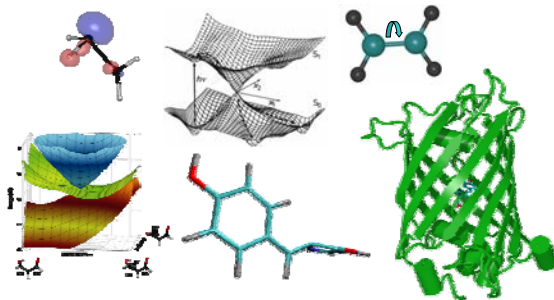


## Ab Initio Multiple Spawning Dynamics

Todd J. Martinez  
Department of Chemistry & The Beckman Institute  
University of Illinois at Urbana-Champaign

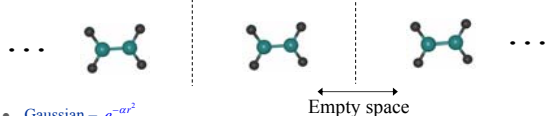


## Ab Initio Molecular Dynamics Terminology

	Electronic Structure	Electronic Basis	Extended Lagrangian?	Dynamics
Direct Dynamics	DFT <i>Ab initio</i> Semiempirical	Any	No	Classical
BOMD Born-Oppenheimer Molecular Dynamics	DFT <i>Ab initio</i>	Any	No	Classical
CPMD Car-Parrinello Molecular Dynamics	DFT	Plane Wave	Yes	Classical
ADMP Atom-Centered Density Matrix Propagation	DFT or SCF	Gaussian	Yes	Classical

## Electronic Basis Sets

- Plane waves -  $e^{ikr}$ 
  - Natural for periodic systems
  - Hellman-Feynman Forces are exact
  - Very inefficient for nonperiodic systems (large empty spaces between periodic replicas; in almost all cases, this empty space is filled with basis functions)
  - Obvious, well-defined convergence hierarchy



- Gaussian -  $e^{-ar^2}$ 
  - Periodicity is more difficult to incorporate (but not impossible, e.g. **Crystal**)
  - Generally atom-centered ("floating" Gaussians also possible)
    - Electrons like to be near nuclei!
  - Pulay terms in forces for atom-centered Gaussians
  - Convergence hierarchy more subtle, but now well-understood (Dunning)

## "Pulay" Terms

$$\frac{\partial E}{\partial R} = \frac{\partial}{\partial R} \langle \psi_{elec}(r; R) | \hat{H}_{elec} | \psi_{elec}(r; R) \rangle_r$$

$$= \left\langle \psi_{elec}(r; R) \left| \frac{\partial \hat{H}_{elec}}{\partial R} \right| \psi_{elec}(r; R) \right\rangle_r \quad \text{"Hellmann-Feynman Force"}$$

$$+ \underbrace{\left\langle \frac{\partial \psi_{elec}(r; R)}{\partial R} \left| \hat{H}_{elec} \right| \psi_{elec}(r; R) \right\rangle_r + \left\langle \psi_{elec}(r; R) \left| \hat{H}_{elec} \right| \frac{\partial \psi_{elec}(r; R)}{\partial R} \right\rangle_r}_{\text{"Pulay Force"}}$$

Pulay force *apparently* requires derivatives of electronic wavefunctions!  
Actually, often it does *not*, but it is always more expensive than HF Force

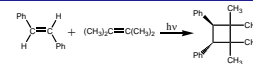
## Extended Lagrangian Technique

- What is it?
  - Electronic degrees of freedom are *propagated* under a new Lagrangian, instead of using the variational principle to determine them at each new geometry
- Benefits
  - Wavefunction does not need to be converged at each time step
    - "1" iteration vs. typical 10-15 iterations (apparently)
    - But*, good BOMD codes require < 5 iter b/c geometry change in one time step is small
- Disadvantages
  - Need to ensure that the electronic coefficients are always "cold" and nuclei are always "hot"
    - Energy transfer between ions and "fictitious" degrees of freedom is *unphysical*
  - Time step needs to be smaller than in BOMD - fictitious degrees of freedom are *high-frequency* relative to nuclei
- Bottom line (according to TJM)
  - EL schemes have 1/2 time step to save 5 iterations/time step. Works out to a 2.5x speed advantage in favor of EL
  - But* need to be careful to maintain adiabatic separation of nuclei and electrons.
  - Both are reasonable and choice depends on taste

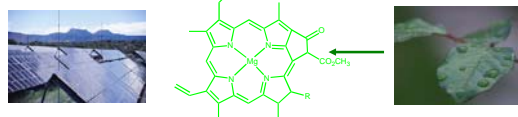
**EL expands dynamic range of frequencies to reduce SCF iterations**

## Electronic Excited States

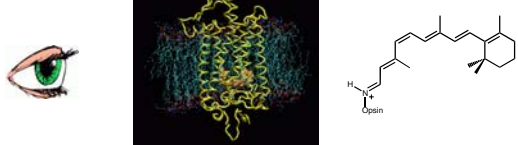
### Chemical Synthesis



### Energy Conversion



### Vision



### Light-Driven Molecular Devices

Light → Mechanical Work

Hugel, et al, Science (2002)

Yu, et al, Nature (2003)

Other Applications...  
 Optical Memory  
 Molecular Logic  
 Local control of pH –  
 “chemical circuits”  
 Drug delivery

Switch electron transport on and off

### More Light-Driven Devices

Tour, Org. Lett. (2006)

Balzani, Stoddart, PNAS (2006)

### Breakdown of Born-Oppenheimer Approximation

Avoided Crossings  
 Degeneracy lifted in  
 N-dimensional space

Conical Intersections  
 Degeneracy lifted in  
 2-dimensional space

**CIs are the rule, not the exception: e.g., Michl, Yarkony, Robb, ...**

### Including Quantum Effects

- Classical with “*ad hoc* corrections”
  - Not guaranteed to converge to the right answer...
  - No well-defined nuclear wavefunction
- Mixed Quantum/Classical (See Iyengar Talk)
  - Based on time-dependent self-consistent field approximation
  - Not obvious that QM and CM are strictly compatible!
- Fully Quantum Mechanical
  - Approach is well-defined
  - But difficult (in fact, exponentially difficult in general case)
  - Basis set and path integral approaches
    - Feynman Path integrals
      - Imaginary time (quantum statistics) is easy
      - “Sign” problem in real time – progress, but still unsolved
  - Basis set
    - What kind of functions?
    - How to choose them?

### Nonadiabatic Dynamics

- Ehrenfest Methods
 
$$\dot{c}_j = -i \sum_l H_{jl}(\vec{R}) c_l \quad V_{ave}(\vec{R}) = \sum_l c_l^* c_l V_l(\vec{R})$$

Hamilton’s Eqns with  $V_{ave}$  for R and P

$V_{ave}$  is unphysical asymptotically!  
 Why? - Wavepacket splits into two parts  
 and averaging becomes senseless
- Surface Hopping (Tully, Truhlar, many more...)
 

Avoid unphysical averaging  
 Stochastic “hops”  
 No systematic hierarchy  
 to improve approximations

### Ab initio Quantum Dynamics

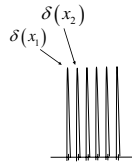
- Ab Initio Quantum Dynamics → “On-the-fly” solution of electronic and nuclear Schrödinger equations
  - Multiple electronic states/Tunneling → Need quantum nuclear dynamics
  - Bond rearrangement → Need to solve electronic Schrödinger equation
- Exact numerical solution of the nuclear Schrödinger equation is impractical for large systems.
  - Ab initio quantum chemistry is local
  - Nuclear Schrödinger equation is global
  - Not a problem in Car-Parrinello b/c Newtonian mechanics is local...

**Further considerations:**

- Need PESs for both ground and excited states.
- Matrix elements which couple electronic states  $\langle \psi_i^{electronic} | \frac{\partial}{\partial R} | \psi_j^{electronic} \rangle$
- Minimize the number of PESs evaluations b/c of extreme expense.

*Tailor the requirements of quantum dynamics to quantum chemistry and vice-versa!*

## Basis Set Approaches to Quantum Dynamics



Orthogonal basis of  $\delta$  functions  $\psi(x) \approx \sum_i c_i \delta(x_i)$   
 $c_i = \psi(x_i)$

Determine  $c_i(t)$  using FFT method, as described by Batista yesterday...

For cognoscenti – the basis functions in the FFT method are actually sinc functions



Nonorthogonal basis  
 $\psi(x,t) \approx \sum_i c_i(t) \chi_i(x)$

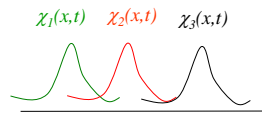
$$\int \chi_j(x) \psi(x,0) dx = \sum_i c_i(0) \int \chi_j(x) \chi_i(x) dx = \sum_i c_i(0) S_{ji}$$

$$\mathbf{S}^{-1} \vec{w}(0) = \vec{c}(0)$$

Insert into t-Dep Schrödinger Equation:  $\frac{d\mathbf{c}}{dt} = -i\mathbf{S}^{-1}\mathbf{H}\mathbf{c}$

Set of ODE's – integrate as discussed by Martyna

## Basis Set Approaches to Quantum Dynamics



t-dependent nonorthogonal basis set

$$\psi(x,t) \approx \sum_i c_i(t) \chi_i(x,t)$$

$$\int \chi_j(x,0) \psi(x,0) dx = \sum_i c_i(0) \int \chi_j(x,0) \chi_i(x,0) dx = \sum_i c_i(0) S_{ji}(0)$$

$$\mathbf{S}^{-1}(0) \vec{w}(0) = \vec{c}(0)$$

Insert ansatz into t-Dep Schrödinger Equation:  $\dot{\mathbf{C}} = -i\mathbf{S}^{-1}[(\mathbf{H} - i\dot{\mathbf{S}})\mathbf{C}]$

$$(\dot{\mathbf{S}}(t))_{ij} = \int \chi_i(x,t) \frac{\partial}{\partial t} \chi_j(x,t) dx$$

Note this is NOT the time derivative of the overlap matrix!

## Ideal Basis Set

- Ideally, our basis set would be
  - Compact
  - Accurately describe the wavefunction at all times
  - Easily determined at any point in time
- Fixed basis sets (orthogonal and nonorthogonal)
  - Must span all Hilbert space which is sampled by the wavefunction from beginning to end of simulation!
  - Recall Batista's example of a Gaussian basis function evolving in a harmonic potential – it does *not* deform and its center follows classical mechanics
  - With a fixed basis set, we must cover the entire configuration space accessed
  - Even in 1D, the problem is much worse if wavefunction is unbound – for free particle, we MUST have basis functions covering ALL space uniformly

## Time Evolution

- Batista already showed us one way to get around this – adaptively expanding a Gaussian basis set at each point in time
- Could we make a good guess at the evolution of these basis functions?
- If we really believe that classical mechanics is usually sufficient, there should be a way to take advantage of it!
- Why Gaussians (“coherent states”)?
  - Exhibit classical motion without deformation in harmonic potential
  - Minimum uncertainty states – as p/q localized as possible in QM
    - Localization is good for scaling – analogy to local bases in quantum chemistry
    - Localization lends itself well to numerical approximations (e.g. integrals)
    - Localization is needed for interface to electronic structure!
    - Overcomplete if all p,q allowed – this will be good for us!
- Would a basis set of Gaussians with classical EOM be sufficient in principle?
  - Need to have classical energy width!
  - Otherwise, energy conservation will restrict allowed space
  - If no hidden conserved quantities and all energies are allowed, infinite basis by this prescription will be overcomplete, hence the answer is YES

## The Full Multiple Spawning (FMS) Method

Wavefunction ansatz:  $\Psi(\mathbf{R};t) = \sum_I \sum_j C_j^I(t) \chi_j^I(\mathbf{R};t) |I\rangle$   
 Nuclear wavefunction      Electronic state

Nuclear wavefunction on each electronic state is a product of  $3N$  frozen Gaussian basis functions:

$$\chi_j^I(\mathbf{R};t) = e^{i\vec{p}_j^I(t) \cdot \mathbf{R}} \prod_{\rho=1}^{3N} \tilde{\chi}_{\rho}^I(R_{\rho}; \vec{R}_{\rho}(t), \vec{P}_{\rho}(t), \alpha_{\rho})$$

Semiclassical phase      Cartesian degrees of freedom      Position, momentum, width       $\text{Re}(\chi_j^I(\vec{R},t))$

Classical evolution for  $R(t)$  and  $P(t)$ .

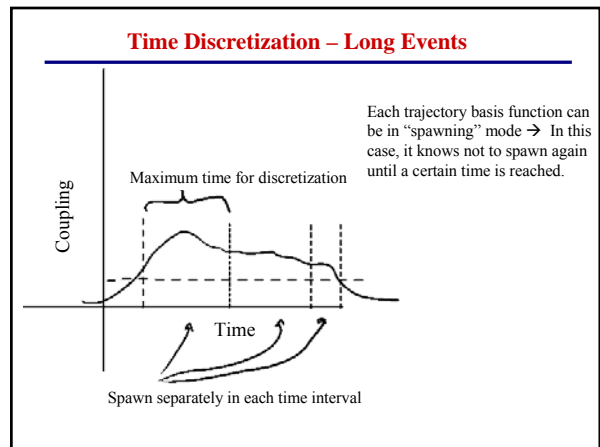
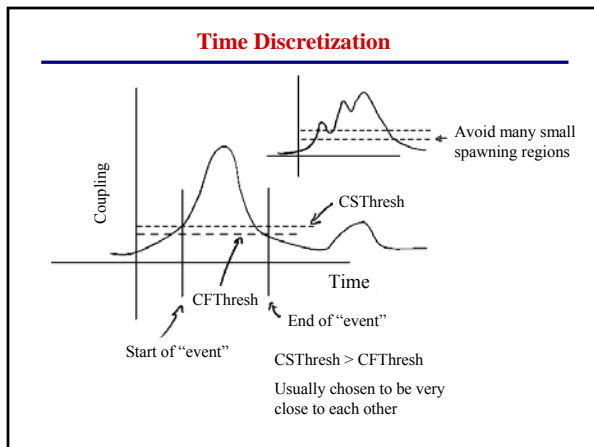
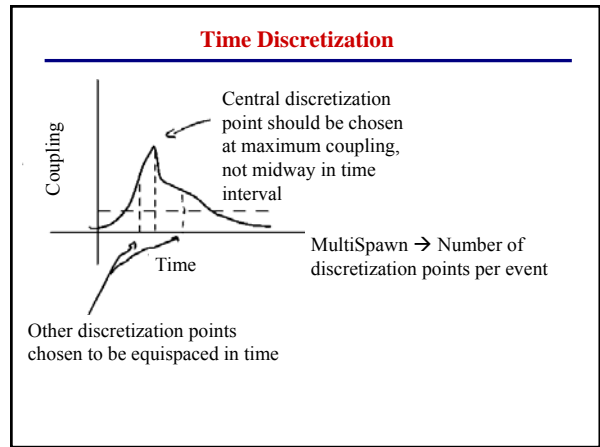
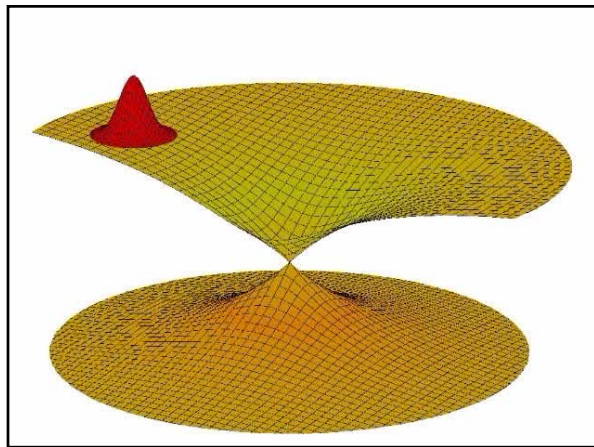
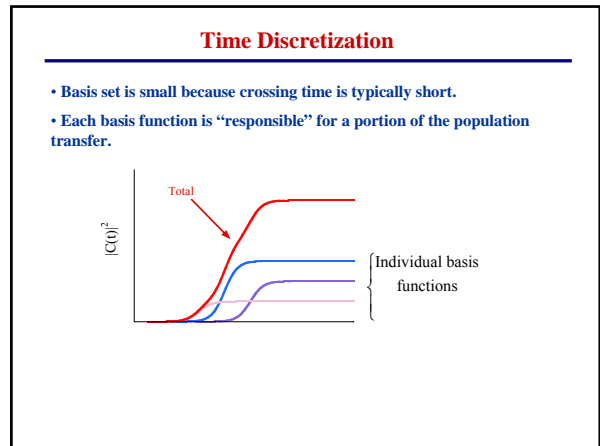
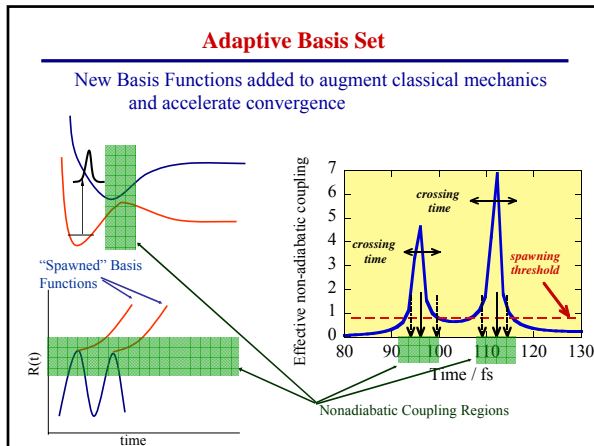
Variational principle for coefficients:  $\dot{\mathbf{C}}_I = -i\mathbf{S}_n^{-1}[(\mathbf{H}_n - i\dot{\mathbf{S}}_n)\mathbf{C}_I + \mathbf{H}_D \mathbf{C}_I]$

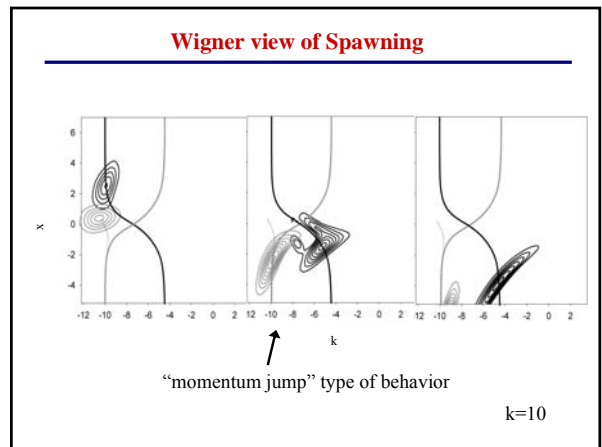
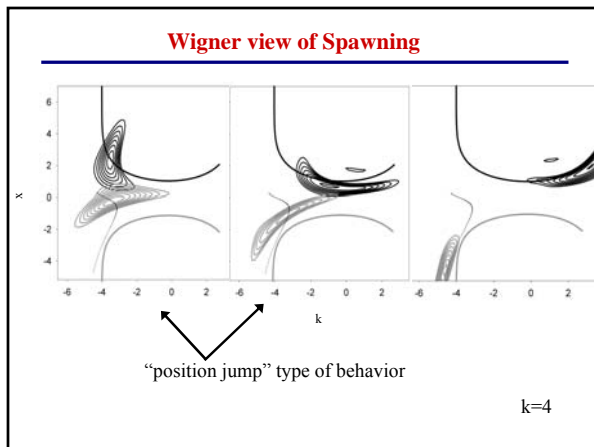
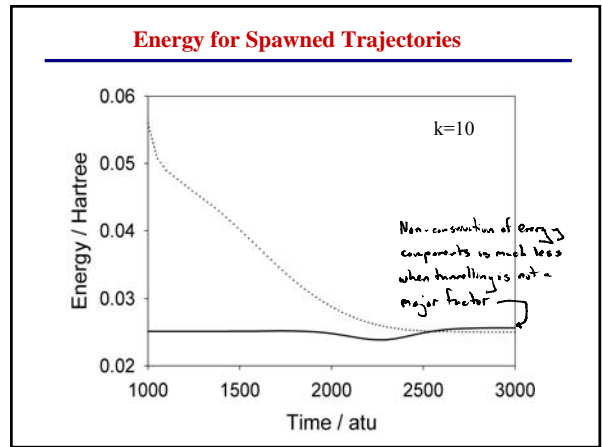
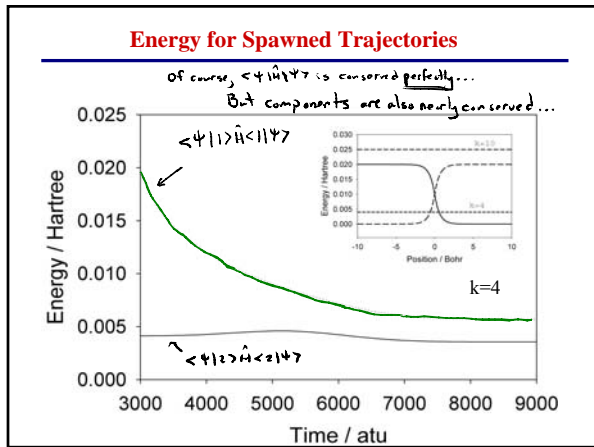
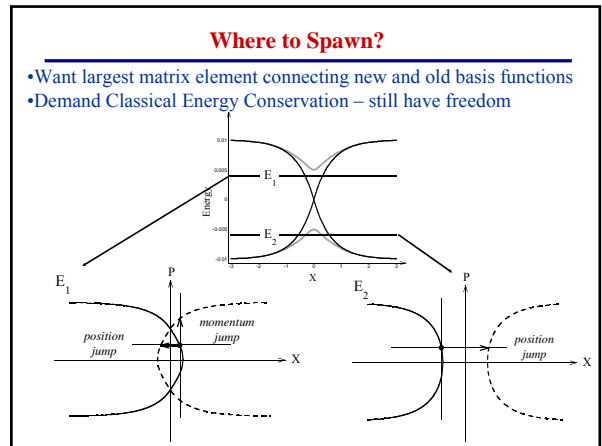
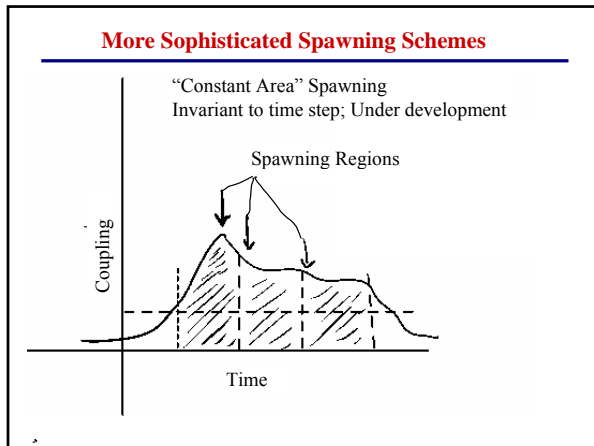
Nuclear overlap matrix

Hamiltonian matrix

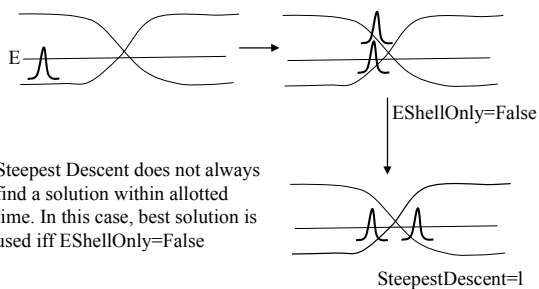
## Principle to Practice

- In principle, we do not need to do anything special – just to have enough “trajectory basis functions”
- But who cares if the basis set prescription would be sufficient in *principle*!?
- Our computers have limited memory and we have limited lifespans...
- Our basis set needs to be able to adapt to the problem!





### “Frustrated” Spawns



### Linear Dependence and Matrix Inversion

- When many gaussian basis functions are used, linear dependence may become an issue
- Controlled by regularization
  - Singular value decomposition of Overlap Matrix
  - Singular values below a threshold are discarded
  - Norm conservation is affected
- Overlap matrix does *not* have to be inverted. Solve by conjugate gradient (nice regularizing properties!):

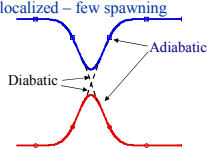
$$\mathbf{S}\dot{\mathbf{C}} = -i[(\mathbf{H} - i\dot{\mathbf{S}})\mathbf{C}]$$

Cost is  $N^2$  instead of  $N^3$ , but sparsity makes it  $O(N)$

similar scaling as surface-hopping...

### Diabatic vs Adiabatic Representations

- Diabatic
  - Smoother, therefore easier to integrate classical equations of motion for trajectories
  - Couplings can be large – much spawning required
  - If diabatic model is purely quadratic, benefit from exact propagation when couplings are small
  - Also, may be able to avoid integral approximations
  - Requires global information about PES – not suitable for *ab initio* MD
- Adiabatic
  - Nonadiabatic events are spatially/temporally localized – few spawning events lasting for short time
  - Classical mechanics is more nearly correct because electronic states are usually independent

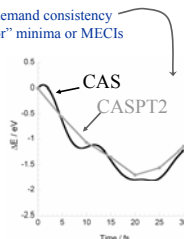


### Running A Simulation – FMS Dynamics

- FMS Dynamics
  - Widths need to be determined – these need to be tested for robustness – 25% changes should not affect amount of population transfer
  - Need to determine appropriate values for CSThresh and CFThresh – this needs to be checked for every new molecule
  - Run several trajectories without spawning, monitor nonadiabatic coupling, choose thresholds low enough to capture all population transfer but otherwise as large as possible

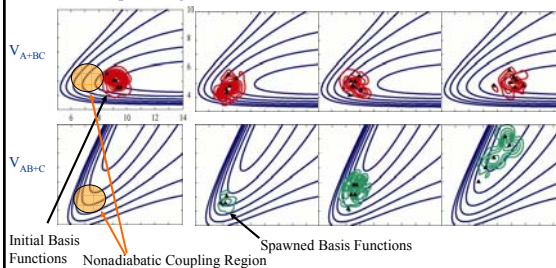
### Running a Simulation – AIMS Dynamics

- *Ab initio* multiple spawning
  - Need to ensure that electronic structure method is accurate
  - This involves *iteration* between AIMS and high-level electronic structure
  - Example with CASSCF – need to choose an active space and state-averaging
    - State ordering and S2/S1 gap at Franck-Condon point
    - Preliminary dynamics calculation
    - Calculate CASPT2 PESs along CAS trajectories – demand consistency
    - Minimize snapshots from dynamics to find “attractor” minima or MECIs
    - Verify energetics of these points with CASPT2 / MS-CASPT2
    - If inconsistent, dynamics results are discarded – continue search for active space

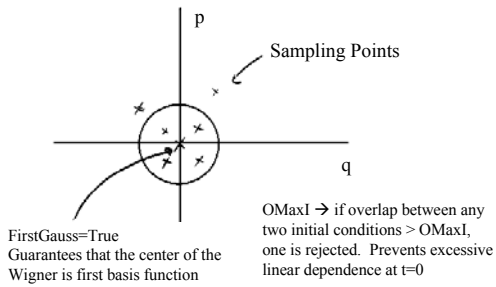


### Multiple Spawning

- Two Diabatic Surfaces (A+BC → AB+C collinear model)
- Triangles denote centroids of Gaussians – not all are populated!
- Linear dependence “prunes” number of Gaussians spawned
- “Back-spawning” is allowed



### Initial Conditions



### Initial Conditions

- Wigner distribution – only obtainable in practice within harmonic approximation
- Problematic above  $v=0$  because of negative regions; difficult to sample
- Not appropriate for condensed phase because of many low frequency vibrations
- Quasiclassical + Wigner – Use Wigner for chromophore and quasiclassical for remainder – for systems where chromophore/solvent decomposition is obvious

### Absorption and Resonance Raman Spectra

Time-domain Formulation of Spectroscopy (Heller)

Electronic Absorption Spectrum:

$$\sigma_A(\omega_i) = C \omega_i \int_{-\infty}^{\infty} \langle \phi_i | \phi_j(t) \rangle \exp(i\bar{\omega}_i t) dt$$

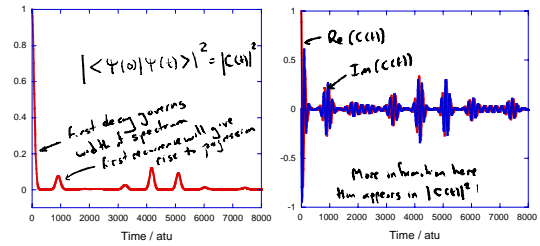
$$|\phi_i\rangle = \mu(\mathbf{R}) |i\rangle ; |\phi_j(t)\rangle = \exp(-i\hat{H}_{el} t) |\phi_j\rangle$$

Resonance Raman Excitation Profiles:

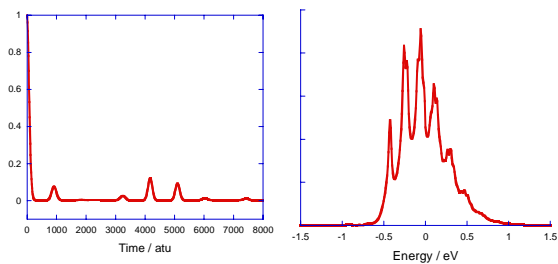
$$\sigma_R^{\omega_i}(\omega_i) = C' \omega_i \omega_i^3 \left| \int \langle \phi_j | \phi_i(t) \rangle \exp(i\bar{\omega}_i t) dt \right|^2$$

- Anharmonicity and Duschinsky rotation included
- Coordinate dependence of transition dipole can be included

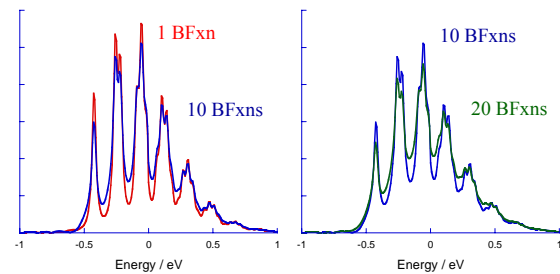
### Correlation Functions



### Correlation Function $\rightarrow$ Spectrum

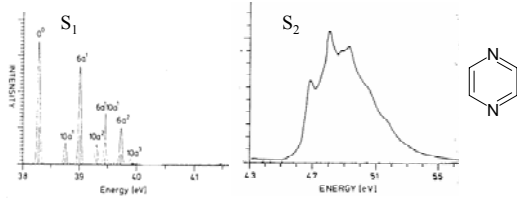


### Convergence



Ethylene V State, Vibronic Coupling Model

### Pyrazine Electronic Absorption Spectra

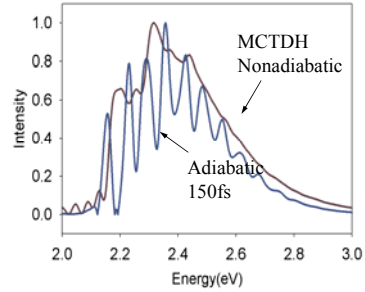


- Structureless  $S_2$  spectrum implying fast  $S_2 \rightarrow S_1$  internal conversion
- 3D/4D/24D vibronic coupling (Domcke/Cederbaum/Meyer/Koppel)

$$H_0 = \frac{1}{2} \sum \omega_j \left( -\frac{\partial^2}{\partial Q_j^2} + Q_j^2 \right)$$

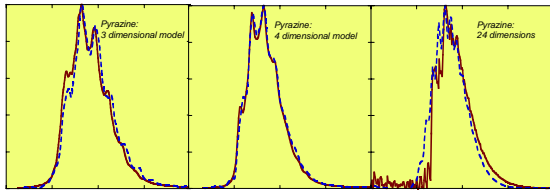
$$H = \begin{bmatrix} E_1 + H_0 + \kappa_1^{(1)} Q_1 + \kappa_{6a}^{(1)} Q_{6a} & \lambda Q_{10a} \\ \lambda Q_{10a} & E_1 + H_0 + \kappa_1^{(2)} Q_1 + \kappa_{6a}^{(2)} Q_{6a} \end{bmatrix}$$

### Effect of Nonadiabaticity on Spectrum



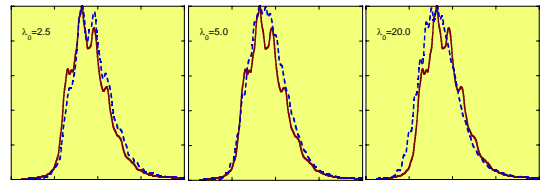
- $C(t)$  limited to 150fs – still leads to significant structure w/o nonadiabaticity
- MCTDH for comparison

### Results for Electronic Spectra



- Prespawning used in all of these calculations
- Final number of basis functions ranges from 100-900
- Somewhat better agreement from IVR methods w/  $10^6$  trajectories (Thoss, Miller and Stock, JCP (2000))
- Fewer basis functions may suffice in adiabatic representation

### Dependence on Spawning Threshold

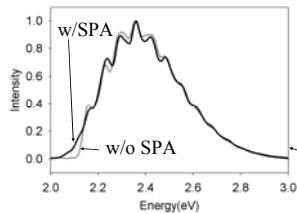


- Large spawning thresholds get basic envelope correct
- Small thresholds required to reproduce detailed structure
- Smooth convergence observed

### Saddle-Point Approximations

- Integrals which are difficult to evaluate in AIMS are treated with saddle point approximation:

$$\langle \chi'_i | V_D | \chi'_j \rangle \approx \langle \chi'_i | \chi'_j \rangle V_D(\bar{R})$$



Centroid of Product Gaussian (Higher order variants possible, but require Hessian)

Minimal effect on spectrum

### Accuracy of FMS Method: The Spin Boson Model

- Two level system linearly coupled to a Harmonic bath:

$$H = H_S + H_B + H_{S-B}$$

- In the diabatic representation:

$$H = \sum_{k=1,2} |\varphi_k\rangle h_k \langle \varphi_k| + \{|\varphi_1\rangle \Delta \langle \varphi_2| + c.c.\}$$

$$h_k = h_0 + \sum C_j X_j \quad ; \quad h_0 = \frac{1}{2} \sum \omega_j (P_j^2 + X_j^2)$$

- $\omega_j$  -- vibrational frequency of the  $j$ th oscillator
- $C_j$  -- dimensionless linear coupling of the  $j$ th oscillator
- $\Delta$  -- electronic coupling
- $C_j$  -- dimensionless position and momentum
- $X_j, P_j$

In the form of Domcke-Cederbaum-Koppel vibronic coupling models  
Often used as a model for conical intersection problems



## The Spin Boson Model

- Bath properties are determined by the spectral density:

$$J(\omega) = \frac{\pi}{2} \sum_j C_j^2 \delta(\omega - \omega_j)$$

- The case of an Ohmic bath:

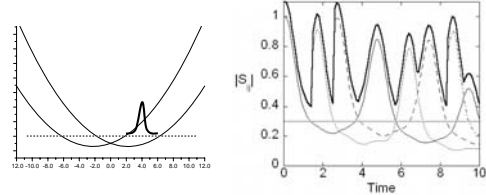
$$J(\omega) = \frac{\pi}{2} \alpha \cdot e^{-\omega/\omega_c} \quad C_j = \left[ \frac{2}{\pi} \Delta \omega J(\omega_j) \right]^{1/2}$$

### Exact Results:

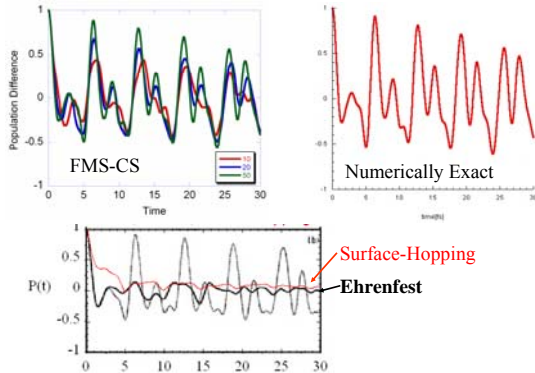
- 400 dimensional model
  - C. H. Mak and D. Chandler, *Phys. Rev. A* **44**, 2352 (1991)
  - D. E. Makarov and N. Makri, *Chem. Phys. Lett.* **221**, 482 (1994)
  - R. Egger and C. H. Mak, *Phys. Rev. B* **50**, 15210 (1994)
- 4 dimensional model
  - G. Stock, *J. Chem. Phys.* **103**, 1561 (1995)
  - Multiconfigurational Time-Dependent Hartree (MCTDH)
    - Manthe, Meyer, Cederbaum *Chem Phys Lett* **165**, 163 (1990)

## Extended Coupling Regions

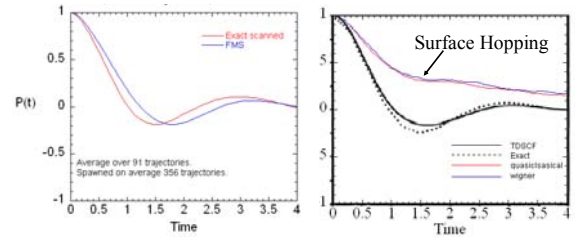
- Adaptive expansion is tailored to time/space-local breakdowns of the Born-Oppenheimer approximation
- What about cases where the BOA breaks down completely?
- Continuous spawning – ensure that basis functions always have “partners” on other electronic states when they are coupled. Why is this even practical? PESs tend to be nearly parallel in extended coupling regions!



## Spin Boson Tests – 4 DOF

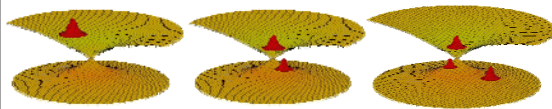


## Spin Boson Tests – 400 DOF



In high dimensionality and finite T, convergence is actually *faster* – basis function separation is *physically correct*. (See early work by Neria & Nitzan, Rossky, Bittner)

## Multiple Spawning



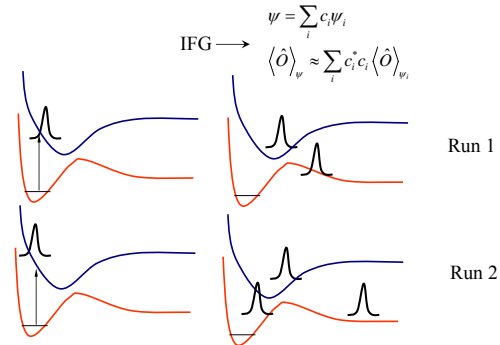
Time →

- FMS is a **hierarchy** of methods
- Dynamics on a single electronic state → coupled frozen Gaussians (Heller, Metiu)
- Useful Approximations in *Ab Initio* Dynamics
  - Independent First Generation Approximation
    - Different initial Gaussian wavepackets are uncoupled
    - Includes coherences between basis function and its “children”
    - Neglects coherence between initial basis functions
  - Saddle-Point Approximation for Integrals
    - Use locality of Gaussians to evaluate integrals using local information

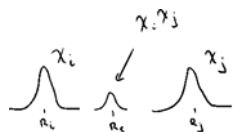
$$\int \chi_i(R) f(R) \chi_j(R) dR \approx f(R_c) \int \chi_i(R) \chi_j(R) dR$$

Centroid of  $\chi_i, \chi_j$

## Independent First-Generation Approximation



### Saddle-Point Approximations



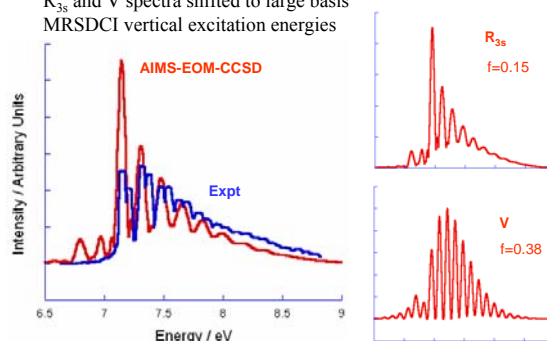
$$\int \chi_i(R) f(R) \chi_j(R) dR =$$

$$\int \chi_i(R) \chi_j(R) \left[ f(R_0) + (R-R_0) \frac{\partial f}{\partial R} \Big|_{R_0} + \frac{(R-R_0)^2}{2} \frac{\partial^2 f}{\partial R^2} \Big|_{R_0} + \dots \right] dR \approx f(R_0) \int \chi_i(R) \chi_j(R)$$

- Taylor expansion of potential around maximum of product
- First-order term requires gradient at maximum of product
- Second-order term can be included if Hessian of potential available

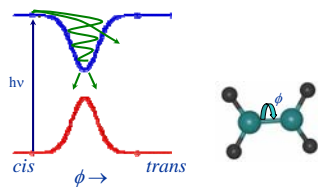
### EOM-CCSD Spectra for Ethylene

$R_{3s}$  and V spectra shifted to large basis MRSDCI vertical excitation energies



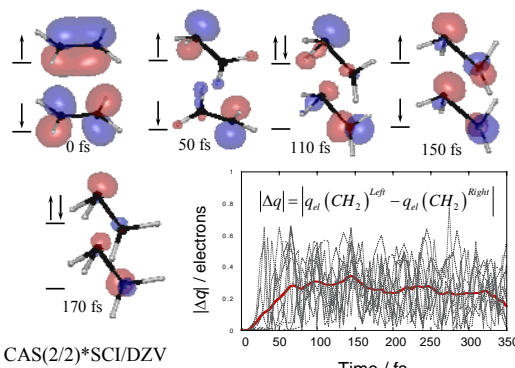
### Photochemistry /Photophysics of Ethylene

- Prototype for *cis-trans* isomerization
- Conventional Picture:

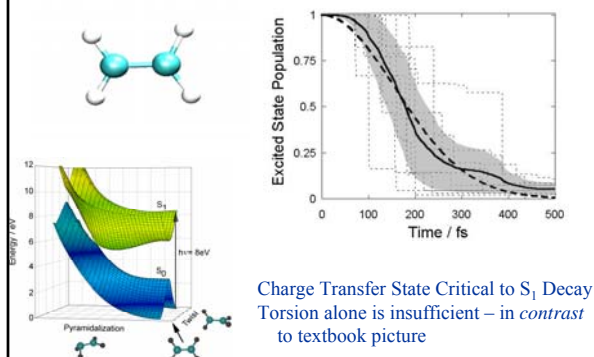


- One-dimensional nature - emphasizing torsion
- Chemistry and Isomerization occur on  $S_0$
- Experimental Photoproducts: *cis-trans* isomers,  $HC\equiv CH$ ,  $H_2$ , H
- Excited State Lifetime from Absorption Spectrum: < 50 fs
- No fluorescence

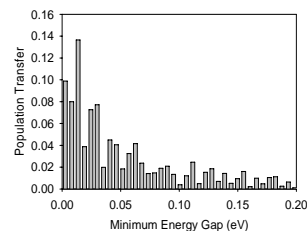
### AIMS Excited State Dynamics of Ethylene



### Ethylene Dynamics Overview

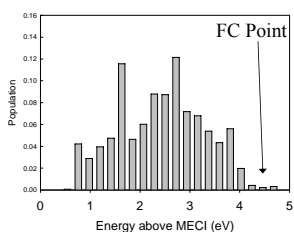


### Do Conical Intersections Matter?



Regions near intersections dominate nonadiabatic events

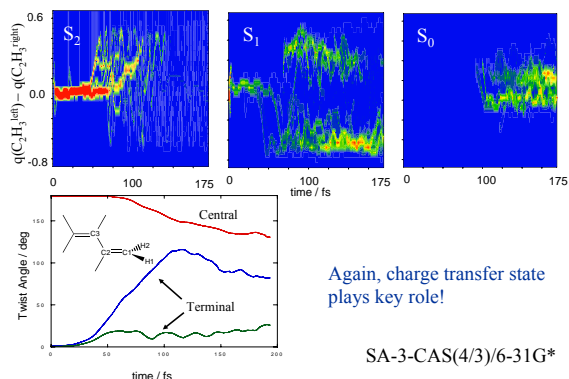
### Do Minimal Energy Conical Intersections Matter?



Minimal energy point along seam may have little significance!  
Still useful in cartoon pictures of mechanisms



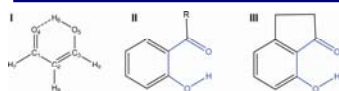
### Photoinduced *cis-trans* Isomerization - Butadiene



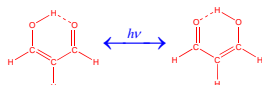
Again, charge transfer state plays key role!

SA-3-CAS(4/3)/6-31G\*

### Excited State Intramolecular Proton Transfer

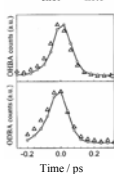
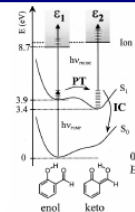


- I) Malonaldehyde
- II) R = H o-hydroxybenzaldehyde (OHBA)
- OH salicylic acid (SA)
- CH<sub>3</sub> o-hydroxyacetophenone (OHAP)
- NH<sub>2</sub> salicylamide (SAM)
- OCH<sub>3</sub> methyl salicylate (MS)
- III) 7-hydroxy-1-indanone (7HIN)



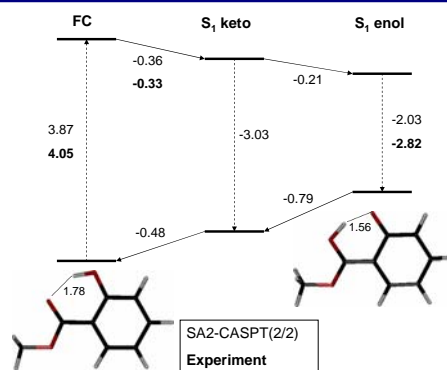
No H/D isotope effect!

Experiments: Lochbrunner, Stolow, Riedle, Zewail ...



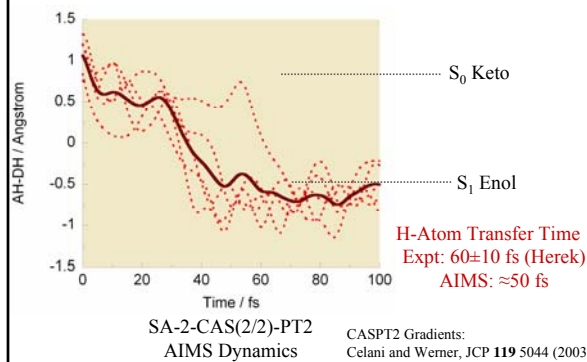
Lochbrunner, JCP (2001)

### Methyl Salicylate Energy Diagram



SA2-CASPT(2/2)  
Experiment

### H-Atom Transfer in Methyl Salicylate

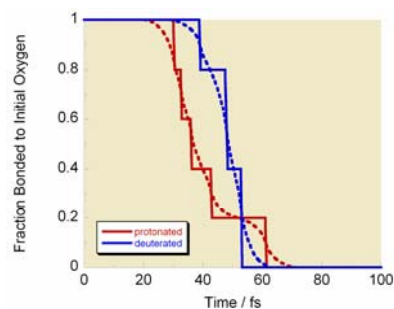


H-Atom Transfer Time  
Expt: 60±10 fs (Herek)  
AIMS: ≈50 fs

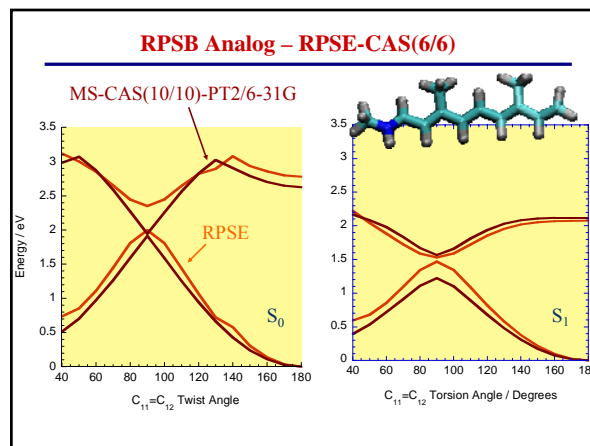
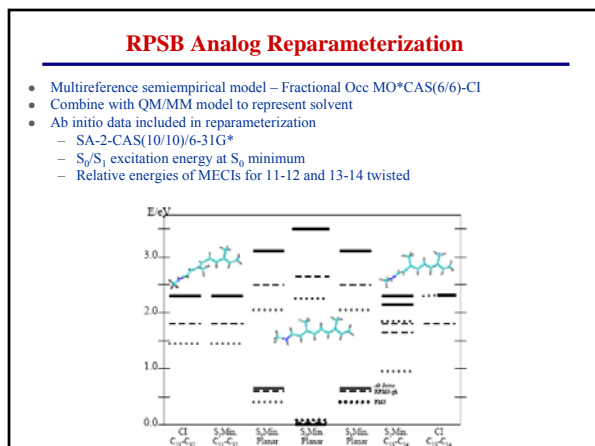
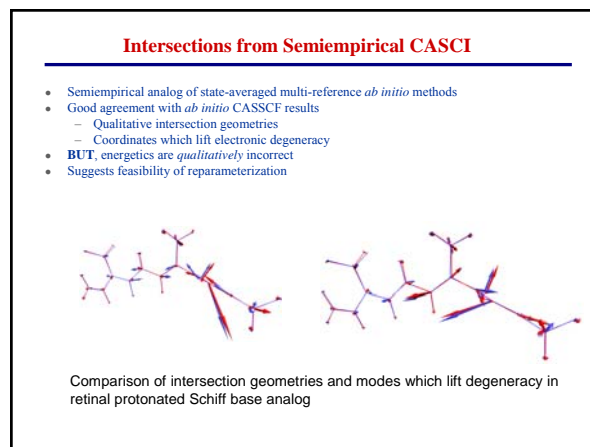
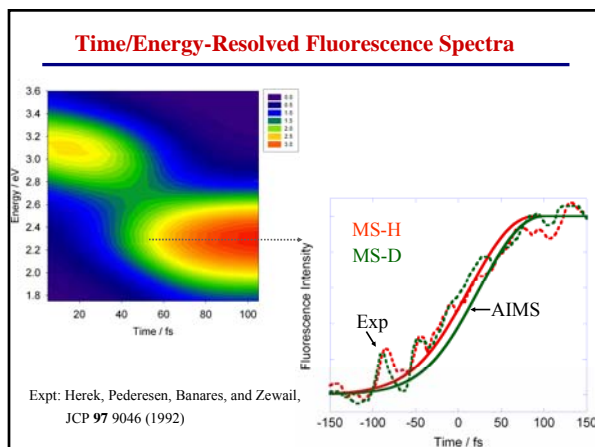
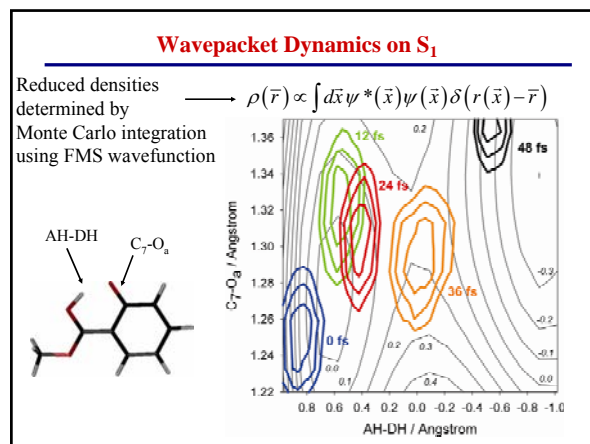
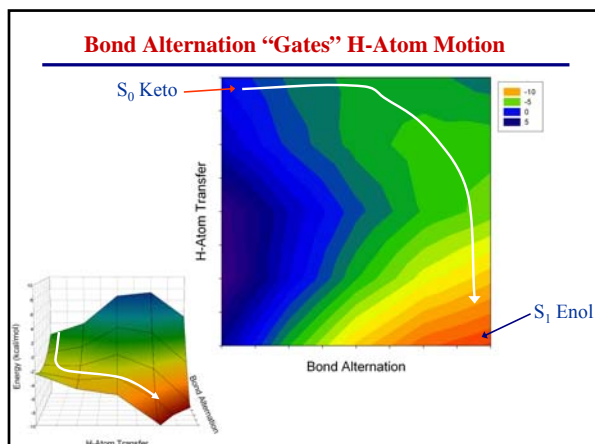
SA-2-CAS(2/2)-PT2  
AIMS Dynamics

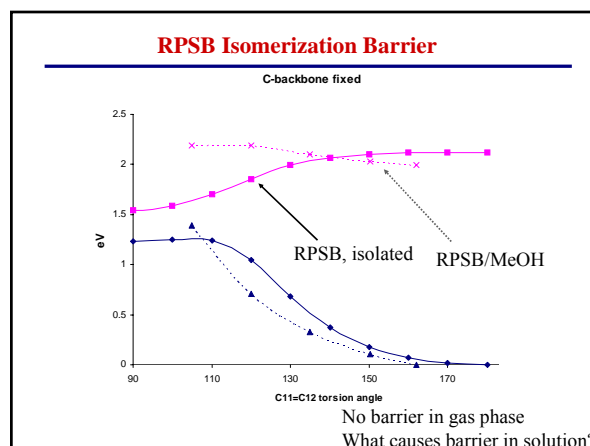
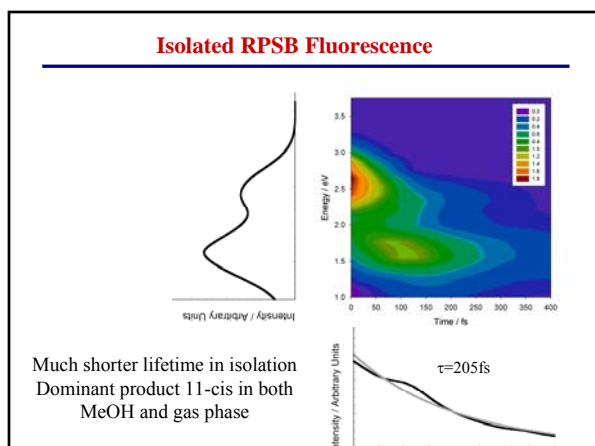
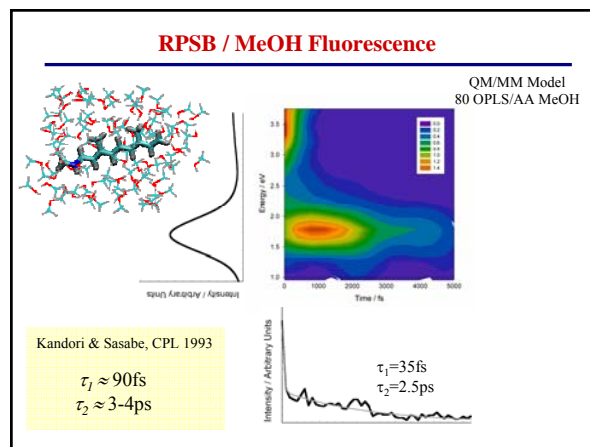
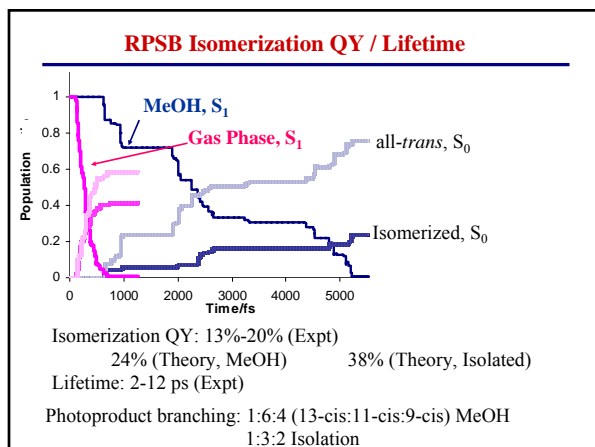
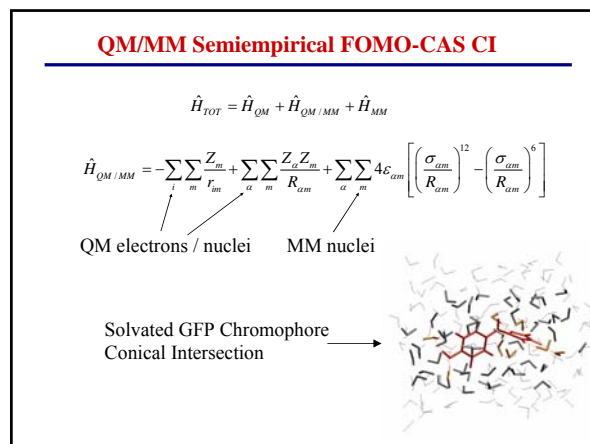
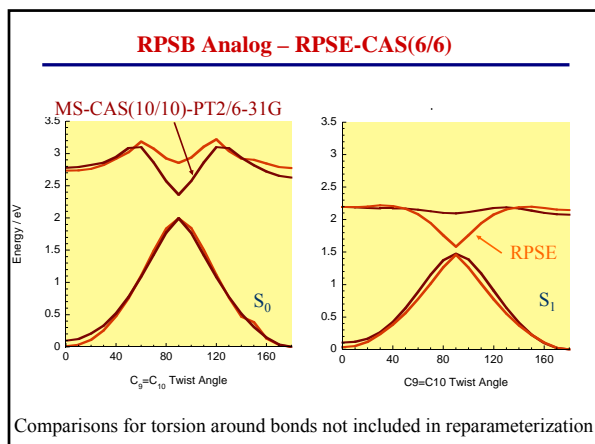
CASPT2 Gradients:  
Celani and Werner, JCP 119 5044 (2003)

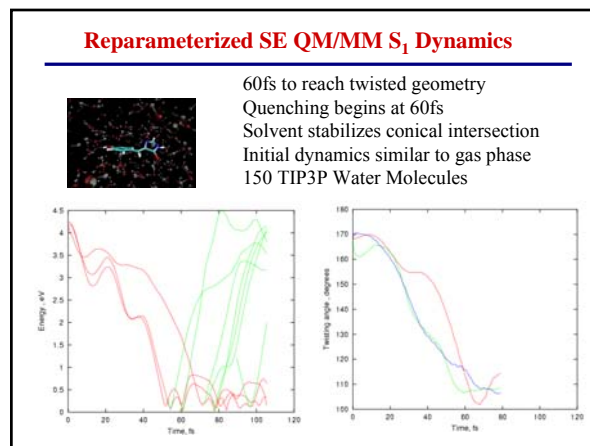
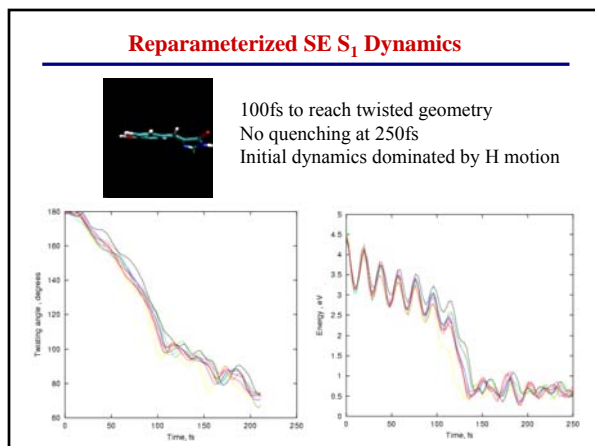
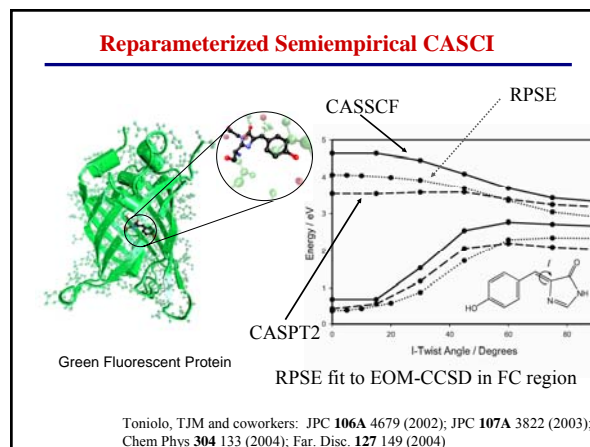
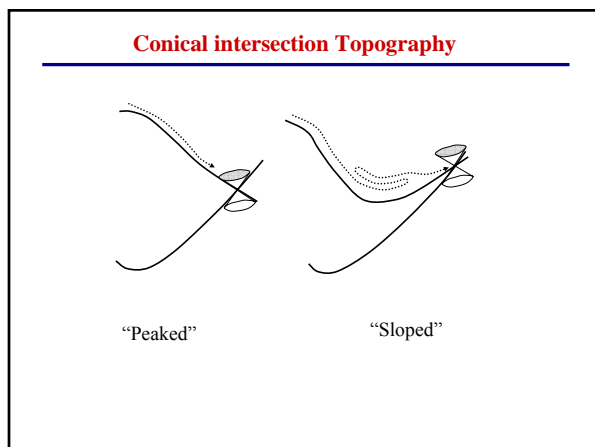
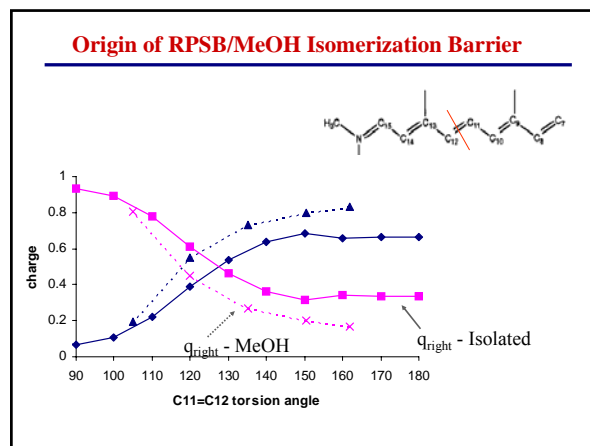
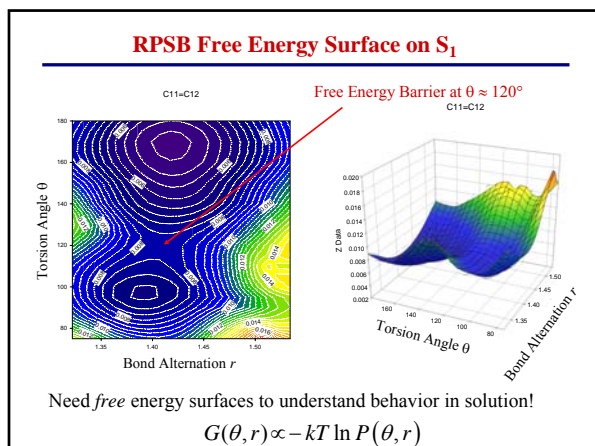
### Isotope Effects in MS ESIPT

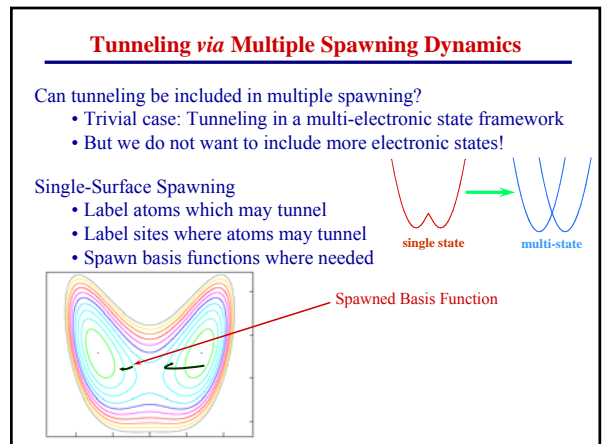
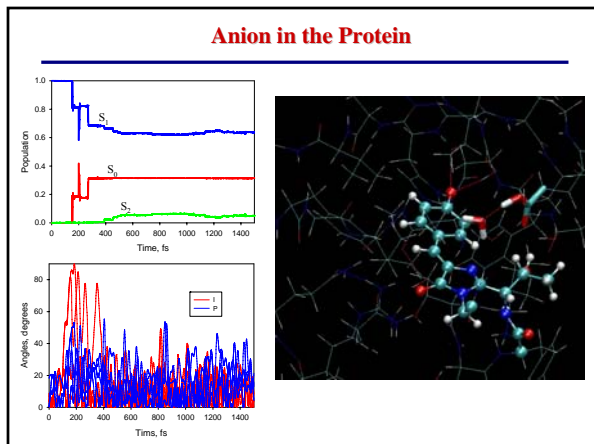
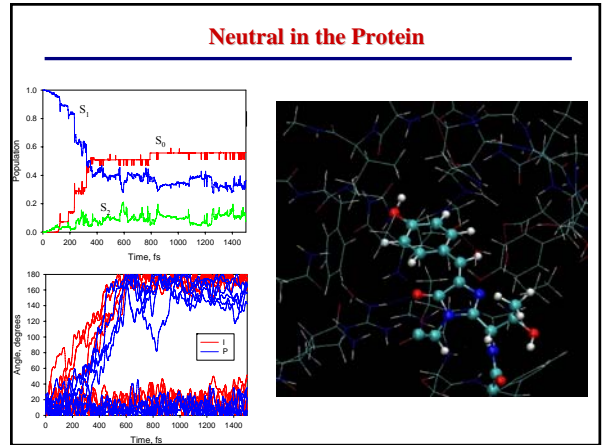
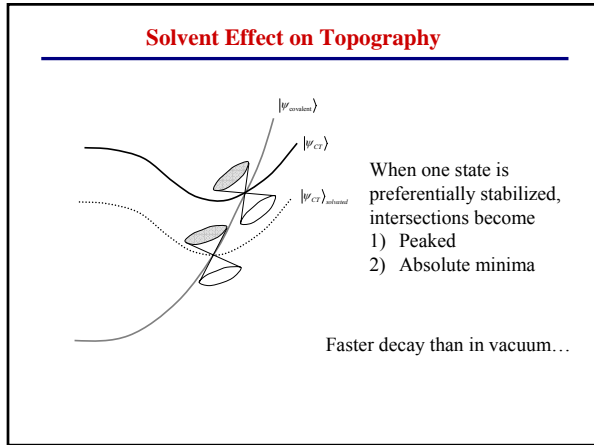
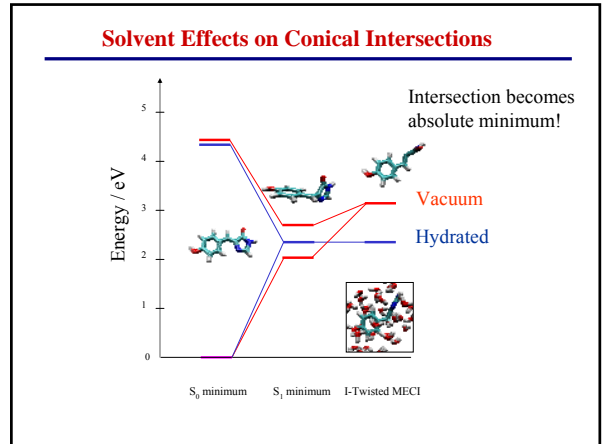
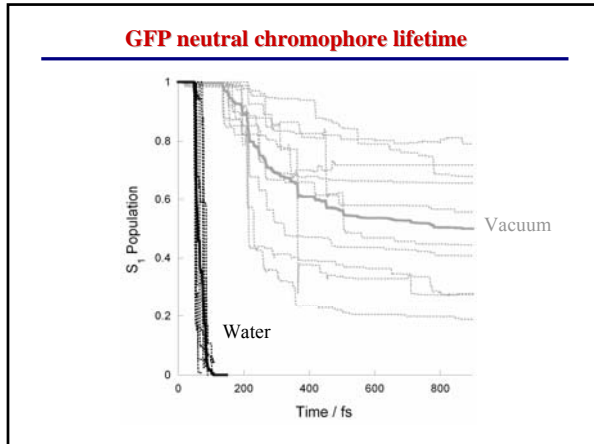


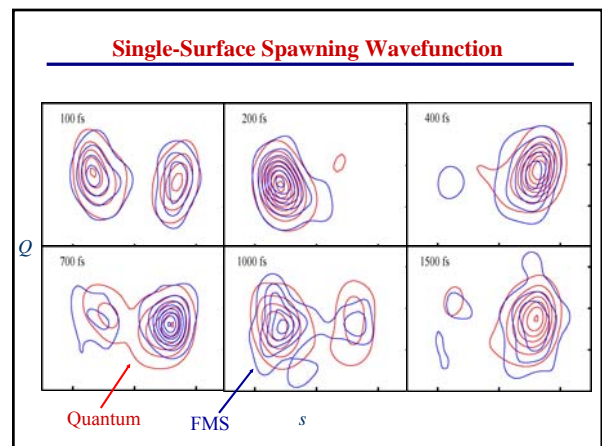
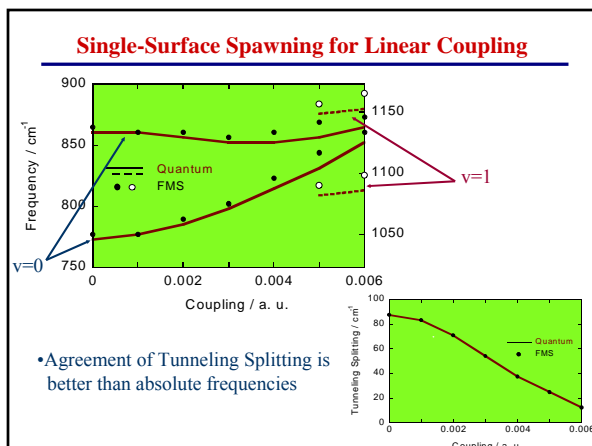
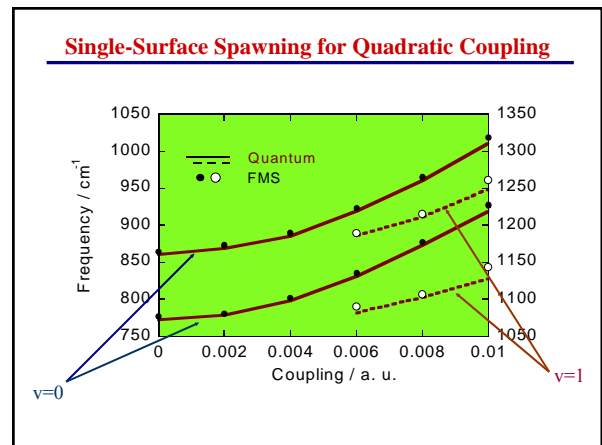
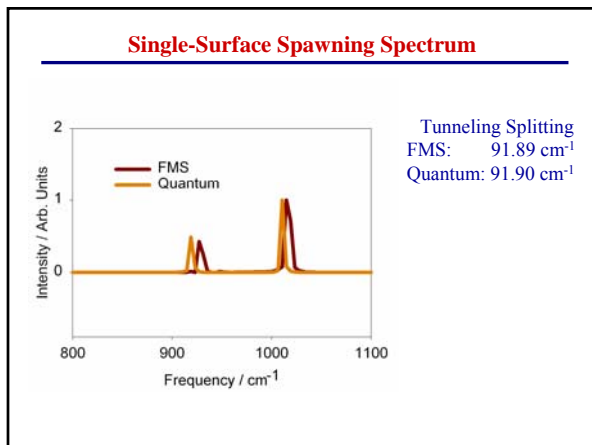
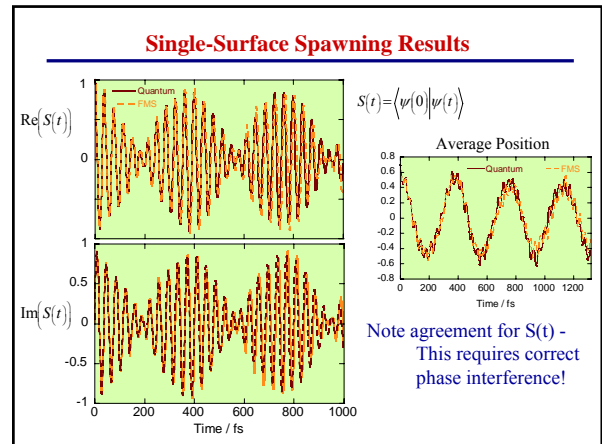
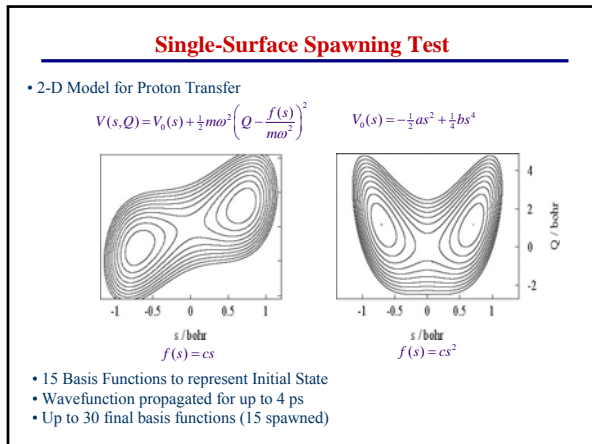
No significant isotope effect!













## Acknowledgments

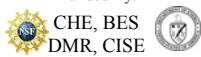


Martinez Group, University of Illinois at Urbana-Champaign, May 11, 2006

### Collaborators

H.-J. Werner – FMS-MolPro  
J. J. P. Stewart – FMS-MOPAC  
M. Persico – FMS-MOPAC  
A. Stolow  
C. Bardeen  
J. Moore  
K. Schulten

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