

# Chemical Dimensions of Quantum Dynamics

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## Quantum Dynamics

- Problem: ultrafast (fs-ps) coupling of multiple electronic and nuclear degrees of freedom in chemical systems

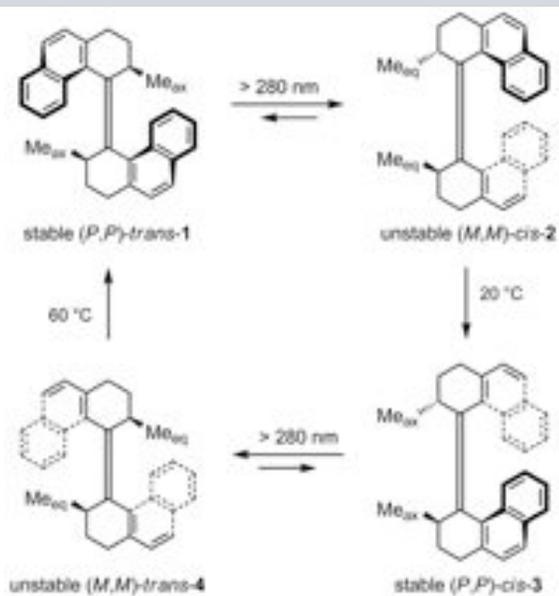
- Solution:

$$i \frac{\delta \psi}{\delta t} = H \psi$$

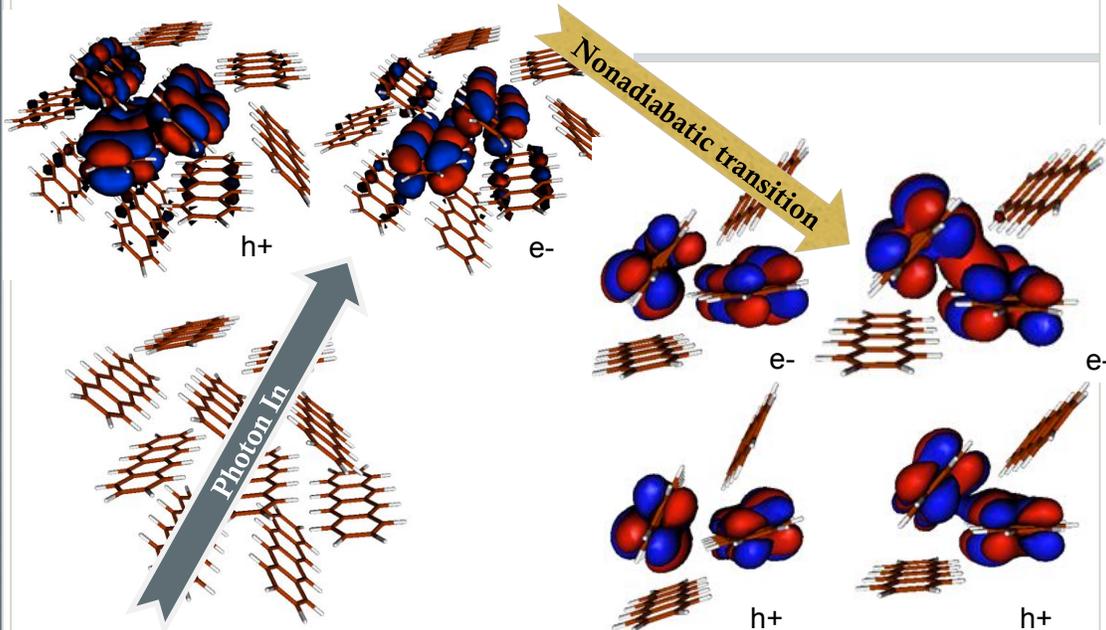
- *Scaling with system size is poor*
- *Have to create potentials  $V(R)$*
- *Computations are cumbersome*

# Molecular Quantum Dynamics

- Photo chemistry:
  - Molecular motors
- Singlet Fission in organic solar cells:
  - $S_0 + \text{photon} \rightarrow T_1T_1$
  - Charge multiplication, increased efficiency



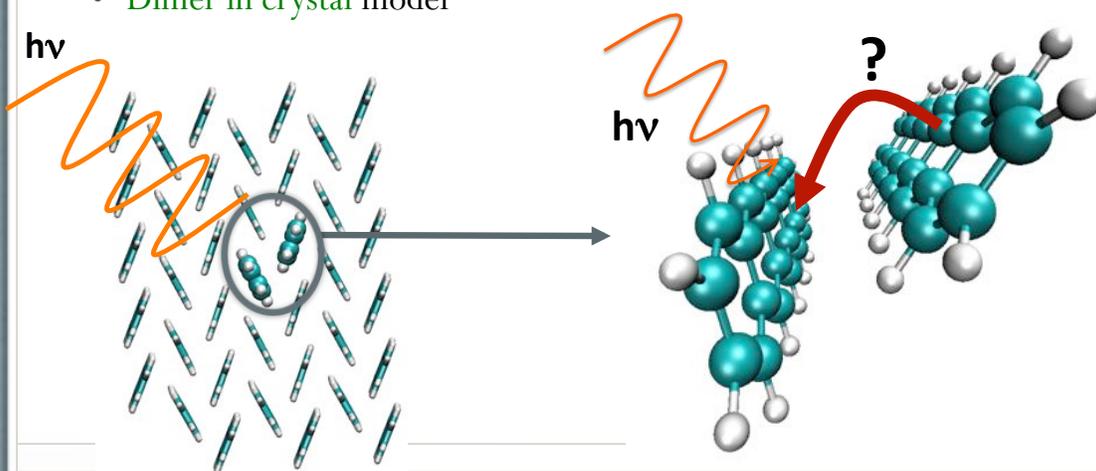
## Singlet Fission



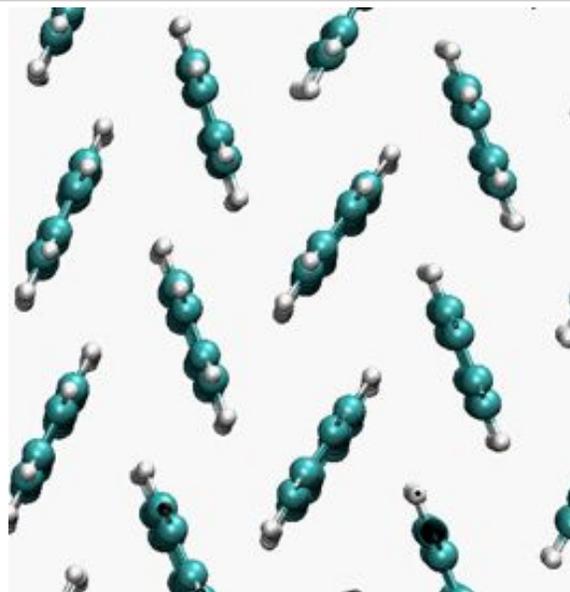
Zimmerman et al, *Nature Chem.* 2010, *J. Am. Chem. Soc.* 2011, *Acc. Chem. Res.* 2013

# Crystal Mechanism

- Electronic-vibrational coupling responsible for ultrafast events
  - Need to understand degrees of freedom in nuclei
  - Electronic structure difficult to obtain
- **Dimer in crystal** model



# Intermolecular Vibration



# Strong Correlations

- To treat multiple excitons by *ab initio* theory:
  - Need low-cost many-body theory for electrons
  - Most-popular method will not work: TD-DFT

- CASSCF (and variants including MR-CI, MRMP)

$$|\Psi\rangle = \sum c_n |\phi_n\rangle$$

$\phi_n$ =Slater determinants with “complete” set of electron configurations  
**Optimized orbitals (expensive!)**

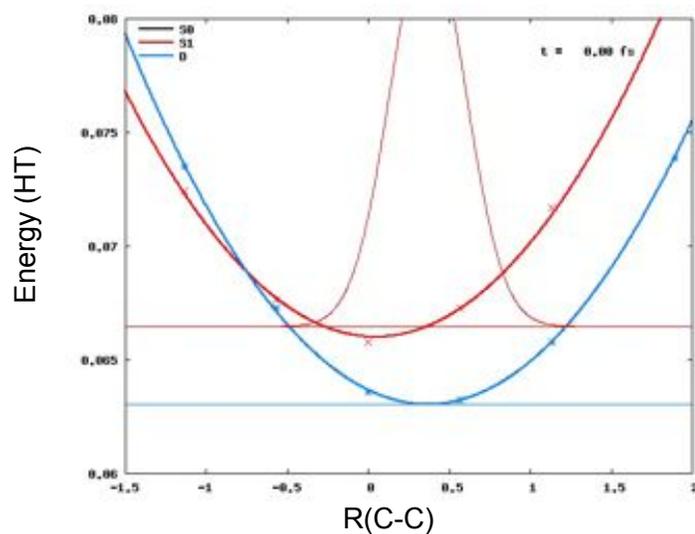
- RAS Spin Flip**

$$|\Psi\rangle = \sum_{\lambda \in A,h,p} r_\lambda |\phi_\lambda\rangle$$

$\phi_\lambda$ =Slater determinants with reduced set of electron configurations  
**High spin orbitals (inexpensive)**

Zimmerman, Head-Gordon et al. *J. Chem. Phys.* 2012, *Phys. Chem. Chem. Phys.* 2013

# Singlet Fission Mechanism



— S1  
 — D

1D solution of

$$i \frac{\delta \Psi}{\delta t} = H \Psi$$

Initial condition:  
 Zero-point state of  
 S0 excited to S1

Thanks  
 David Swenson

- Experiment: 80% converted by 200 fs in pentacene

# Coordinates for Dynamics

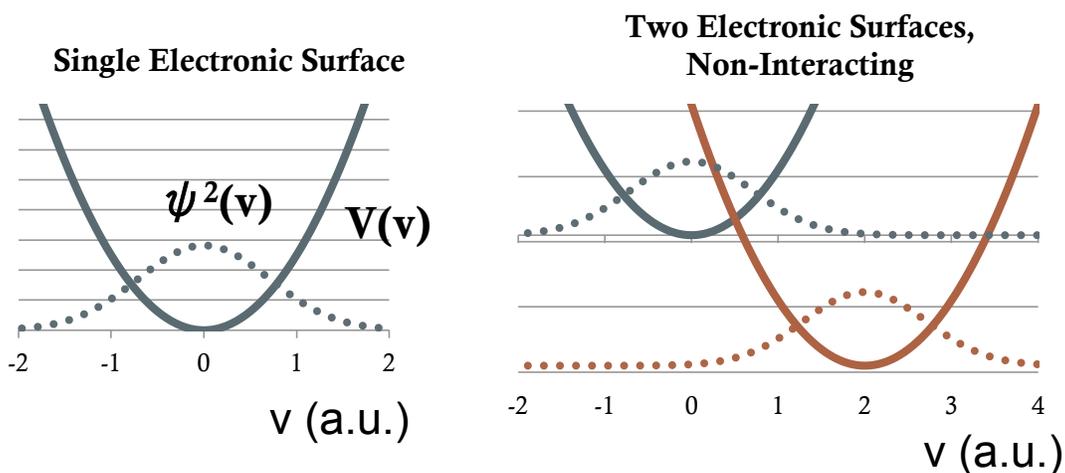
$$H = T + V \quad \longrightarrow \quad \begin{aligned} T &= 1/2 \dot{x}^T M \dot{x} \\ V &= 1/2 \Delta x^T F \Delta x \end{aligned}$$

$$F_{ij} = \frac{\delta^2 E}{\delta x_i \delta x_j} \quad \longrightarrow \quad \begin{aligned} &v_i \quad \text{Vibrational coordinates} \\ F_{ij}^v &\cong \delta_{ij} \omega_i^2 \quad \text{Coordinates minimally interact} \\ E_{i,n} &= \hbar \omega_i \left( n + \frac{1}{2} \right) \end{aligned}$$

*Quadratic approximation for atomic motion*

These quantized states of  $H\psi = E\psi$  are experimentally measurable

# Oscillator Stationary States



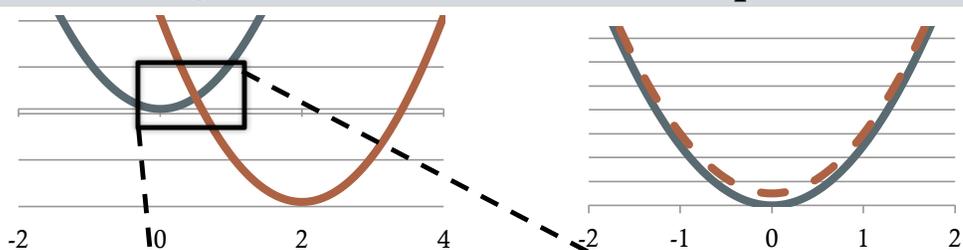
Harmonic oscillator coordinates:

- Lengths and energies are normalized
- Small (*not zero!*) off-diagonal coupling in  $F$

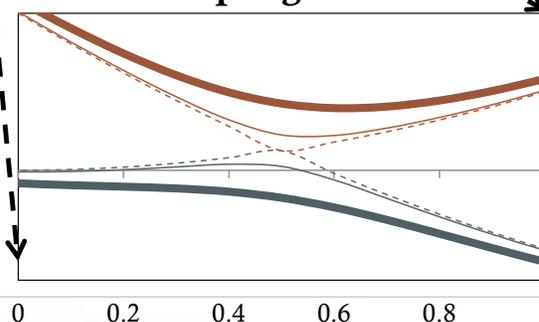
# Vibration Classification

Tuning modes

Inconsequential modes

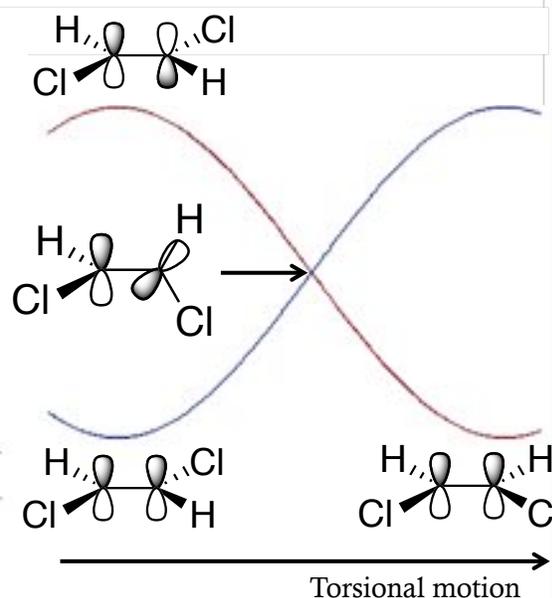
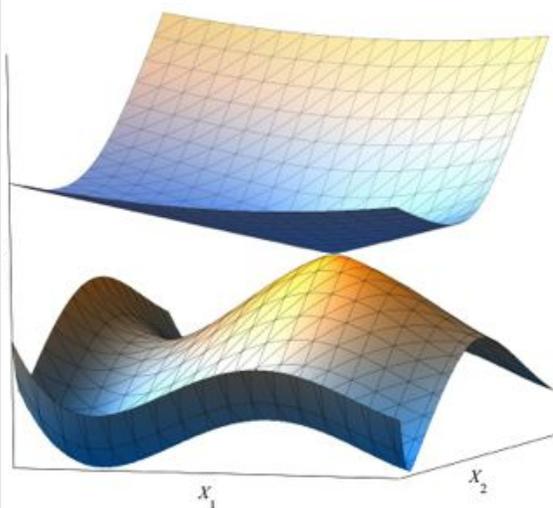


Coupling modes

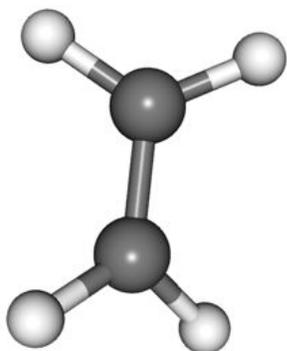


$$\begin{matrix}
 H_{11}(v_t) & H_{12} = \lambda v_c \\
 H_{12} = \lambda v_c & H_{22}(v_t)
 \end{matrix}$$

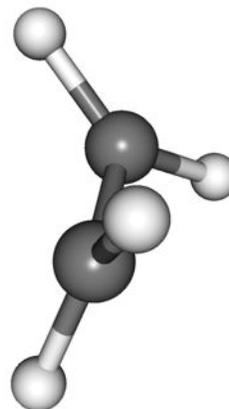
# Conical Intersections



## Internal Coordinates



## Cartesian Coordinates



Bond stretches during dihedral rotation an artifact of Cartesian vibrational vectors – “large amplitude” motions

## Delocalized Internal Coordinates

- Starting with ( $>3N-6$ ) primitive internals

$$B_{ij} = \frac{\delta q_i}{\delta x_j} \quad B^p B^{p,T} (UR) = \begin{pmatrix} \Lambda & 0 \\ 0 & 0 \end{pmatrix} (UR)$$

- U: non-redundant internal coordinates ( $3N-6$ )
- R: redundant set

$$B = U^T B^p \quad X(k+1) = X(k) + \left[ (BB^T)^{-1} B \right]^T (q - q(k))$$

Baker JCP 1996

# Coordinates for Vibrations

## Cartesians

$$F_{ij} = \frac{\delta^2 E}{\delta x_i \delta x_j}$$

$$F_{ij}^v \cong \delta_{ij} \omega_i^2$$

## Internal Coordinates

$$F_{ij}^{IC} = \frac{\delta^2 E}{\delta q_i \delta q_j}$$

$$F_{ij}^{v,IC} \cong \delta_{ij} \omega_i^2$$

At  $v_i=0$ , vibration vectors are parallel for Cartesians vs. ICs  
 At  $|v_i|>0$ , vibrations are linear (or curvilinear)

***Internals are a natural coordinate system for molecules.***

# IC Vibrations

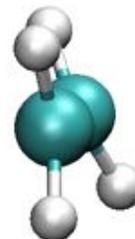
$$T = \frac{1}{2} \dot{x}^T M \dot{x} = \frac{1}{2} \dot{q}^T G_m^{-1} \dot{q} \quad V = \frac{1}{2} \Delta x^T F \Delta x = \frac{1}{2} \Delta q^T F_q \Delta q$$

$$G_m = B M^{-1} B^T \quad F_q = (B^{-1})^T F B^{-1}$$

$$G_m F_q L = \omega^2 L \quad \text{not symmetric}$$

$$(G_m^{1/2} F_q G_m^{1/2})(G_m^{-1/2} L) = \omega^2 (G_m^{-1/2} L)$$

$$G_m^{-1/2} L \quad \text{Curvilinear, mass-weighted vibrational coordinates}$$



# Vibronic Coupling Hamiltonian

$$\hat{H} = T(\mathbf{v}) + \begin{bmatrix} \Delta & 0 \\ 0 & -\Delta \end{bmatrix} + \sum_{i=1}^{3N-6} \left\{ \frac{\omega}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} v_i^2 + \begin{bmatrix} a_i^{(1)} & 0 \\ 0 & a_i^{(2)} \end{bmatrix} v_i + \begin{bmatrix} 0 & b_i \\ b_i & 0 \end{bmatrix} v_i \right\}$$

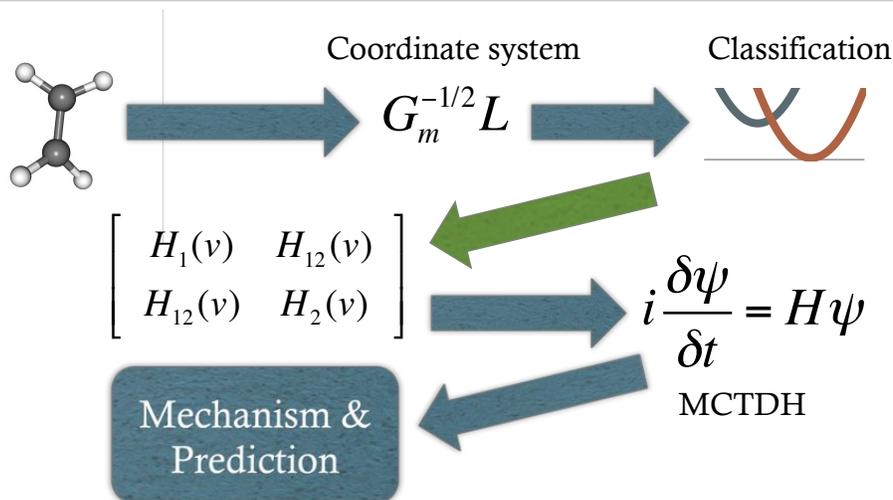
$$+ \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} \left\{ \begin{bmatrix} c_{i,j}^{(1)} & 0 \\ 0 & c_{i,j}^{(2)} \end{bmatrix} v_i v_j + \begin{bmatrix} 0 & d_{i,j} \\ d_{i,j} & 0 \end{bmatrix} v_i v_j \right\} + \dots$$

$$= \begin{bmatrix} H_1(\mathbf{v}) & H_{12}(\mathbf{v}) \\ H_{12}(\mathbf{v}) & H_2(\mathbf{v}) \end{bmatrix}$$

- H expressed in normal mode coordinates

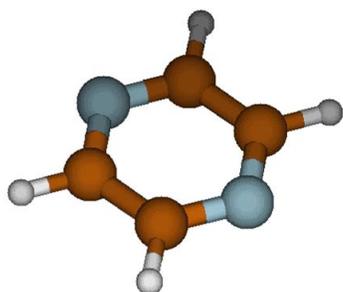
$$i \frac{\delta \psi}{\delta t} = H \psi$$

# Tool Summary

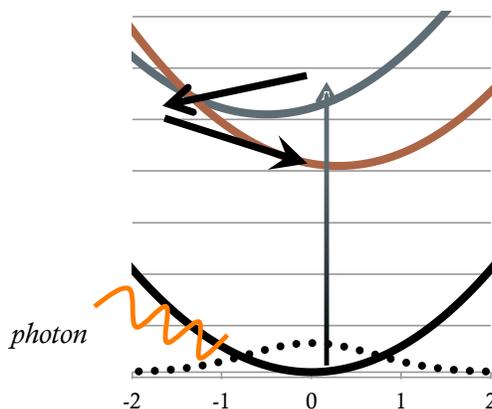


**How to achieve mode classification?**

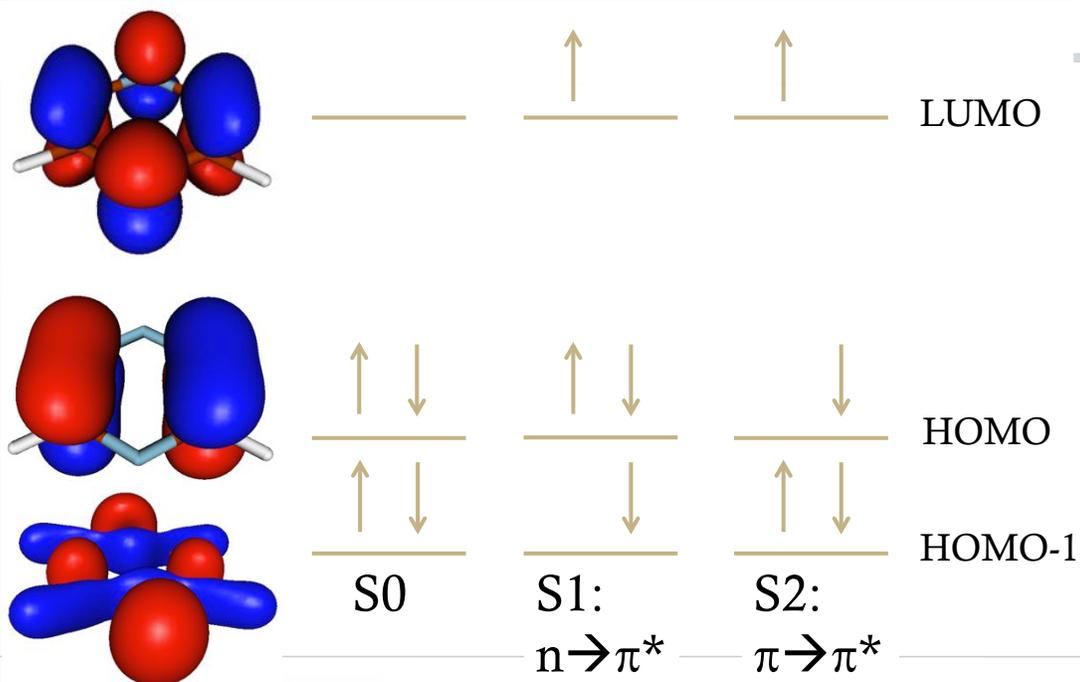
# Example: Pyrazine



- 24 degrees of freedom
- Excited manifold has 2 eigenstates/surfaces
  - Non-interacting at planar structure

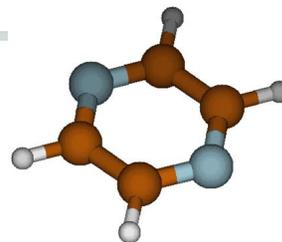


## Pyrazine Electronic States

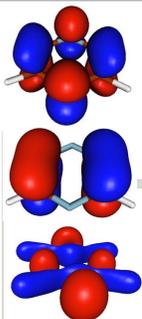


# Pyrazine Model

- Previous studies:
  - Mode 7 is coupling vibration
  - Modes 3, 12, 15 (20, 24) are tuning modes
  - Minimal coordinates: 3, 7
  - *Identified using symmetry arguments (e.g. Werner J. Chem. Phys. 1994)*
- **Can these modes be identified without resorting to symmetry?**

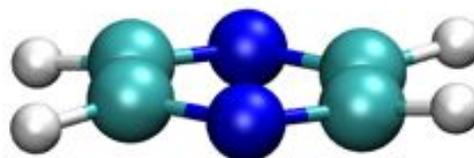
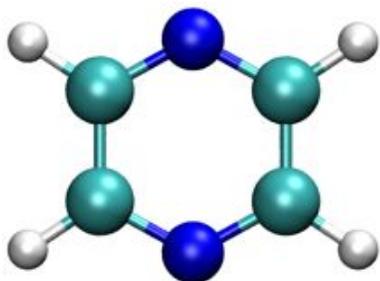


# Pyrazine Vibrations



**Mode 3**

**Mode 7**



Vibrational surfaces minima for mode 7 exist at **planar** structures in electronic states S<sub>0</sub>, S<sub>1</sub>, and S<sub>2</sub>

# Dimension Reduction

**Can motion along vibrational coordinates be quantified using approximate quantum dynamics?**

Advantages:

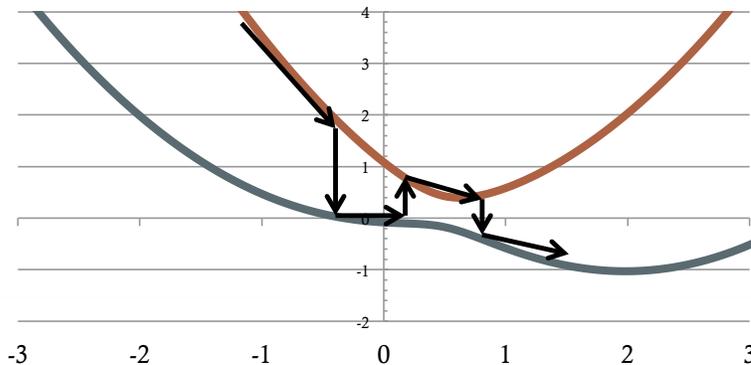
- Simplified representation of dynamics (chemical heuristics)
- Easier to integrate time-dependent Schrodinger
- Easier to produce fit of  $V(R)$
- More accurate fitting possible by using more powerful electronic structure techniques

# Surface Hopping

Classical trajectory  $R = R(t)$  Moves on single electronic state

Electronic wave function  $\psi(r, R, t) = \sum_i c_i(t) \phi_i(r; R)$

Wave function propagation  $i\hbar \dot{c}_j = \sum_i c_i (V_{ji} - i\hbar \dot{R} \cdot d_{ji})$



Transition rate

$$\propto \dot{R} \cdot d_{ji}$$

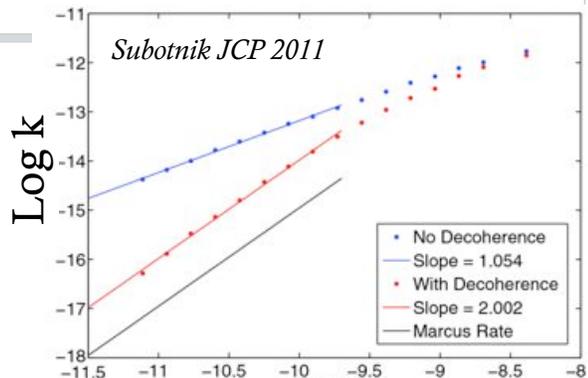
$$\propto V_{ji}$$

$$\propto \frac{1}{E_i - E_j}$$

# Hopping Rates: Realistic?

Marcus rate constant  
(weak coupling)

$$k = \frac{2\pi |V_{12}|^2}{\hbar \sqrt{4\pi\lambda kT}} \exp\left(-\frac{(\lambda + \Delta E)^2}{4\lambda kT}\right)$$



Recent arguments about accuracy:

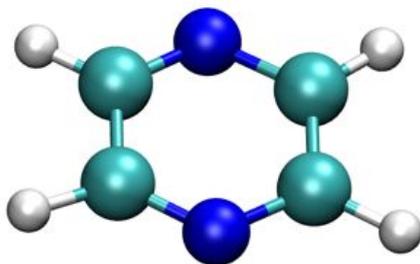
- Rate according to Marcus theory should scale as  $V_{12}^2$  for small  $V_{12}$
- Tully: regions near conical intersections do not have small  $V_{12}$

$\text{Log } V_{12}$

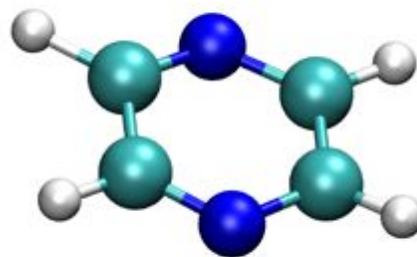
# Hopping Trajectories

Initial positions and momenta sampled from quasi-classical distribution  $\psi(v_i)^2 = \frac{1}{\sqrt{\pi}} \exp(-v_i^2)$

Trajectory 28



Trajectory 91

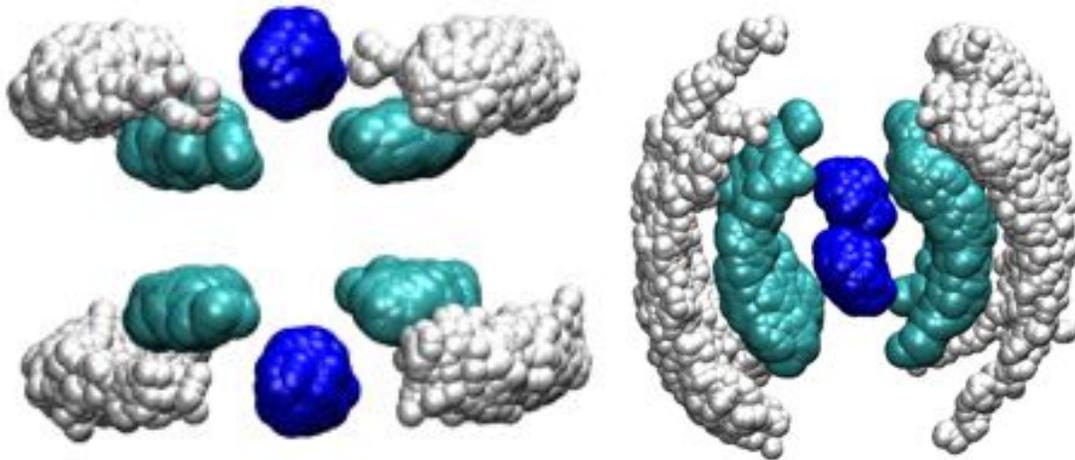


Cyan/Blue: S2

Pink/Red: S1

# Sampled Space

- Sampled ~100 trajectories for 200 fs each
- After 200 fs, all but 2 trajectories are on S1



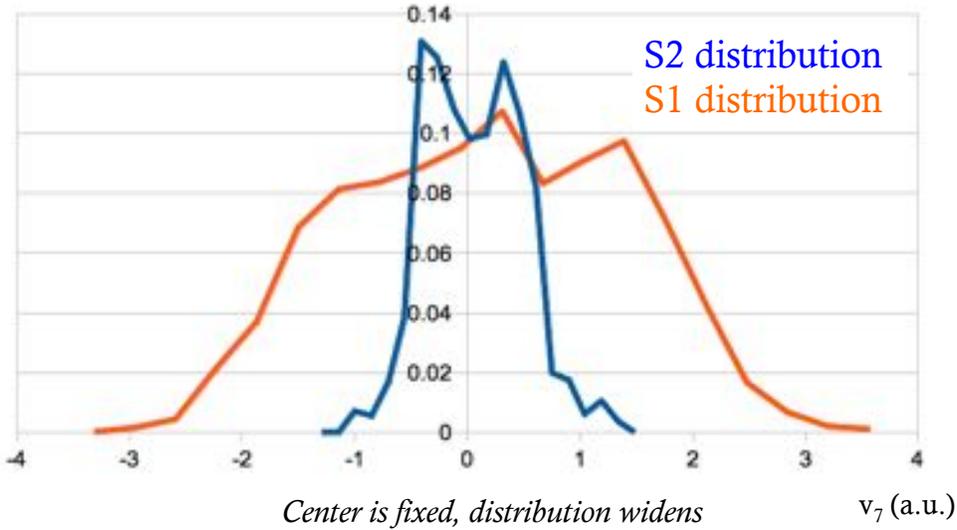
## Vib. Mode 3

$$d_i(j) \propto v_i \cdot G_m^{-1/2} (q(j) - q_0)$$

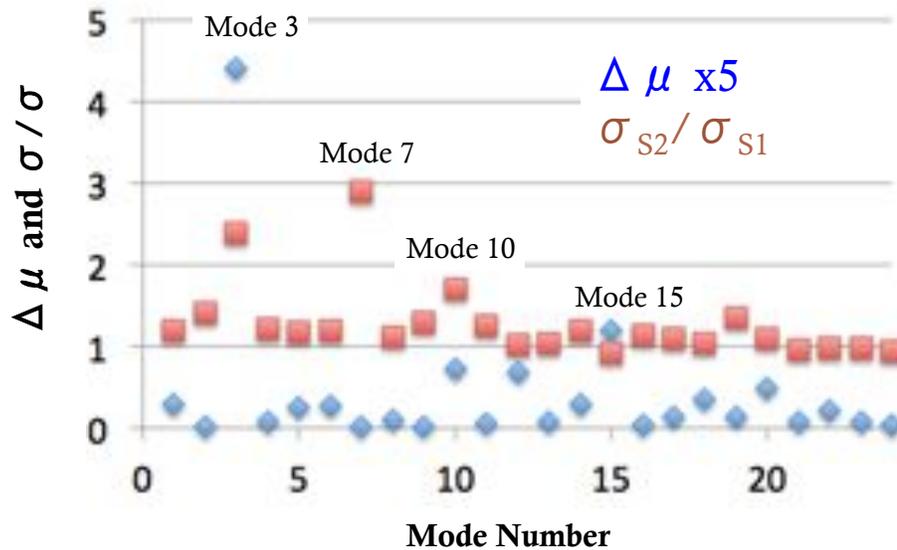


# Vib. Mode 7

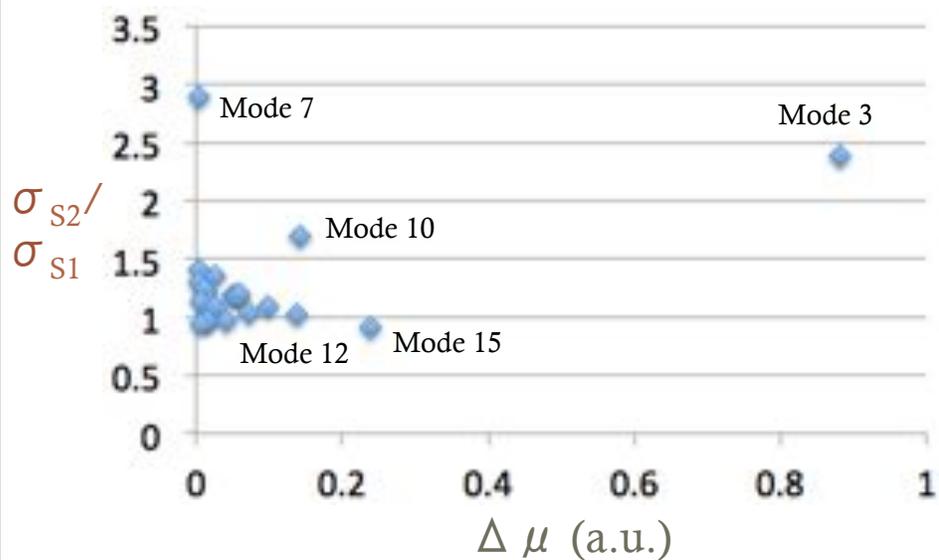
$$d_i(j) \propto v_i \cdot G_m^{-1/2} (q(j) - q_0)$$



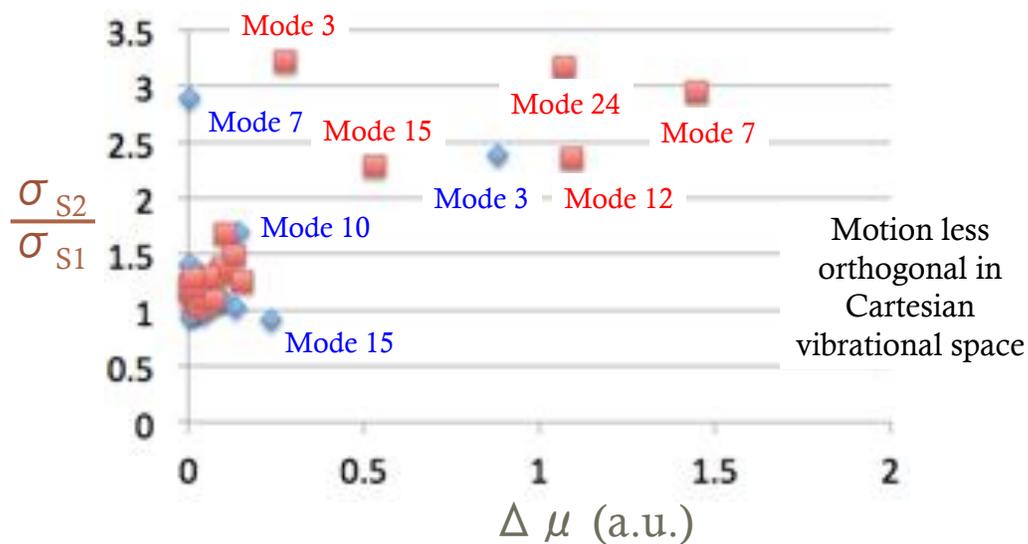
# Vibrational Statistics



# Vibrational Statistics



# Cartesian vs. IC Statistics

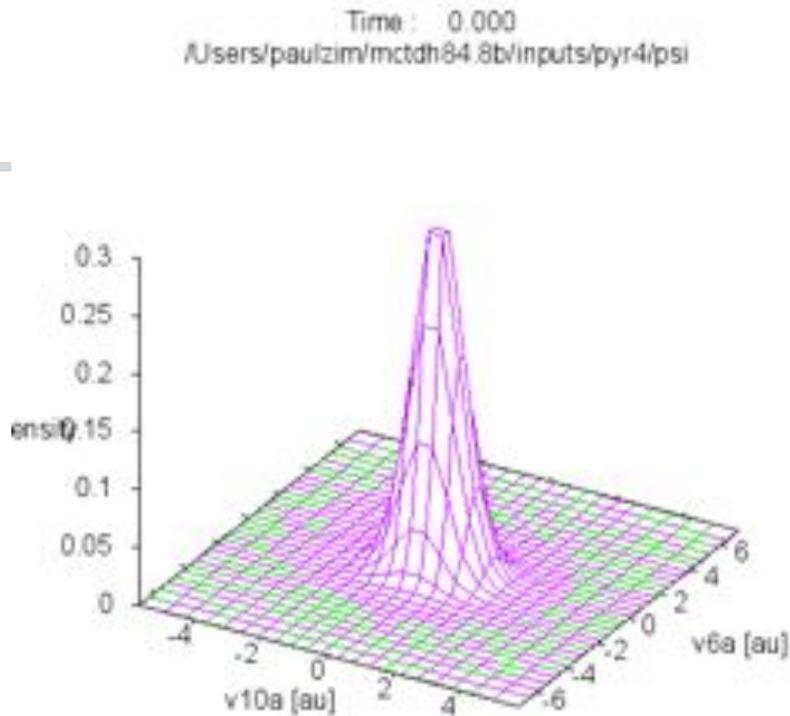


# Pyrazine Dynamics

- Linear vibronic coupling Hamiltonian, integrated for 200 fs using MCTDH

$$\hat{H} = T(\mathbf{v}) + \begin{bmatrix} \Delta & 0 \\ 0 & -\Delta \end{bmatrix} + \sum_{i=1}^{3N-6} \left\{ \frac{\omega}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} v_i^2 + \begin{bmatrix} a_i^{(1)} & 0 \\ 0 & a_i^{(2)} \end{bmatrix} v_i + \begin{bmatrix} 0 & b_i \\ b_i & 0 \end{bmatrix} v_i \right\}$$

- Comparison set:
  - Modes 3, 7
  - Modes 3, 7, 15
  - Modes 3, 7, 10, 15
  - Modes 3, 7, 10, 12, 15



# Conclusions

- Internal coordinates allow quick access to molecular properties
  - See also Zimmerman *J. Chem. Phys.* 2013 and *J. Chem. Theor. Comput.* 2013 for IC's used to locate reaction paths
- Projection of direct dynamics into vibrations reduces arbitrariness of coordinate system choice for quantum dynamics

Surface Hopping:  
Tractable, full dimensional  
Not wave mechanics



Exact Quantum Dynamics:  
Reduced dimensions  
Quantitative

# Acknowledgements

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- Alex Nett

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- Aiman Faruqi

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