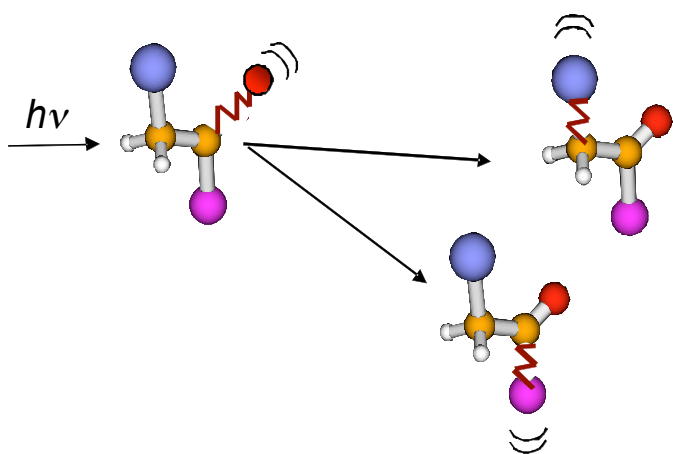


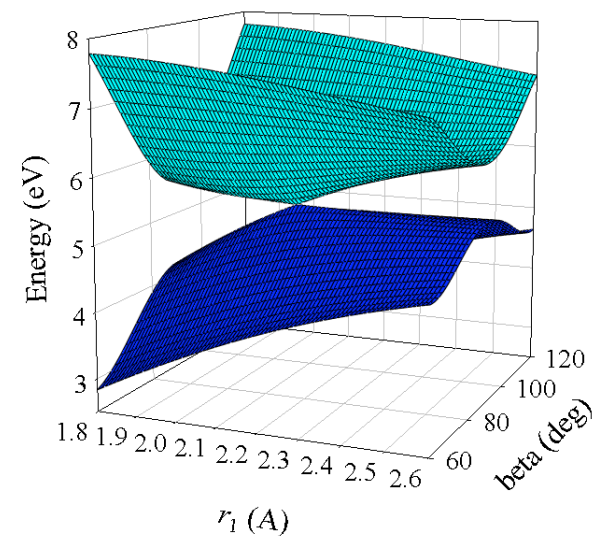
Photochemical Dynamics in the Truhlar Group

Developing new methods for studying photochemical
and other non-Born-Oppenheimer processes

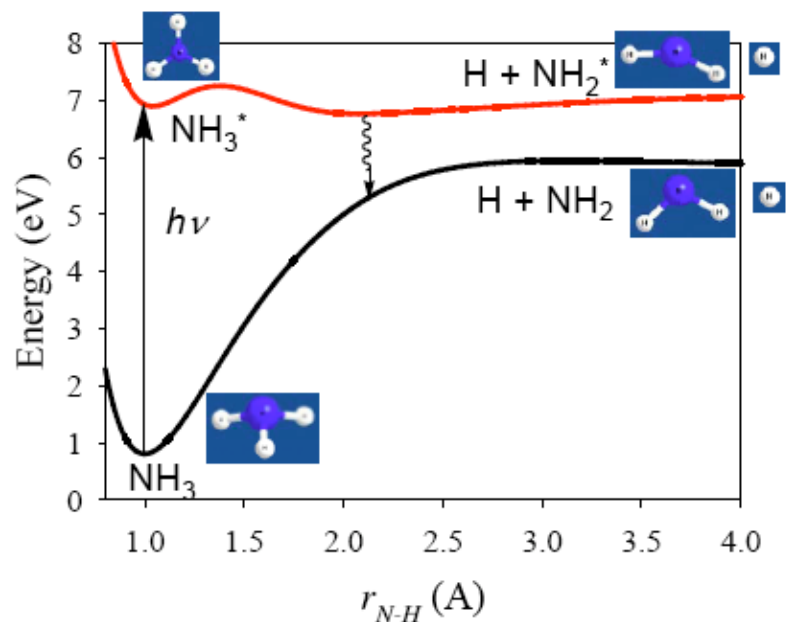


David Bonhommeau
Zhen Hua Li
Oksana Tishchenko
Rosendo Valero
Don Truhlar

February 2007



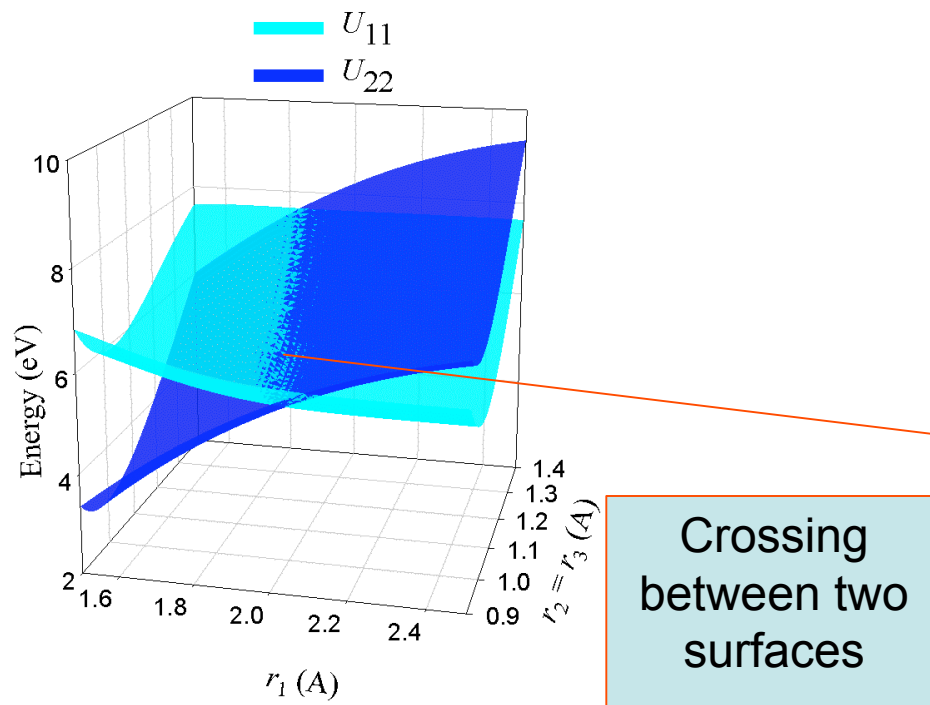
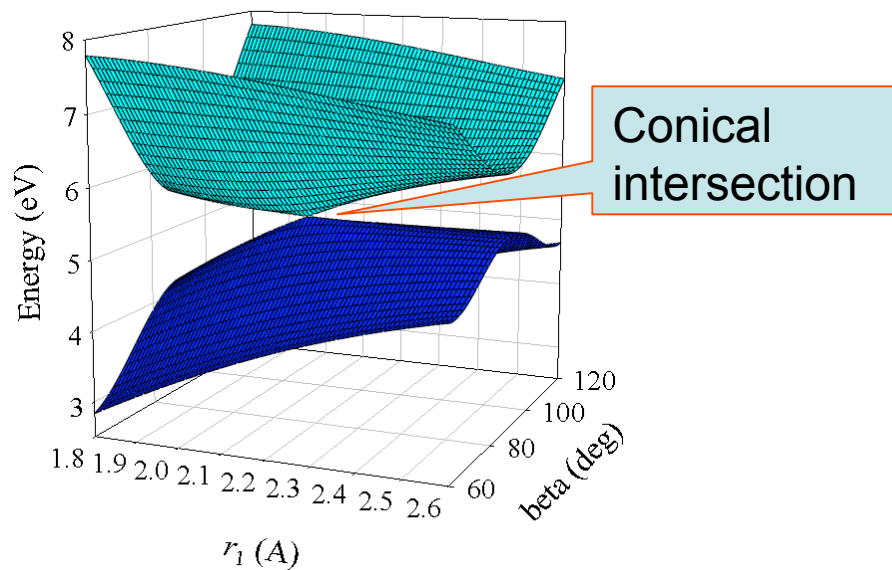
Coupled potential energy surfaces of NH₃ molecules



NH₃ has two low-lying electronic states; the higher one (excited state) is planar. Experimentalists found that the excitation of a particular vibration of the planar structure leads to the adiabatic dissociation of NH₃ into H + NH₂^{*}, where * denotes an excited electronic state, while exciting other vibrations leads to amino radical in the ground electronic state.

We are using computational methods to understand *why*.

The first step of our study consists in building a multi-dimensional surface.



Dynamical study of NH₃ molecules

Methods	Quantum methods	Mixed quantum-classical methods	Classical adiabatic methods	Statistical methods
Number of surfaces	$N_{\text{surf}} \leq 5-10$	$N_{\text{surf}} \leq 50-100$	$N_{\text{surf}} = 1$	No
Number of atoms	$N_{\text{at}} \leq 4$	$N_{\text{at}} \leq 20$	$N_{\text{at}} \leq \text{a few } 100$	$N_{\text{at}} \geq 100$
Simulation time	$t_{\text{end}} \leq 100 \text{ fs}$	$t_{\text{end}} \leq 100 \text{ ps}$	$t_{\text{end}} \leq 10 \text{ ns}$	$t_{\text{end}} \leq 1 \text{ ms} - 1 \text{ s}$
Example of Method	Multi-Configuration Time-Dependent Hartree	Mean-field and surface hopping methods	Molecular dynamics	Kinetic Monte Carlo

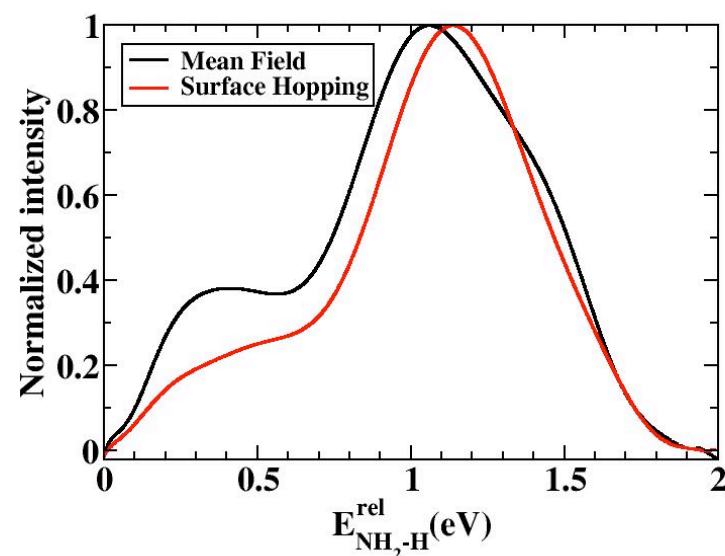
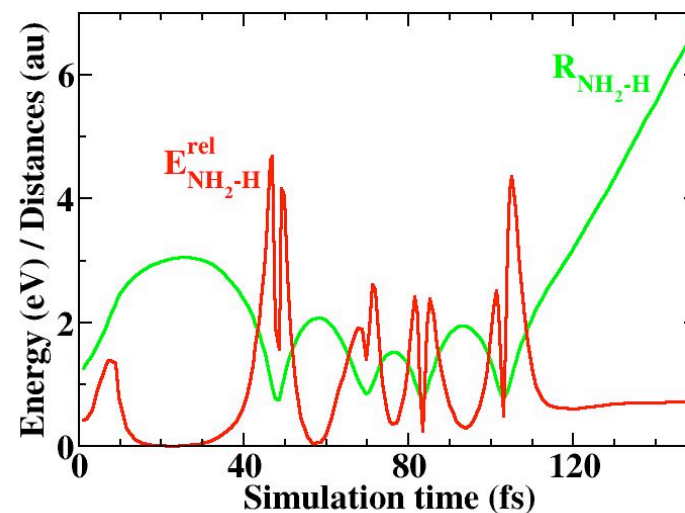
Photofragmentation of NH₃ Molecules

Mixed quantum-classical method:

- Nuclei are treated classically by following classical equation of motion in Cartesian coordinates
- The electronic part is treated quantum mechanically (wave function)
- The existence of two surfaces is taken into account by allowing for hops between surfaces (surface hopping techniques) or generating an average surface (mean field techniques)

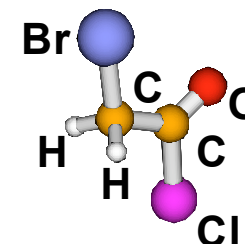
Results:

- Following the fragmentation process as a function of time (energies, distances, electronic state populations, mode populations,...) → top figure
- Determining speed and kinetic energy distributions of departing H atoms (comparison to experiments) → bottom figure
- Testing the reliability of mean field and surface hopping techniques in diabatic and adiabatic representations



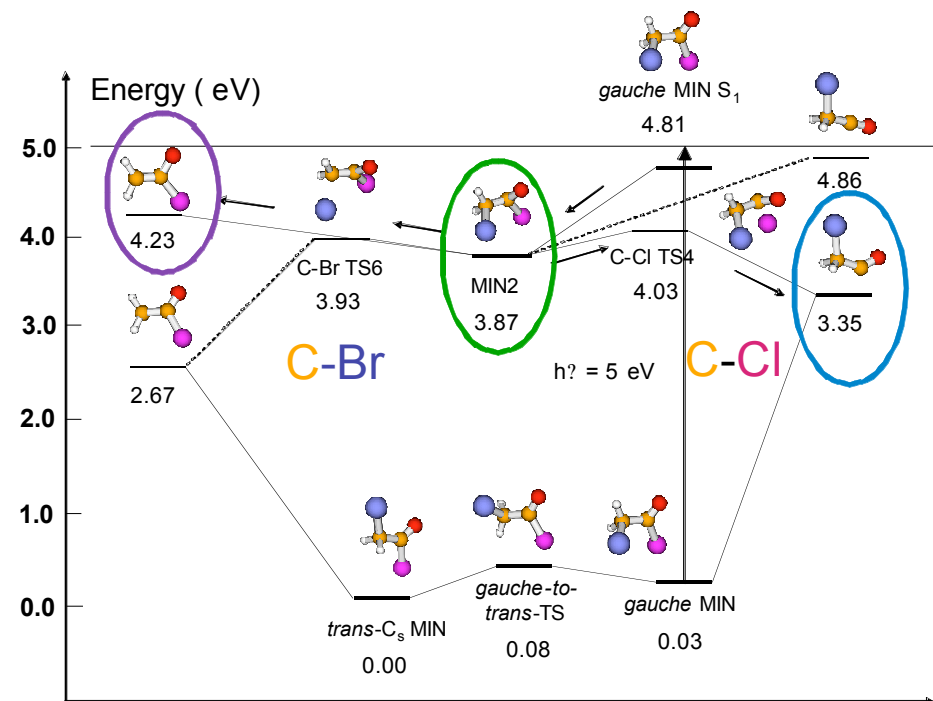
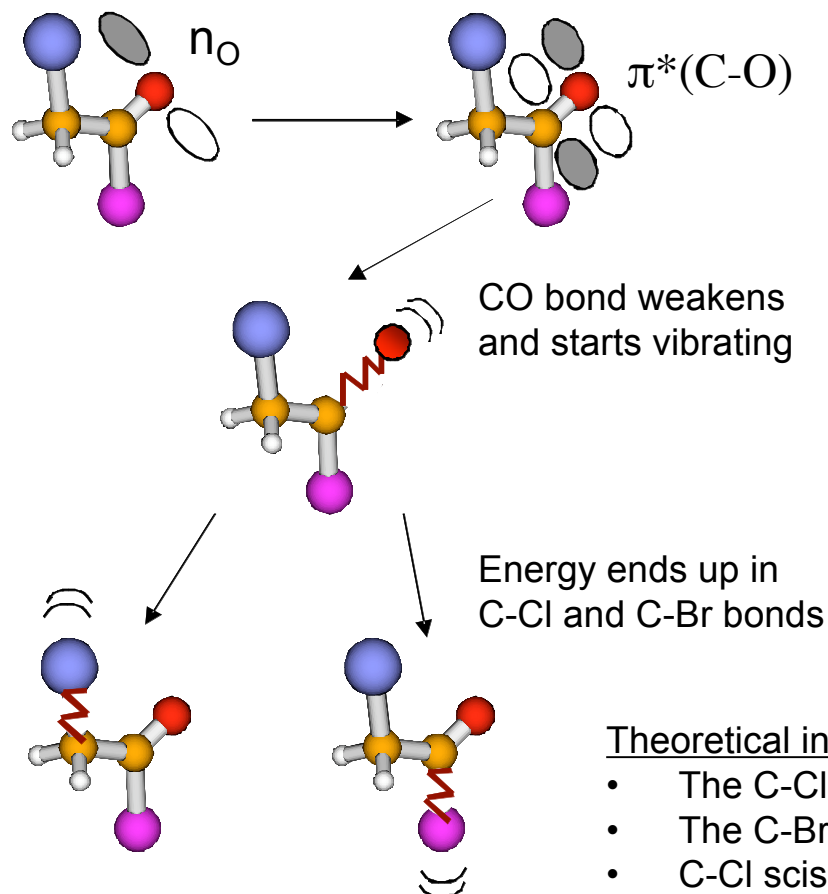
Bromoacetyl chloride photochemistry: Using electronic structure calculations to explain experiments

- Laser excites nonbonding electron of oxygen to C-O antibonding orbital
- Electronic excitation redistributes to break the C-Cl and C-Br bonds



Experimental (puzzling) fact:

- C-Cl has a higher barrier than C-Br but scission is easier for C-Cl! Why?



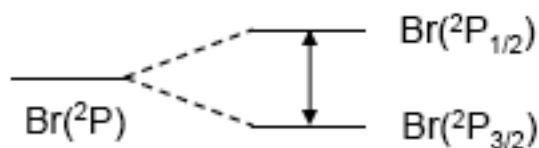
Theoretical interpretation:

- The C-Cl rupture is adiabatic: the molecule goes over the barrier
- The C-Br rupture is diabatic: the molecule goes to excited products
- C-Cl scission (right-hand side of figure) now needs less energy than C-Br scission (left-hand side of figure)!

A simple model to include spin-orbit effects in photochemistry

Spin-orbit interaction has two very important effects

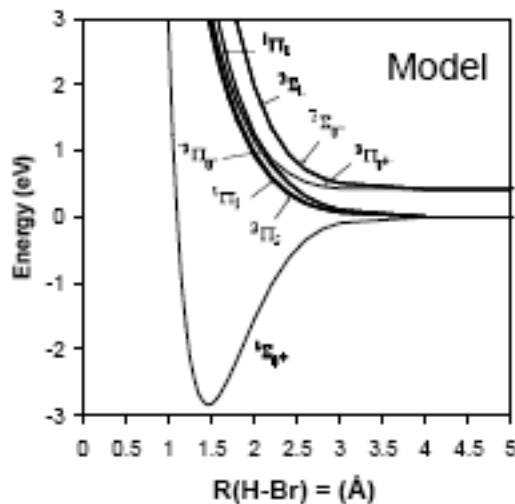
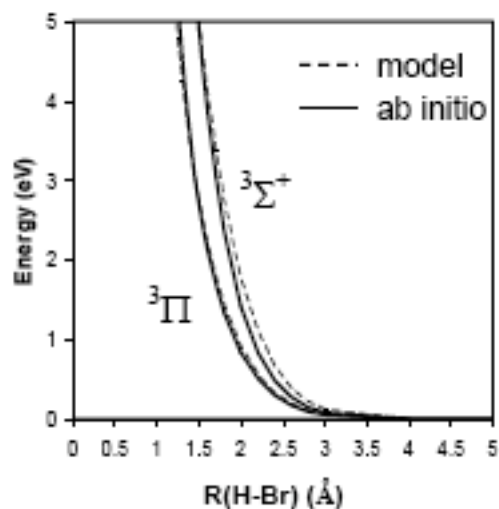
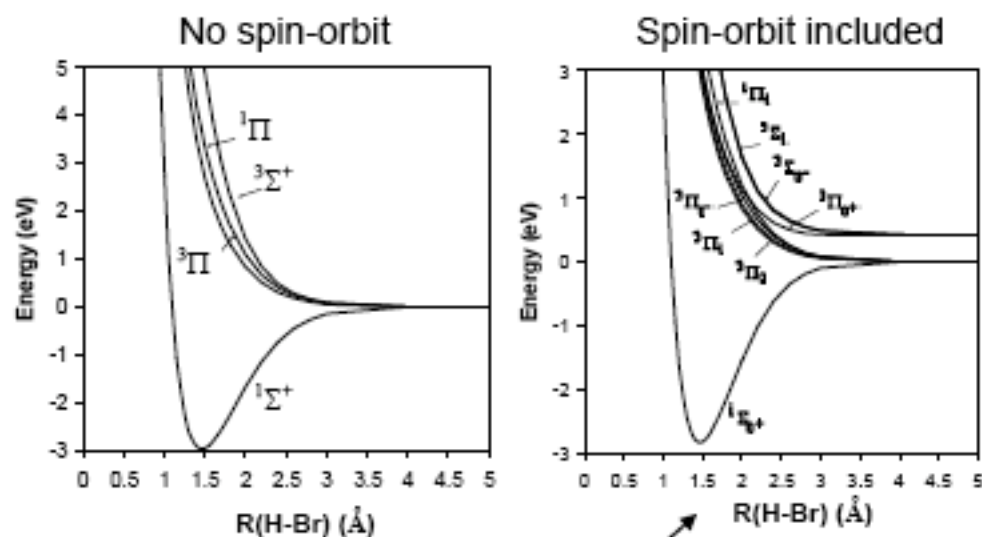
1) Fine-structure splitting



Formulation of the model

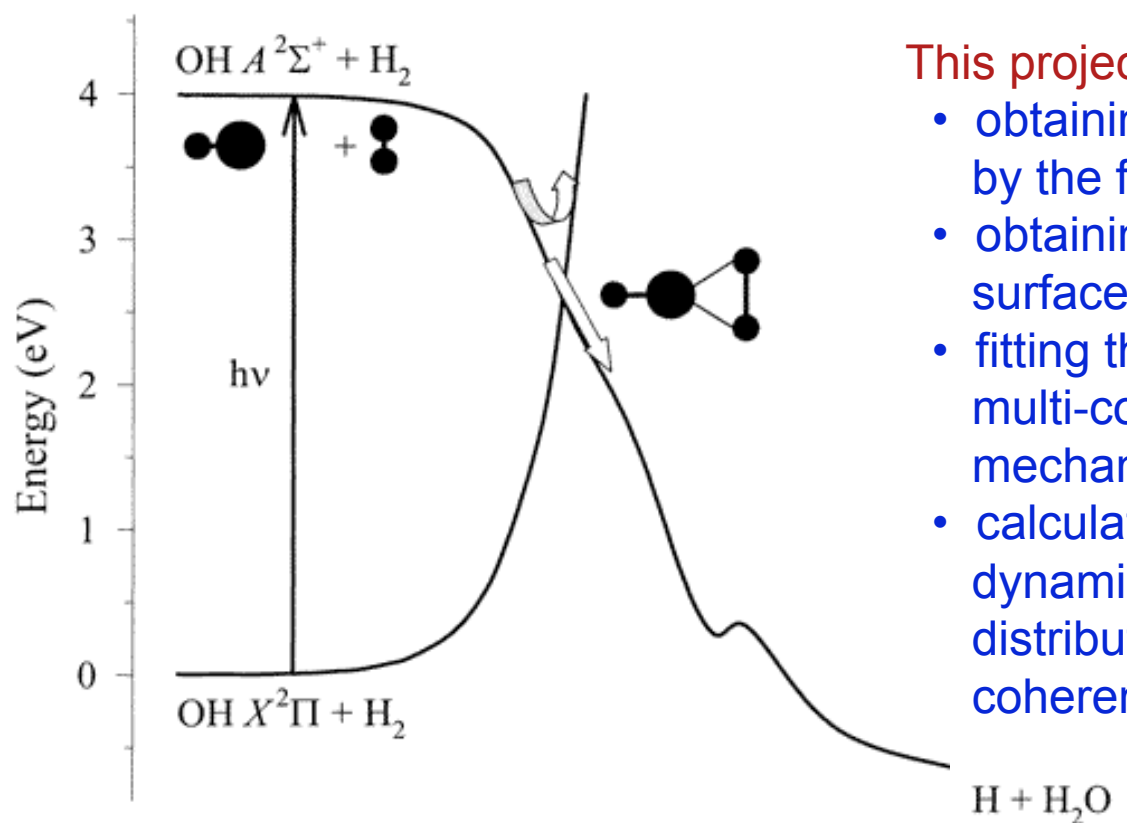
- Express the energy of triplet states in terms of the energy of singlet states
- Assume spin-orbit coupling does not depend on internuclear distances
- With these two approximations compute potential energy curves

2) Singlet-triplet interaction and mixing. Example: HBr molecule



The model does a good job of generating a set of approximate potential curves with spin-orbit coupling included

Reactive quenching of the excited \tilde{A} state of OH by hydrogen and deuterium molecules



This project involves

- obtaining diabatic molecular orbitals by the fourfold way
- obtaining diabatic potential energy surfaces by configurational uniformity
- fitting the surfaces and couplings by multi-configuration molecular mechanics
- calculating the non-Born-Oppenheimer dynamics and product energy distributions by decay of mixing with coherent switches

Todd, Anderson, and Lester, *JPC A*, 2001