Truhlar Group Research

Snapshot of research on Oct. 2, 2003

Graduate Students	Post Docs	Visiting Researchers
Vanessa Audette	Ahren Jasper	Keith Kuwata
Ari Chakraborty	Hai Lin	
Ben Ellingson	Ben Lynch	
Shikha Nangia	Chaoyuan Zhu	
Jingzhi Pu		
Nate Schultz		
Jason Thompson		
Yan Zhao		

$8 + 4 + 1 = 13$

Subgroups

Kinetics

Ben E., Keith, Hai, Pu, and Yan (emeritus: Ben L.)

Nanotechnology

Ahren and Nate

Solvation (with Chris Cramer)

Ben L., Jason, and Casey Kelly

Quantum

Vanessa, Ari, Shikha, and Chao (emeritus: Ahren)

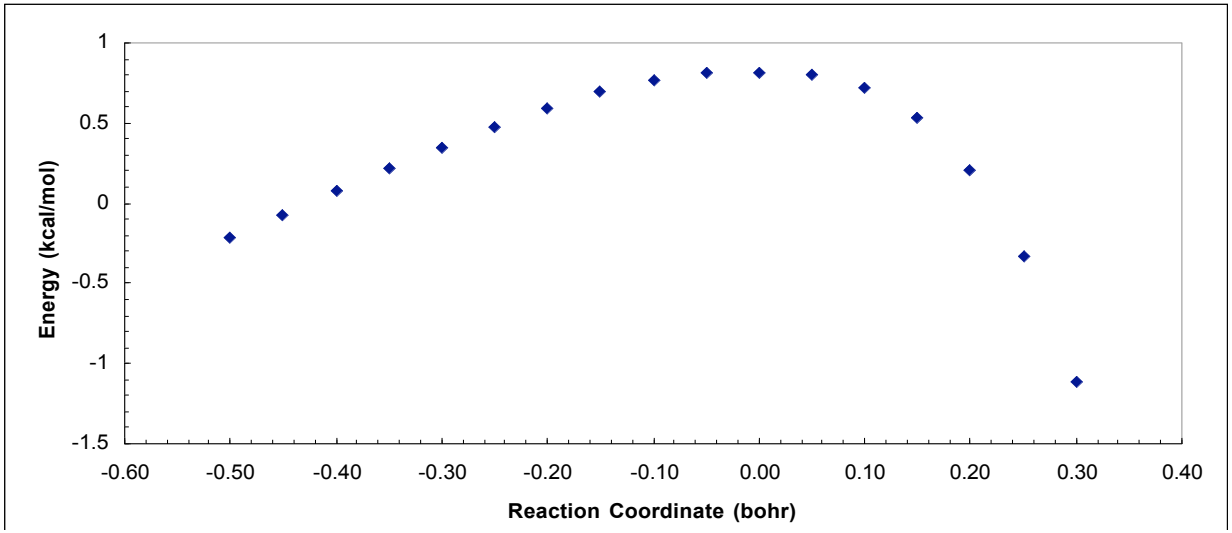
Ben E.

Direct Dynamics

$H_2S + OH \rightarrow SH + H_2O$

A saddle point is found on the potential energy surface (red dot).

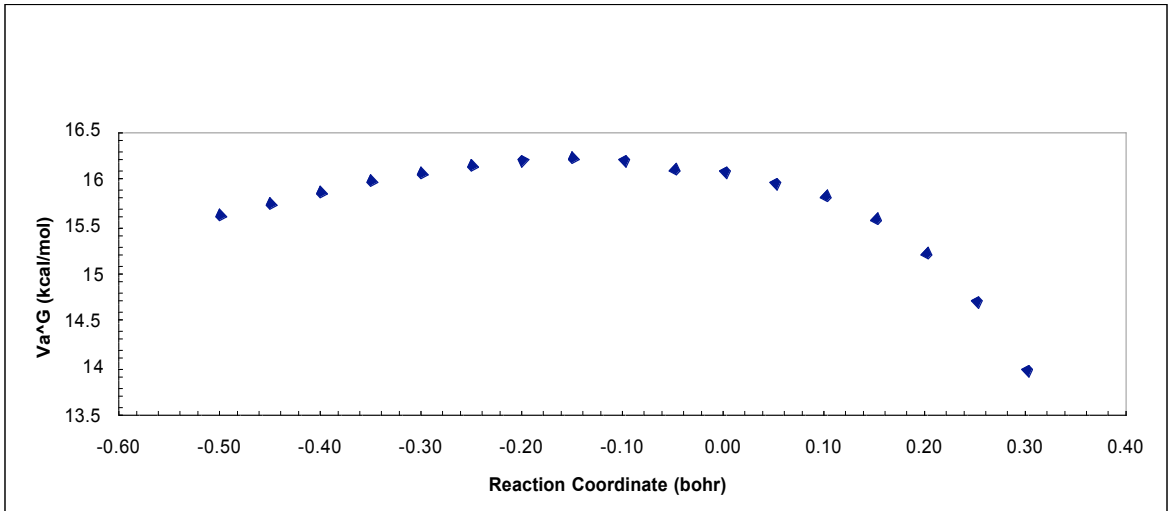
Using an electronic structure program (*Gaussian98*), the gradient is followed down the surface creating the Minimum Energy Path (blue line) by calculating the energy and gradient at every point.



Direct Dynamics
Rate Calculation

The Vibrationally Adiabatic Ground State curve is created by calculating frequencies and adding on zero-point energy. This curve is used for tunneling calculations.

Free energy is calculated using the frequencies and other information. The optimal dividing surface is located at the maximum of free energy. In this reaction, the optimal dividing surface occurs before the saddle point (Reaction Coordinate = 0).



Dynamical Study of the Reactions of OH Radical with Unsaturated Hydrocarbons

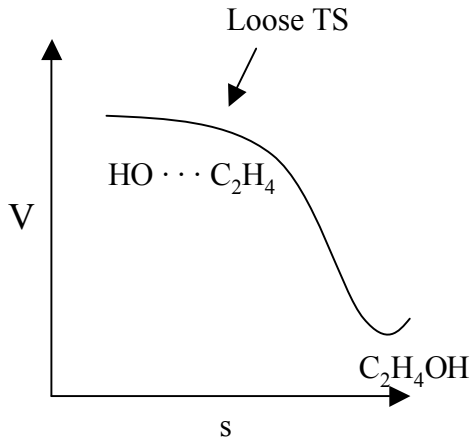
Yan

Two Reaction Channels

Low temperature (<500 K):

Association reaction

$OH + C_2H_4 \rightarrow HOC_2H_4$



*Variational TS Theory for Loose TS

High temperature (~500 – 1000 K):

Hydrogen abstraction

$OH + C_6H_6 \rightarrow C_6H_5 + H_2O$

*Variational Transition State Theory/Multidimensional Tunneling

POLYRATE

*Direct Dynamics

*Multi-Coefficient Molecular Mechanics (MCMM)

MC-TINKERATE, …

*Multi-Coefficient Correlation Methods (MCCMs)

MCG3, MC-QCISD, …

*Hybrid Density Functional Theory

MPW1K, …

Generalized Hybrid Orbital (GHO) method for Combining *Ab Initio* Hartree-Fock Wave Functions with Molecular Mechanics

Pu

GHO Scheme

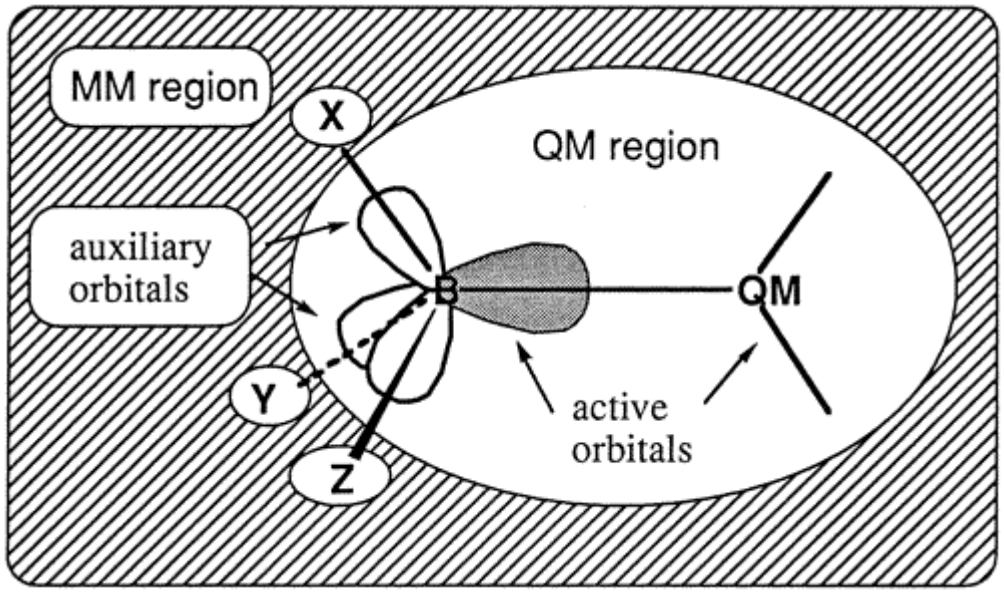


Figure 1. Schematic representation of the QM/MM division along a covalent bond and the hybrid orbitals on the GHO boundary atom B. The shaded orbital is the active hybrid orbital.

Hai

MCMM: Multi-Configuration Molecular Mechanics

$$A + BC \rightleftharpoons AB + C$$

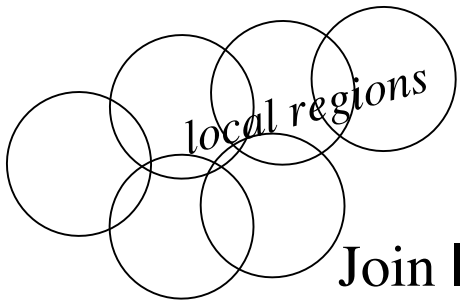
Φ_1 Φ_2 ← valence bond configuration LEPS, Coulson

$$\mathbf{H} = \begin{pmatrix} \langle\Phi_1|H|\Phi_1\rangle & H_{12} \\ H_{12} & \langle\Phi_2|H|\Phi_2\rangle \end{pmatrix}$$ ← molecular mechanics configuration Allinger

$$= \begin{pmatrix} V_1^{MM} & V_{12} \\ V_{12} & V_2^{MM} \end{pmatrix}$$ ← diabatic coupling

Eigenvalue is adiabatic energy.

Choose V_{12} to *make* it accurate:



Use quadratic expansion of V_{12} to reproduce quadratic expansion of adiabatic energy in local regions. Chang, Miller

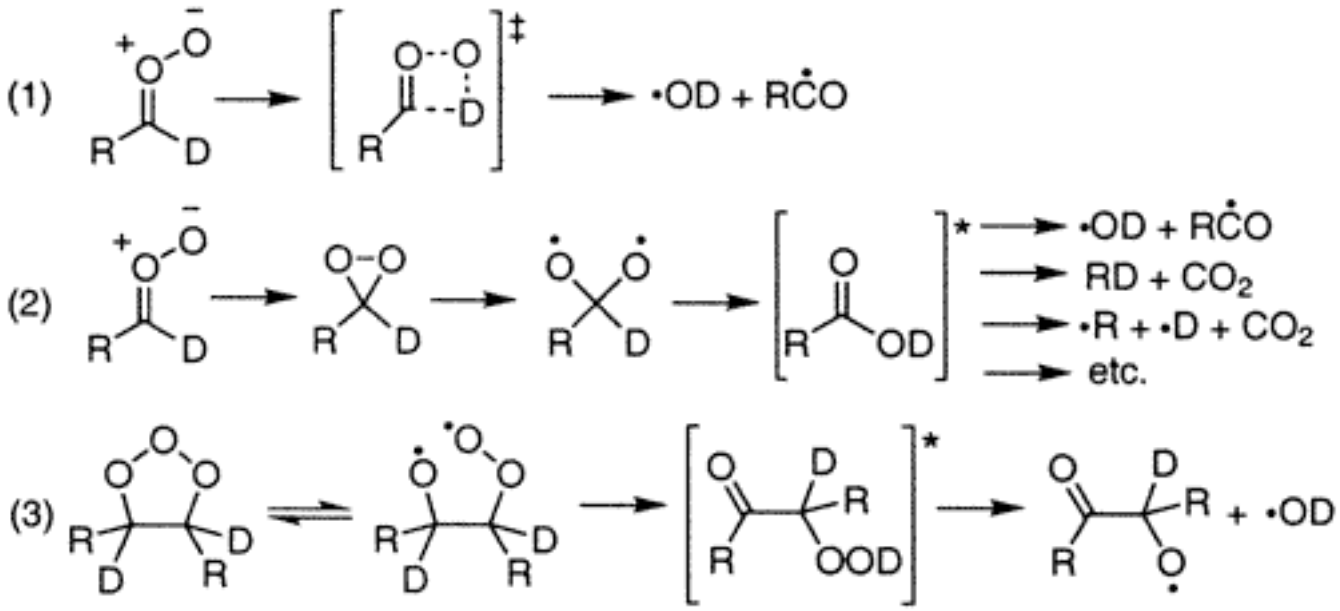
Join local fits of V_{12} by Shepard interpolation. Collins

Put it all together:

MCMM

Keith

Recent experiments on 3-hexenes with vinylic deuteriums (Kroll, J. H. *et al., J. Am. Chem. Soc.* **2002**, *124*, 8518) reveal significant production of OD radicals, perhaps due to the isomerization and decomposition of dioxiranes. Possible mechanisms of OD formation:



These mechanisms are under study by direct dynamics calculations.

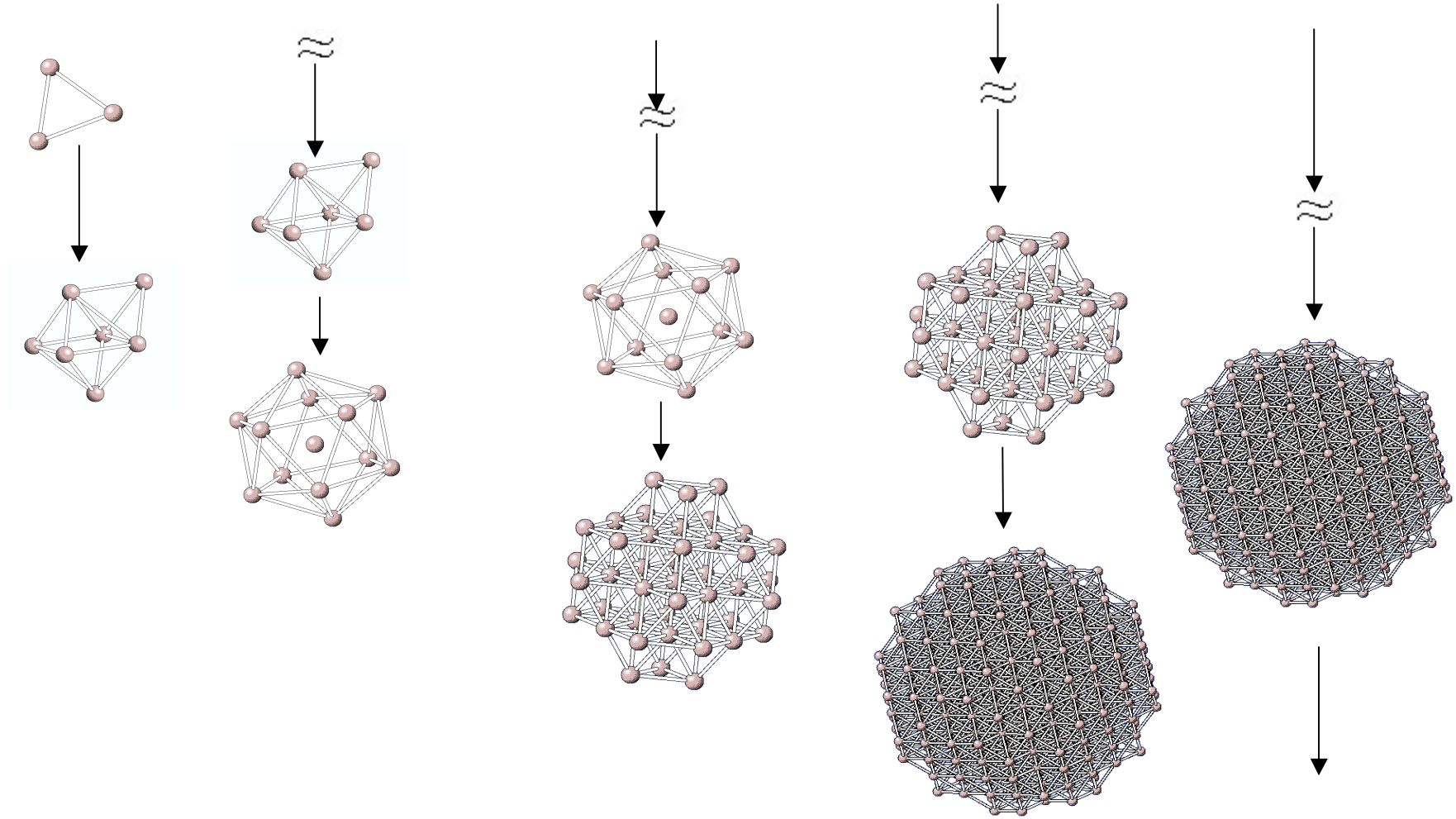
Nanotechnology Subgroup

Ahren

& Nate

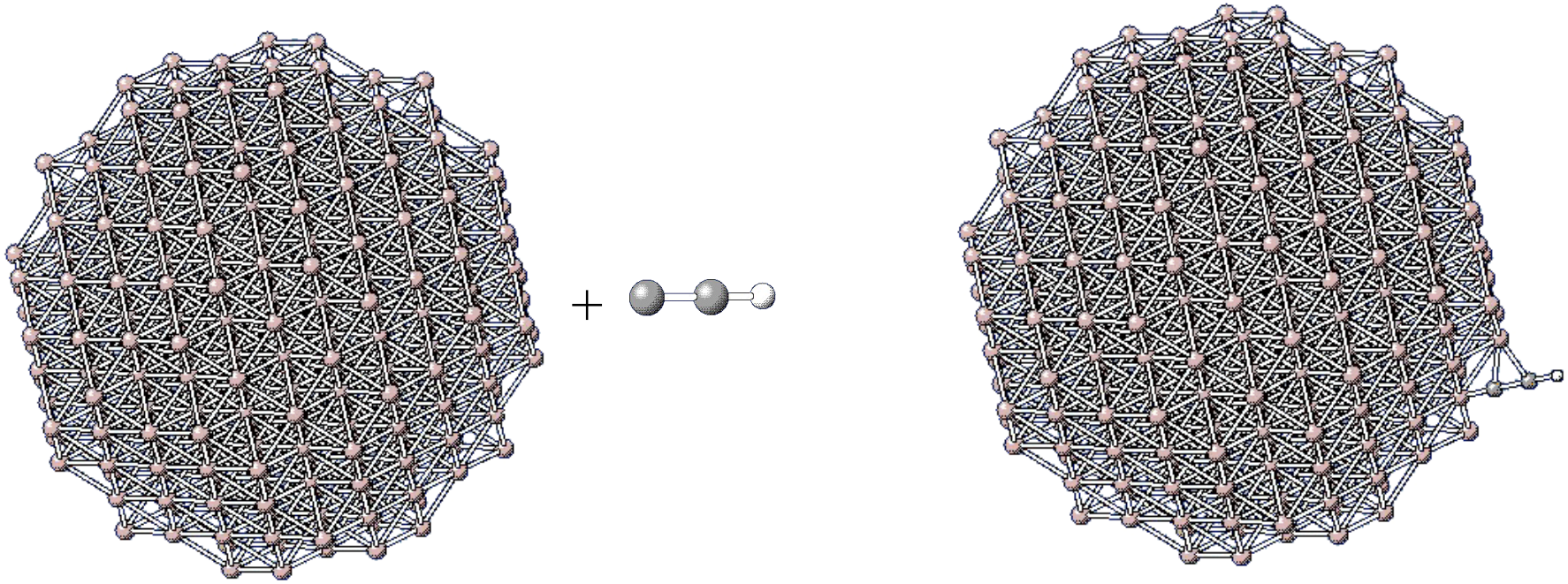
Al_n: A range of methods for a range of sizes

MCG3/3 PBE0/MG3 PBE0/MECP-pTZ MBTB-S LSRGolMB



$n \lesssim 7$ $n \lesssim 13$ $n \lesssim 75$ $n \lesssim 3500$ $n >> 10{,}000$

Future of the Nanotechnology Group

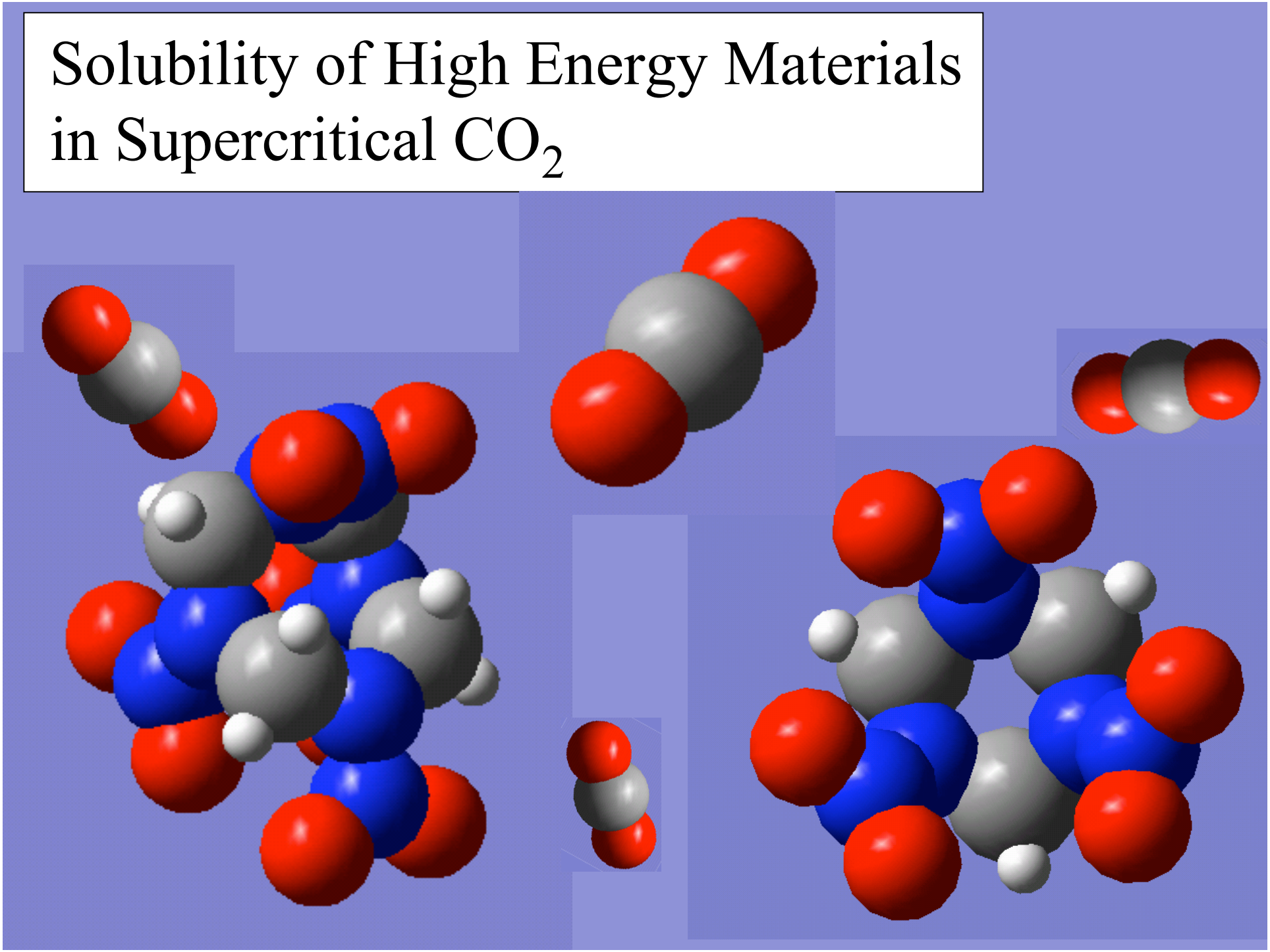


Al_{381} CCH $Al_{381}CCH$

Solvation

Jason

Solubility of High Energy Materials in Supercritical CO_2



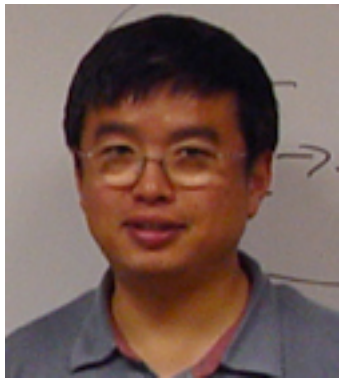
Quantum Subgroup

Ari

Shikha

Vanessa

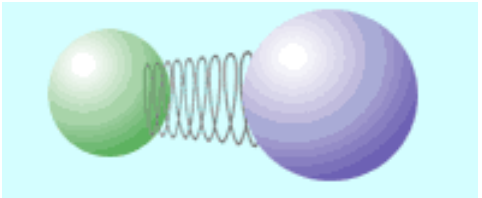
Chao



Calculation of accurate partition functions using rovibrational energy levels

Ari

Conventional method of computing partition function $Q(T)$: Rigid-rotor Harmonic oscillator



Improving the Rigid-rotor Harmonic Oscillator model

- Inclusion of anharmonic effects
- Inclusion of rotational-vibrational interactions, such as Coriolis coupling and centrifugal distortions

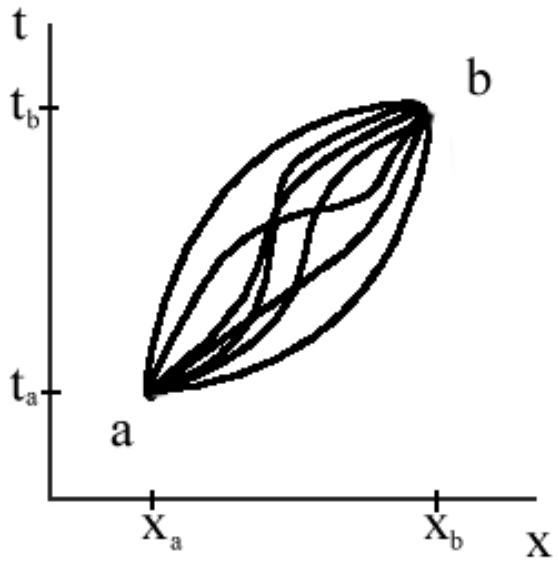
Methodology

Variational Self Consistent Field (VSCF) method is a powerful technique for calculating accurate rovibrational energy levels

Path Integral Monte Carlo Methods

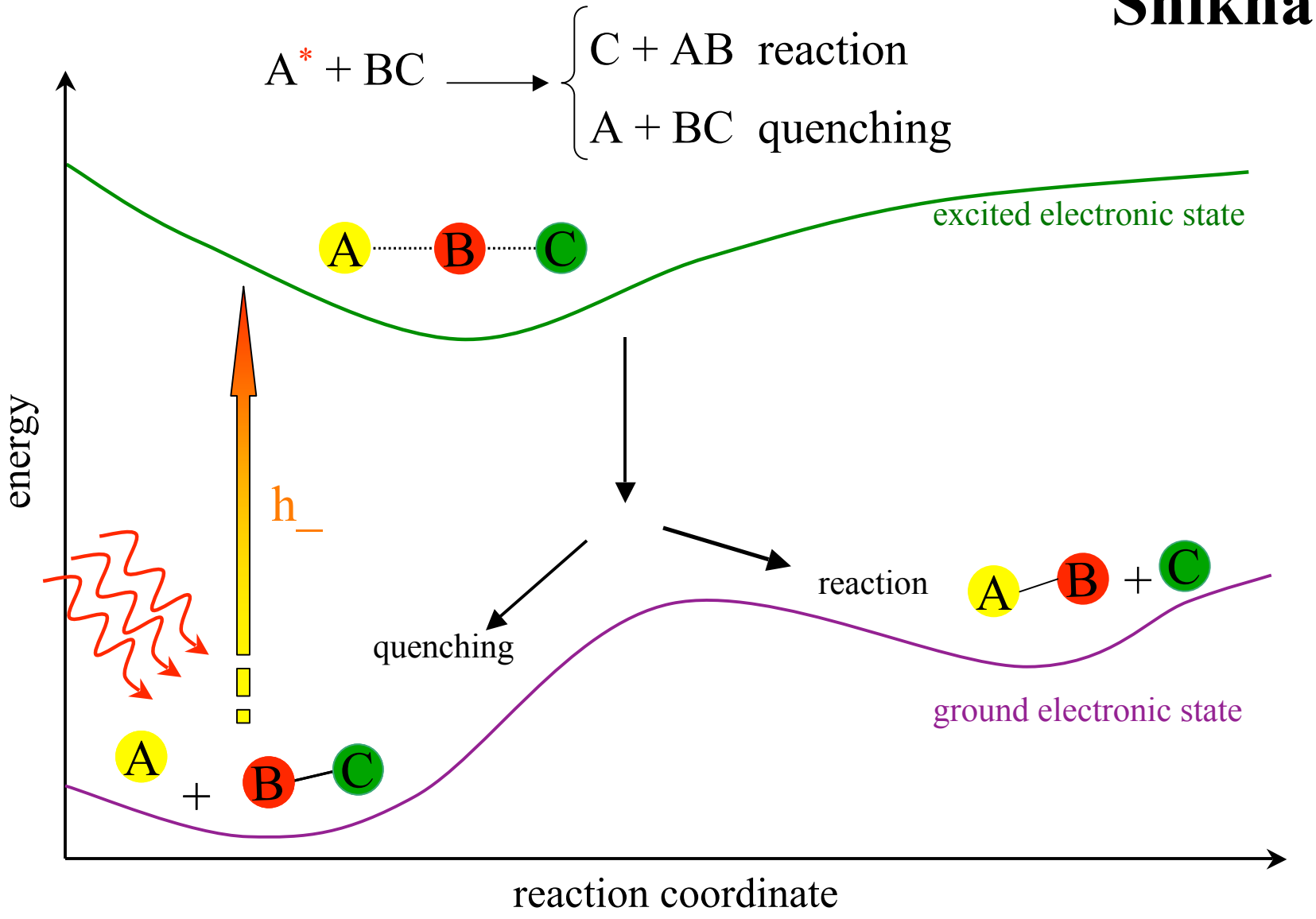
Vanessa

- Propagator is written as a sum over all paths
- Path integrals coupled with Monte Carlo sampling can be used to calculate partition functions



Quantum Photochemistry

Shikha



Self-Consistent Decay of Mixing with Coherent Switching for Photchemical Processes

Chao

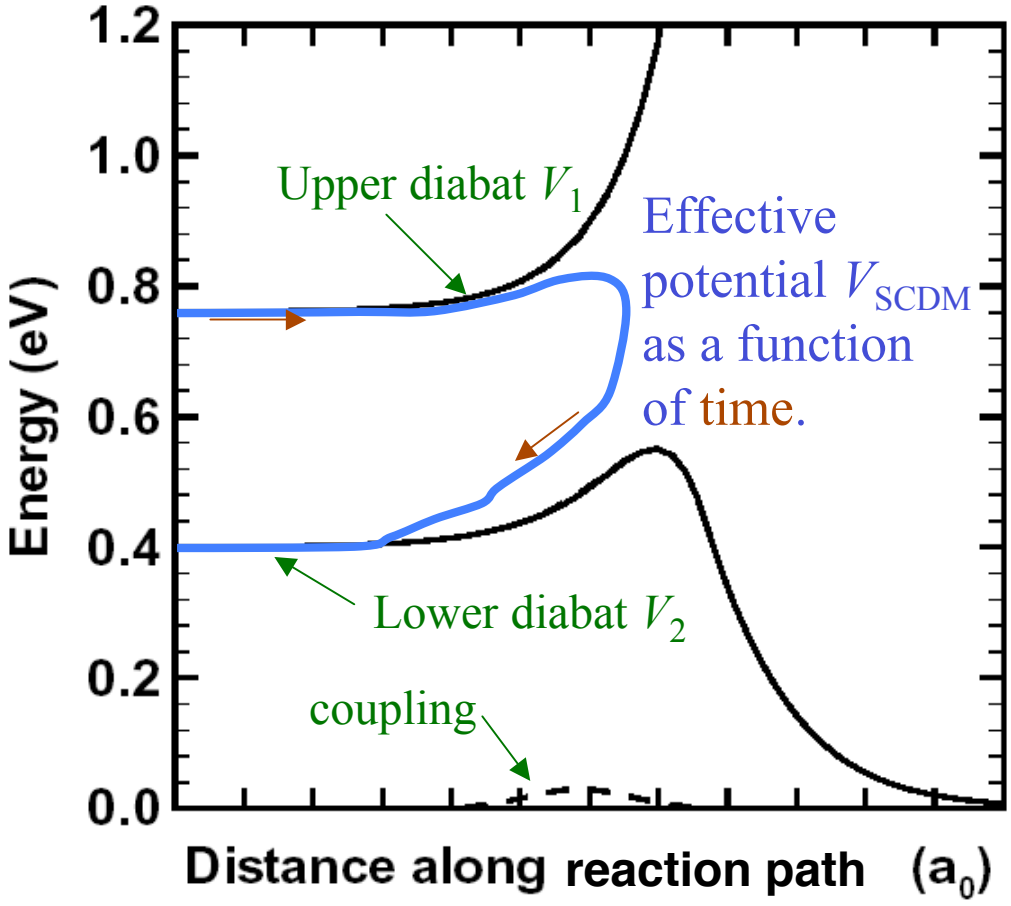
In the strong interaction region:

$$V_{\mathrm{SCDM}} \approx V_{\mathrm{mean}}.$$

Asymptotically:

$$V_{\mathrm{SCDM}} \approx V_1 \text{ or } V_2.$$

However, the transition probabilities are computed coherently, yet self-consistently.



That’s all, folks.

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