct topology in TDDFT
calculations at conical intersections

The first two are a collaboration of Cramer and Truhlar

SciDAC publications from Truhlar group, Year 1

“Combined Self-Consistent-Field and Spin-Flip Tamm-Dancoff Density Functional Approach to Potential Energy Surfaces for Photochemistry,” X. Xu, S. Gozem, M. Olivucci, DGT, *J. Phys. Chem. Lett.* **4**, 253 (2013).

“Valence Excitation Energies of Alkenes, Carbonyl Compounds, and Azabenzenes by Time-Dependent Density Functional Theory: Linear Response of the Ground State Compared to Collinear and Noncollinear Spin-Flip TDDFT with the Tamm-Dancoff Approximation,” M. Isegawa DGT, *J. Chem. Phys.* **138**, 134111 (2013).

“Direct Diabatization of Electronic States by the Fourfold Way: Including Dynamical Correlation by Multi-Configuration Quasidegenerate Perturbation Theory with Complete Active Space Self-Consistent-Field Diabatic Molecular Orbitals,” K. R. Yang, X. Xu, DGT, *Chem. Phys. Lett.* **573**, 84 (2013).

“Diabatic Molecular Orbitals, Potential Energies, and Potential Energy Surface Couplings by the Fourfold Way for Photodissociation of Phenol,” X. Xu, K. R. Yang, DGT, *J. Chem. Theory Comput.* **9**, 3612 (2013).

joint with Cramer group

“Reduced and Quenched Polarizabilities of Interior Atoms in Molecules,” A. Marenich, C. J. Cramer, DGT, *Chem. Sci.* **4**, 2349 (2013).

“Uniform Treatment of Solute–Solvent Dispersion in the Ground and Excited Electronic States of the Solute Based on a Solvation Model with State-Specific Polarizability,” A. Marenich, C. J. Cramer, DGT, *J. Chem. Theory Comput.* **9**, 3649 (2013).

SciDAC publications from Truhlar group, Year 2

"Army Ants Tunneling for Classical Simulations," J. Zheng, X. Xu, R. Meana-Pañeda, DGT, Chem. Sci. **5**, 2091 (2014).

"Configuration Interaction-Corrected Tamm-Dancoff Approximation: A Time-Dependent Density Functional Method with the Correct Dimensionality of Conical Intersections," S. L. Li, A. V. Marenich, X. Xu, DGT, J. Phys. Chem. Lett. **5**, 322 (2014).

"Anchor Points Reactive Potential for Bond-Breaking Reactions," K. R. Yang, X. Xu, DGT, J. Chem. Theory Comput. **10**, 924-933 (2014).

"Testing Noncollinear Spin-Flip, Collinear Spin-Flip, and Conventional Time-Dependent Density Functional Theory for Predicting Electronic Excitation Energies of Closed-Shell Atoms," X. Xu, K. R. Yang, DGT, J. Chem. Theory Comput. **10**, 2070 (2014).

"Including Tunneling in Non-Born-Oppenheimer Simulations," J. Zheng, R. Meana-Pañeda, DGT, J. Phys. Chem. Lett. **5**, 2039 (2014).

joint with Cramer group

"Computational Electrochemistry: Prediction of Liquid-Phase Reduction Potentials," A. V. Marenich, J. Ho, M. L. Coote, C. J. Cramer, DGT, Phys. Chem. Chem. Phys. **16**, 1506 (2014).

joint with Gagliardi group

"Multi-Configuration Pair-Density Functional Theory," G. Li Manni, R. K. Carlson, S. Luo, D. Ma, J. Olsen, D. G. Truhlar, and L. Gagliardi, J. Chem. Theory Comput., online as Just Accepted Manuscript.

Summary of progress in year 2

New methods

Best procedures for spin-flip TDDFT
CIC-TDA for excited states at conical intersections
Multi-Configuration Pair-Density Functional Theory
Simultaneous tunneling and nonadiabatic transitions
in molecular simulations of photochemistry
Refined and new procedures for diabatic
representations with applications to OH_3 , phenol,
and thiosanisole
Anchor Points Reactive Potential

Implementation in user-friendly software

CM5PAC: G09
Solvation: Q-Chem
VEMGAUSS: G09
CIC-TDA:GAMESS
SMD, VEM: NWChem

Credits for the work presented

Alek Marenich
Xuefei Xu
Ke Yang
Shaohong Li
Osanna Tishchenko
Rubén Meana-Pañeda
Giovanni Li Manni
Rebecca Carlson
Dongxia Ma
Sijie Luo
Chad Hoyer

Chris Cramer
Laura Gagliardi