

Solving the Time-Dependent Schrödinger Equation Using the QUANTICS Package

2. Non-Adiabatic QD

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Steps for quantum dynamics simulations

1. Get the Hamiltonian
 - Specify the system coordinates
 - Work out the Kinetic energy operator
 - Work out the potential energy operator
2. Define a *primitive basis set* to represent the Hamiltonian and wavepacket
3. Define an initial wavepacket
4. Select a method to propagate the wavepacket (integrate the TDSE)
5. Analyse wavepacket to obtain (time-evolution) data.

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System has a manifold of coupled states. I.e. **Non-Adiabatic Dynamics**

Describing photo-excitation

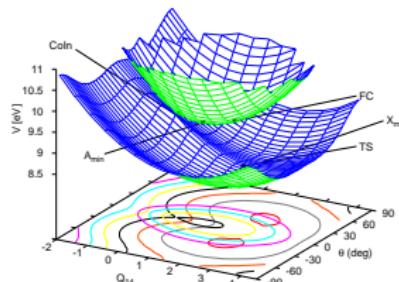
After photo-excitation, molecule can access a number of states.

Nuclear TDSE must include manifold of electronic states coupled by *non-adiabatic* coupling.

In the **adiabatic picture**, coupling gives rise to conical intersections

$$[(T_N \mathbf{1} + \mathbf{F})^2 + \mathbf{V}] \chi = i\hbar \frac{\partial \chi}{\partial t}$$

$$F_{ij} = \langle \Phi_i | \nabla \Phi_j \rangle$$



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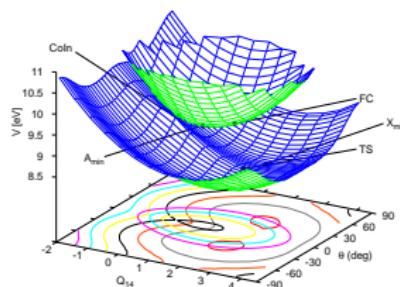
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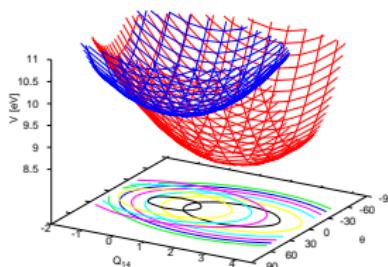
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In the **diabatic picture**

$$[T_N \mathbf{1} + \mathbf{W}] \chi = i\hbar \frac{\partial \chi}{\partial t}$$



where all elements of **W** are potential-like terms. The diabatic and adiabatic representations are related by a transformation

$$\Phi^{di} = \mathbf{S}(\mathbf{q}) \Phi^{ad}$$

The Born-Oppenheimer Approximation

Start using Born representation

$$\Psi(\mathbf{q}, \mathbf{r}) = \sum_i \chi_i(\mathbf{q}) \Phi_i(\mathbf{r}; \mathbf{q}) \quad , \quad (1)$$

where electronic functions are solutions to *clamped nucleus Hamiltonian*

$$\hat{H}_{\text{el}} \Phi_i(\mathbf{r}; \mathbf{q}) = V_i(\mathbf{R}) \Phi_i(\mathbf{r}; \mathbf{q}) \quad . \quad (2)$$

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The full Hamiltonian is

$$\hat{H}(\mathbf{q}, \mathbf{r}) = \hat{T}_n(\mathbf{q}) + \hat{H}_{\text{el}}(\mathbf{q}, \mathbf{r}) \quad , \quad (3)$$

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Integrate out electronic degrees of freedom to obtain

$$\left[-\frac{1}{2M} (\nabla \mathbf{1} + \mathbf{F})^2 + \mathbf{V} \right] \chi = i\hbar \frac{\partial \chi}{\partial t} \quad , \quad (4)$$

The Adiabatic Picture

where

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Assuming $\frac{\mathbf{F}}{M} \approx 0$

$$[\hat{T}_n + V] \chi = i\hbar \frac{\partial \chi}{\partial t} \quad (6)$$

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Unfortunately,

$$\mathbf{F}_{ij} = \frac{\langle \Phi_i | (\nabla \hat{H}_{\text{el}}) | \Phi_j \rangle}{V_j - V_i} \quad \text{for } i \neq j \quad . \quad (7)$$

The Diabatic Picture

First we separate out a group of coupled states from the rest

$$\left[(\hat{T}_n \mathbf{1}^{(g)} + \mathbf{F}^{(g)})^2 + \mathbf{V}^{(g)} \right] \boldsymbol{\chi}^{(g)} = i\hbar \frac{\partial \boldsymbol{\chi}^{(g)}}{\partial t} , \quad (8)$$

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To remove singularities, find a suitable unitary transformation

$$\tilde{\Phi} = \mathbf{S}(\mathbf{q})\Phi \quad (9)$$

such that the Hamiltonian can be written

$$[T_N \mathbf{1} + \mathbf{W}] \boldsymbol{\chi} = i\hbar \frac{\partial \boldsymbol{\chi}}{\partial t} , \quad (10)$$

where all elements of \mathbf{W} are potential-like terms

Köppel, Domcke and Cederbaum. Adv. Chem. Phys. (84) 57:1
 Worth and Cederbaum, Ann. Rev. Phys. Chem. (04) 55: 127

Vibronic Coupling Model

Assume diabatic basis: $\Psi(\mathbf{Q}, \mathbf{r}) = \sum_{\alpha} \phi_{\alpha}(\mathbf{Q}) \psi_{\alpha}(\mathbf{r}; \mathbf{Q})$

$$\mathbf{H}(\mathbf{Q}) = \mathbf{T}(\mathbf{Q}) + \mathbf{W}(\mathbf{Q}) \quad (11)$$

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$$\mathbf{H}(\mathbf{Q}) = \mathbf{T}(\mathbf{Q}) + \mathbf{W}(\mathbf{Q}) \quad (11)$$

$$W_{\alpha\beta} = \langle \psi_{\alpha} | H_{el} | \psi_{\beta} \rangle$$

$$W_{\alpha\beta} \approx V_{\alpha}^0 \delta_{\alpha\beta} + \varepsilon_{\alpha} + \sum_i \underbrace{\frac{\partial}{\partial Q_i} \langle \psi_{\alpha} | H_{el} | \psi_{\beta} \rangle}_{\text{Diagram: A curved arrow points from this term to the condition below}} Q_i + \dots$$

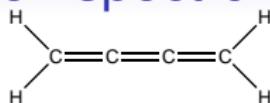
$$\kappa_i, \lambda_i \neq 0 \quad \text{if} \quad \Gamma_{\alpha} \times \Gamma_i \times \Gamma_{\beta} \supseteq A_1$$

$$\hat{T}_{\alpha} + V_{\alpha}^0 = \frac{\omega_i}{2} \left(\frac{\partial^2}{\partial Q^2} + Q^2 \right) \quad (12)$$

Köppel *et al* Adv. Chem. Phys. (1984) 57: 59

Butatriene photoelectron spectrum

18 modes D_{2h}
 X^2B_{2g} ; A^2B_{2u}



$$\begin{aligned}
 \mathbf{H} = & \sum_i \frac{\omega_i}{2} \left(-\frac{\partial^2}{\partial Q_i^2} + Q_i^2 \right) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} \\
 & + \sum_{i \in A_g}^4 \begin{pmatrix} \kappa_i^{(1)} & 0 \\ 0 & \kappa_i^{(2)} \end{pmatrix} Q_i + \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix} Q_{A_u} \\
 & + \dots
 \end{aligned}$$

↗ ↗
 $\langle \psi_\alpha | \frac{\partial H}{\partial Q_i} | \psi_\beta \rangle$ $B_{2g} \times B_{2u} = A_u$

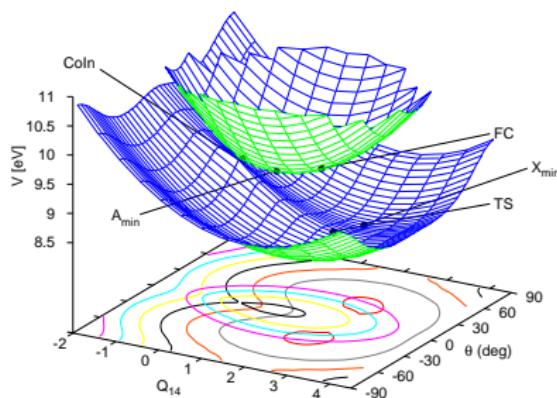
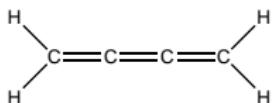
linear: 5 modes, 16 parameters

bilinear: 18 modes, 79 parameters

$$I(\omega) \sim \int_{-\infty}^{\infty} dt \langle \Psi(0) | \Psi(t) \rangle e^{i\omega t}$$

Conical Intersections

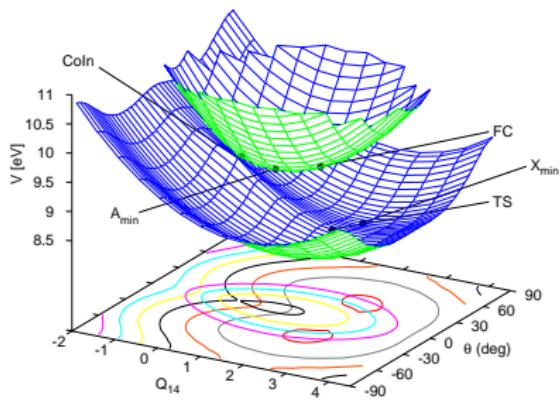
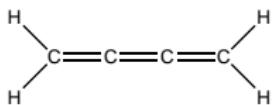
Butatriene Radical Cation



Adiabatic

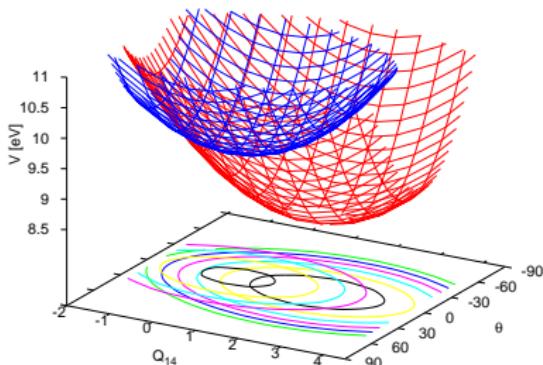
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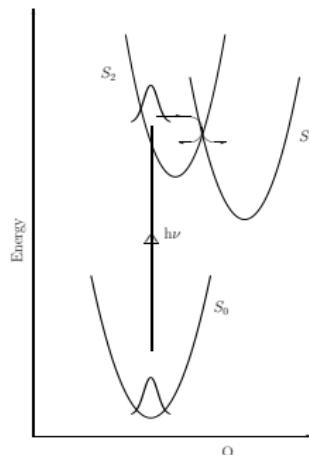
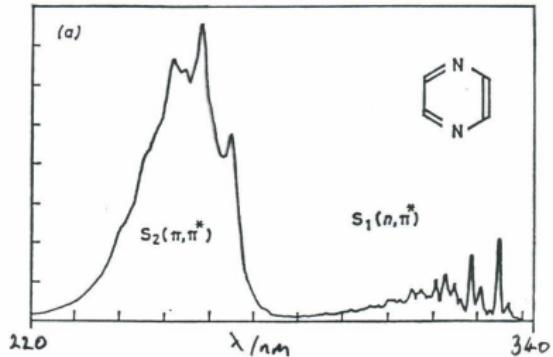


Adiabatic

Diabatic



Pyrazine Excitation: Model Hamiltonian

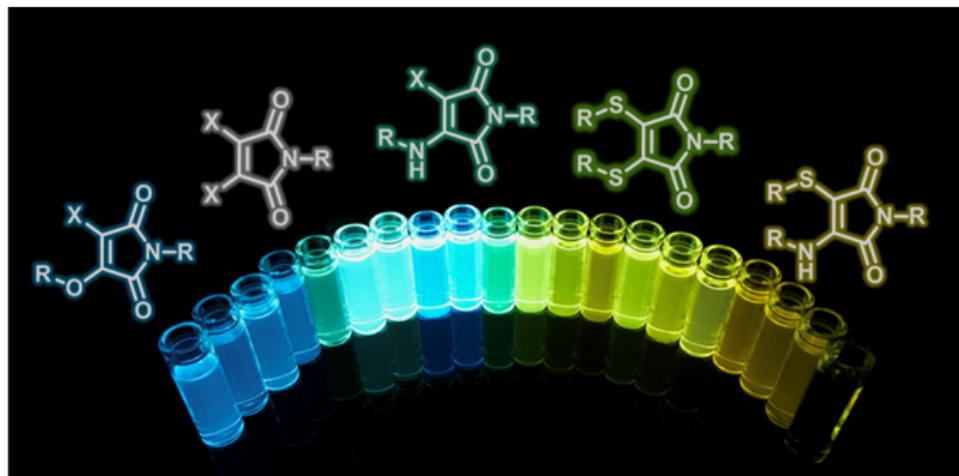


Yamazaki *et al* Farad. Discuss. (83) **75**: 395

The pyrazine molecule has 24 vibrational modes.

$$\mathbf{H} = \sum_i \frac{\omega_i}{2} \left(-\frac{\partial^2}{\partial Q_i^2} + Q_i^2 \right) \mathbf{1} + \begin{pmatrix} -\Delta & 0 \\ 0 & \Delta \end{pmatrix} + \sum_{i \in G_1} \begin{pmatrix} \kappa_i^{(1)} & 0 \\ 0 & \kappa_i^{(2)} \end{pmatrix} Q_i + \sum_{(i,j) \in G_2} \begin{pmatrix} \gamma_{i,j}^{(1)} & 0 \\ 0 & \gamma_{i,j}^{(2)} \end{pmatrix} Q_i Q_j + \sum_{i \in G_3} \begin{pmatrix} 0 & \lambda_i \\ \lambda_i & 0 \end{pmatrix} Q_i + \sum_{(i,j) \in G_4} \begin{pmatrix} 0 & \mu_{i,j} \\ \mu_{i,j} & 0 \end{pmatrix} Q_i Q_j.$$

Maleimide: A small, versatile fluorophore

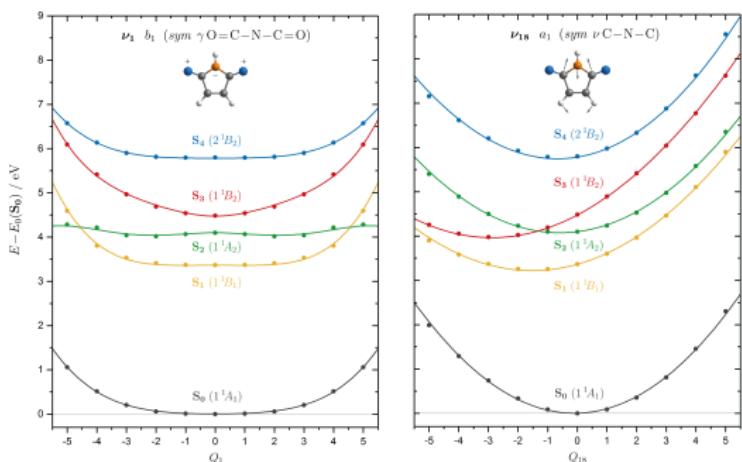


Experimental Group of Rachel O'Reilly, Birmingham

Maleimide Potential Energy Surfaces

CASPT2(12,9)

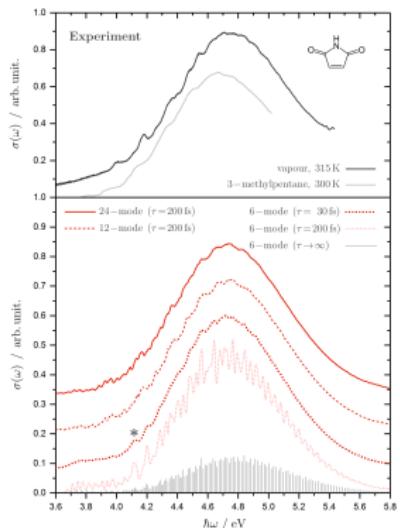
state	sym	cc-pVDZ E/eV	Experiment $E/\text{eV} (f)$
S₀(n₂²)	1 ¹ A ₁	0.00	
S₁(n₂π[*])	1 ¹ B ₁	3.37 (0.00)	3.33 ^b
S₂(n₁π[*])	1 ¹ A ₂	3.96 (0.00)	(-)
S₃(π₂π[*])	1 ¹ B ₂	4.62 (0.03)	4.72 ^a , 4.48 ^b , 4.67 ^c
S₄(π₁π[*])	2 ¹ B ₂	5.80 (0.46)	5.95 ^a , 6.20 ^{b,c}



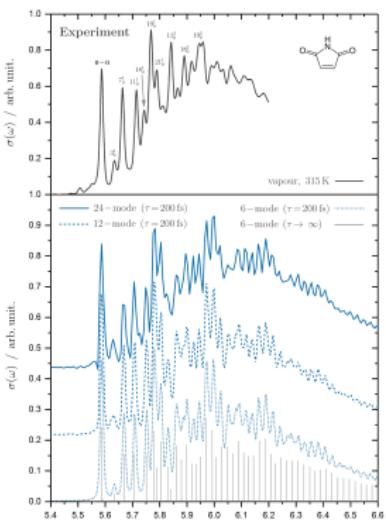
EOM-CCSD/cc-pVDZ
shifted to
CASPT2(12,9)/cc-pVDZ
at FC point.

Maleimide Absorption Spectra

Excitation to S_3



Excitation to S_4

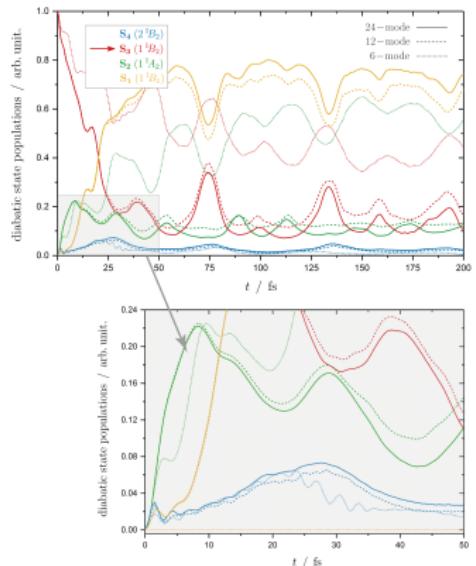


Spectra calculated from dynamics simulation

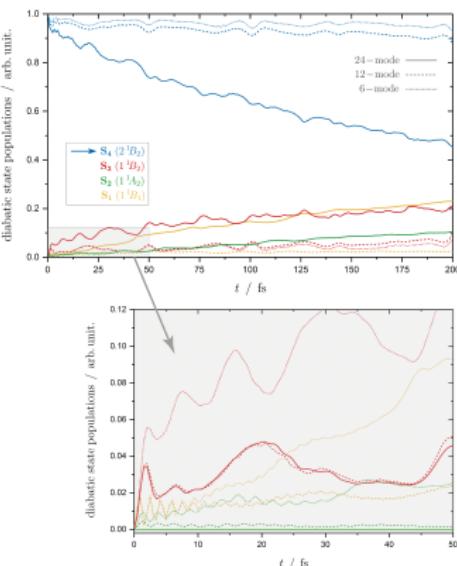
$$I(\omega) \sim \int \langle \Psi(0) | \Psi(t) \rangle e^{i\omega t} dt$$

Maleimide Relaxation Dynamics

Excitation to S_3

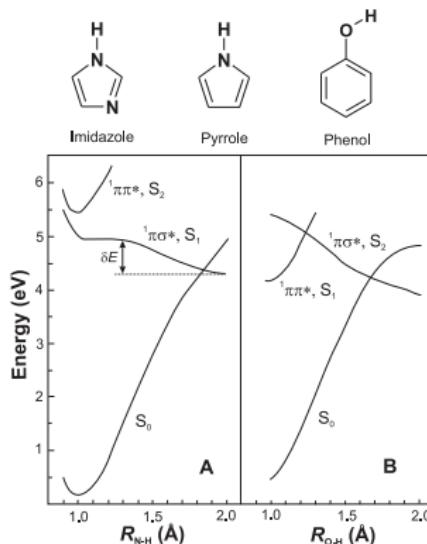


Excitation to S_4



Lehr et al/PCCP (20) 22: 25272

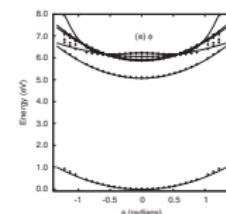
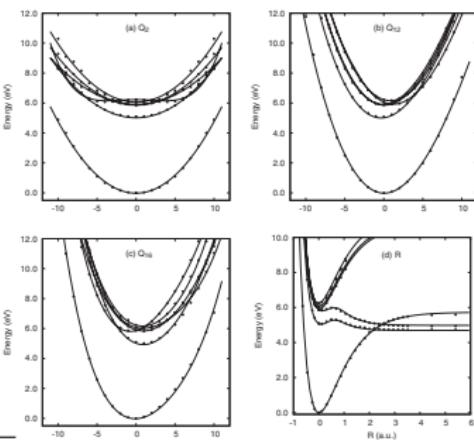
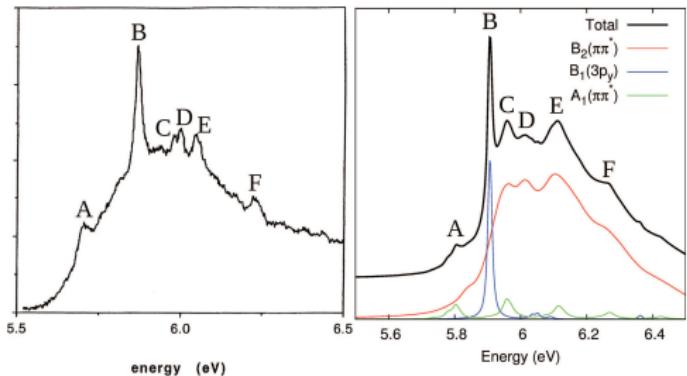
Heteroaromatic Photodissociation



Ashfold *et al* Science (06) 312: 1637

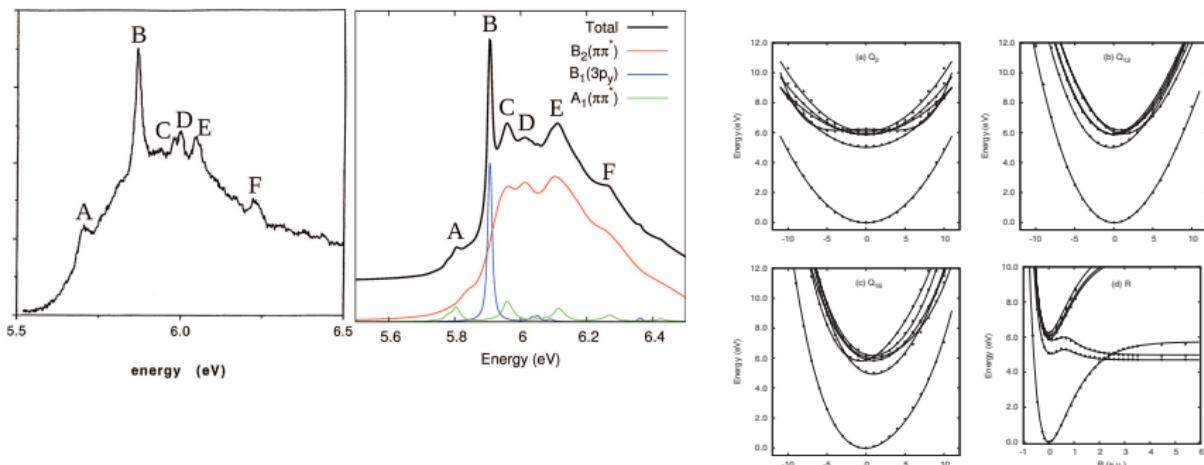
Excitation to $\pi\pi^*$ states
 Dissociation after crossing to $\pi\sigma^*$ states

Electronic Absorption Spectrum of Pyrrole



Symmetry	Character	CASSCF	CASPT2
A_1		0.00	0.00
A_2	$3s/\pi\sigma^*$	4.17	5.06
B_1	$3s/\pi\sigma^*$	4.87	5.86
A_2	$3p_z$	4.91	5.87
A_1	$\pi\pi^*$	6.47	6.01
B_2	$\pi\pi^*$	7.83	6.24
B_1	$3p_z$	5.67	6.69

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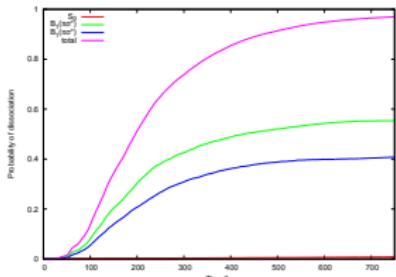
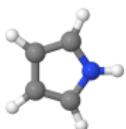
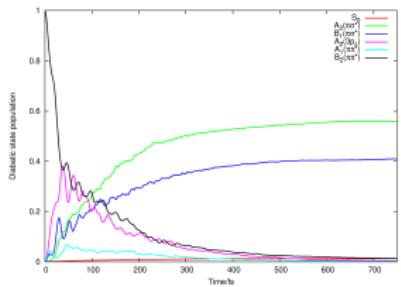


- 6-state, 9-mode model.
- Strong vibronic coupling between states.
- Contribution from excitation to three states.
- Intensity borrowing allows excitation to lower lying Rydberg states.

Pyrrole: 6-State 9(10)-Mode Model

Ignoring ν_2

State populations

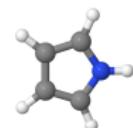
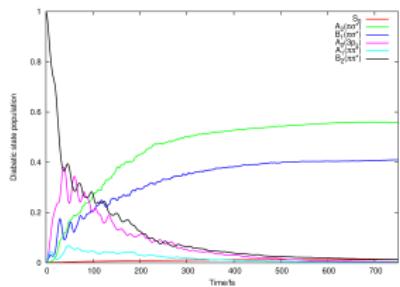


Flux

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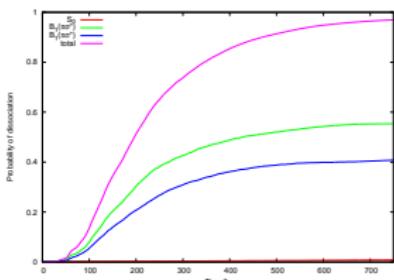
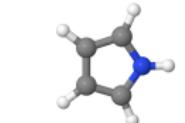
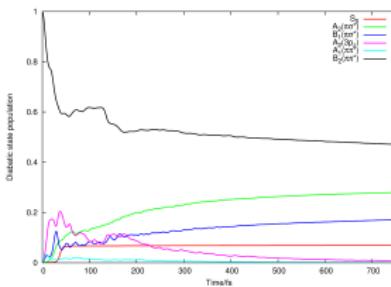
Ignoring ν_2

State populations

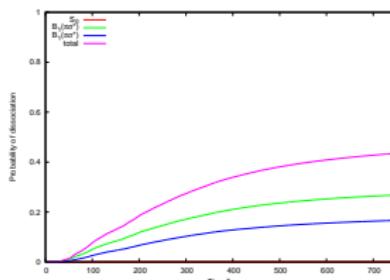


Including ν_2

State populations



Flux



Flux

“Trapped”
“Geometry”

MCTDH Calculations with Multiple PES

If more than one electronic state in system, can use either

1. Single-set

$$\Psi(Q_1, \dots, Q_f, t) = \sum_{j_1=1}^{n_1} \dots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f s}(t) \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) \varphi_s^{(\text{el})} \quad (13)$$

with $\varphi_s^{(\text{el})}$ a time-independent discrete basis for the electronic degree of freedom, e.g. $\{(1, 0), (0, 1)\}$

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```
SPF-BASIS-SECTION
single-set
    v10a =      6
    v6a  =      7
    v1   =      4
    v9a  =      4
end-spf-basis-section
```

OR

2. Multi-set

$$\Psi(Q_1, \dots, Q_f, t) = \sum_s \sum_{j_1=1}^{n_1} \dots \sum_{j_f=1}^{n_f} A_{j_1 \dots j_f}^{(s)}(t) \prod_{\kappa=1}^f \varphi_{j_\kappa}^{(\kappa, s)}(Q_\kappa, t) \quad (14)$$

OR

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SPF-BASIS-SECTION

multi-set

```
v10a =      7, 7
v6a   =    12, 11
v1    =      6, 5
v9a   =      5, 4
```

end-spf-basis-section

```
RUN-SECTION
name = pyr4    propagate
tfinal = 120.0   tout = 0.5   tpsi= 1.0
psi auto=twice steps gridpop
title = pyrazine 4-mode multi-set, linear model, no combinations.
end-run-section

OPERATOR-SECTION
opname = pyrmod4
end-operator-section

SPF-BASIS-SECTION
multi-set
    v10a =    7, 7
    v6a =   12, 11
    v9a =    5, 4
end-spf-basis-section
PRIMITIVE-BASIS-SECTION
    v10a   HO    22  0.0    1.0    1.0
    v6a    HO    32  0.0    1.0    1.0
    v1     HO    21  0.0    1.0    1.0
    v9a    HO    12  0.0    1.0    1.0
    el     el     2
end-primitive-basis-section

INTEGRATOR-SECTION
CMF/var = 0.5,  1.0d-05
BS/spf  = 7 ,  1.0d-05 ,  2.5d-04
SIL/A   = 5 ,  1.0d-05
end-integrator-section

INIT_WF-SECTION
build
    init_state = 2
    v10a HO  0.0    0.0    1.00
    v6a  HO  0.0    0.0    1.00
    v1   HO  0.0    0.0    1.00
    v9a  HO  0.0    0.0    1.00
end-build
end-init_wf-section

end-input
```

```
OP_DEFINE-SECTION
title Pyrazine 4-mode model, linear coupling. end-title
end-op_define-section
```

```
PARAMETER-SECTION
w10a = 0.09357, ev
w6a = 0.0740 , ev
wl = 0.1273 , ev
w9a = 0.1568 , ev
delta = 0.46165, ev
lambda = 0.1825 , ev
k6a1 = -0.0964 , ev
k6a2 = 0.1194 , ev
k11 = 0.0470 , ev
k12 = 0.2012 , ev
k9a1 = 0.1594 , ev
k9a2 = 0.0484 , ev
end-parameter-section
```

HAMILTONIAN-SECTION

modes		e1		v10a		v6a		v1		v9a	
1.0*w10a		1		KE		1		1		1	
0.5*w10a		1		q^2		1		1		1	
1.0*w6a		1		1		KE		1		1	
0.5*w6a		1		1		q^2		1		1	
1.0*wl		1		1		1		KE		1	
0.5*wl		1		1		1		q^2		1	
1.0*w9a		1		1		1		1		KE	
0.5*w9a		1		1		1		1		q^2	
-delta		S1&1		1		1		1		1	
delta		S2&2		1		1		1		1	
lambda		S1&2		q		1		1		1	
k6a1		S1&1		1		q		1		1	
k6a2		S2&2		1		q		1		1	
k11		S1&1		1		1		q		1	
k12		S2&2		1		1		q		1	
k9a1		S1&1		1		1		1		q	
k9a2		S2&2		1		1		1		q	

```
end-hamiltonian-section
```

State Populations

Diabatic state populations are obtained from

$$P_\alpha = \langle \Psi(t) | \alpha \rangle \langle \alpha | \Psi(t) \rangle$$

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Note on MCTDH

Some evaluations that are straightforward using the standard method are impossible in MCTDH due to the form of the wavefunction. For example application of an operator such as the diabatic - adiabatic transformation is only completely defined on the full primitive grid.

Expectation values are always possible, e.g. Monte-Carlo integration

Golden Rule Spectrum

This is the Fourier Transform of the autocorrelation function

$$\sigma(\omega) \propto \omega \int_{-\infty}^{\infty} dt C(t) e^{i(E_0 + \omega)t} , \quad (15)$$

where E_0 denotes the ground-state energy and where the autocorrelation function is defined as

$$C(t) = \langle \Psi(0) | \Psi(t) \rangle = \langle \Psi^*(\frac{t}{2}) | \Psi(\frac{t}{2}) \rangle \quad (16)$$

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Using eigenvalue representation,

$$C(t) = \sum_i c_i^* c_i e^{iE_i t} \quad (17)$$

and

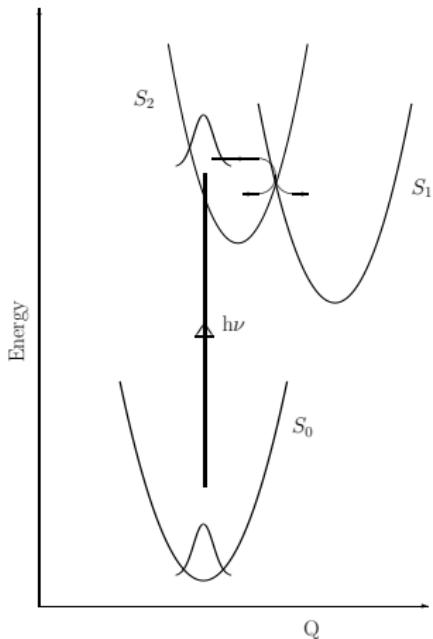
$$\begin{aligned} \int_{-\infty}^{\infty} dt C(t) e^{i(E_0 + \omega)t} &= \int_{-\infty}^{\infty} dt \sum_i c_i^* c_i e^{-i(E_i - E_0)} e^{i\omega t} \\ &= \sum_i c_i^* c_i \delta(E_i - E_0) \end{aligned} \quad (18)$$

pyrazine absorption spectrum

$$\frac{I}{I_0} = e^{-\sigma Cl} \quad (19)$$

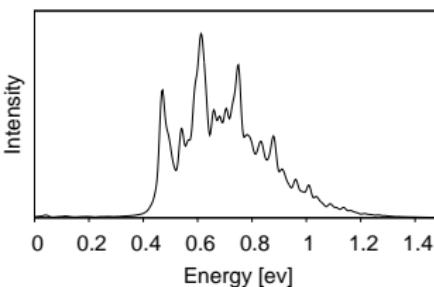
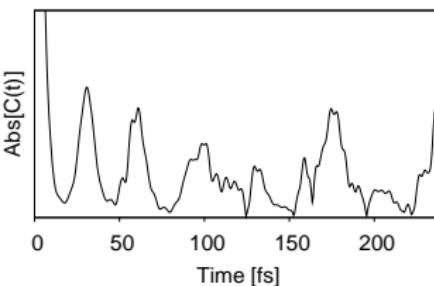
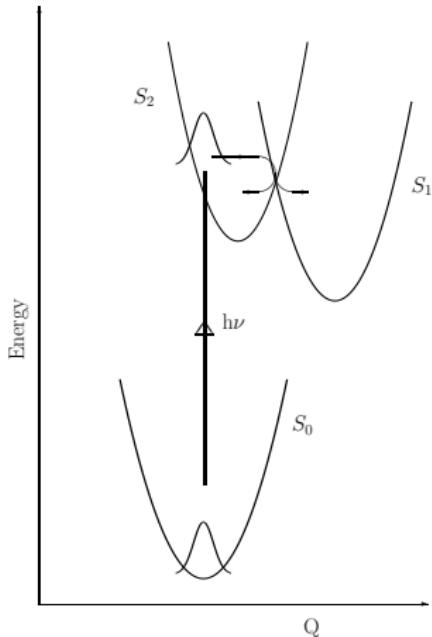
pyrazine absorption spectrum

$$\frac{I}{I_0} = e^{-\sigma Cl} \quad (19)$$



pyrazine absorption spectrum

$$\frac{I}{I_0} = e^{-\sigma C t} \quad (19)$$



Golden Rule derived from first-order perturbation theory. Spectrum valid for:

- weak fields
- direct processes

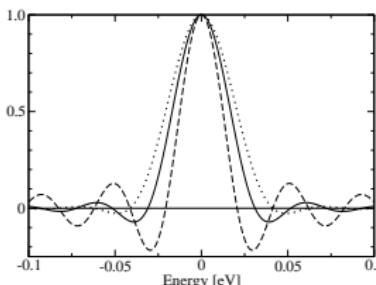
Due to finite propagation multiply C(t) by

$$f(t) = \exp(-t/\tau) \quad . \quad (20)$$

and

$$g_k(t) = \cos^k \left(\frac{\pi t}{2T} \right) \Theta \left(1 - \frac{|t|}{T} \right) \quad (21)$$

$k = 1$ usually best choice



$T=100$ fs.

Time-independent Picture

For a time-independent Hamiltonian, can also treat system using

$$H\psi_i(\mathbf{q}) = E_i\psi_i(\mathbf{q}) \quad (22)$$

to obtain quantum states (eigenvalues). Using a basis set (DVR) and variational principle, states found by diagonalising the matrix

$$H_{JL} = \sum_{\ell_1, \dots, \ell_f} \langle \chi_{j_1}^{(1)} \cdots \chi_{j_f}^{(f)} | H | \chi_{\ell_1}^{(1)} \cdots \chi_{\ell_f}^{(f)} \rangle \quad (23)$$

Once eigenvalues are known, dynamics also known as

$$\Psi(\mathbf{q}, t) = \sum_i c_i \psi_i e^{-\frac{i}{\hbar} E_i t} \quad (24)$$

where

$$\Psi(\mathbf{q}, 0) = \sum_i c_i \psi_i \quad (25)$$

Thus time-independent and time-dependent views equivalent.

Equivalence is important for interpretation of wavepacket.

Thus time-independent and time-dependent views equivalent.

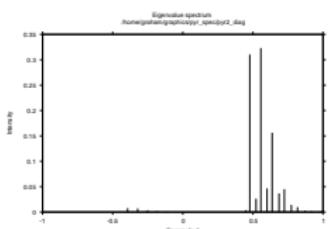
Equivalence is important for interpretation of wavepacket.

Time-dependent has advantages that

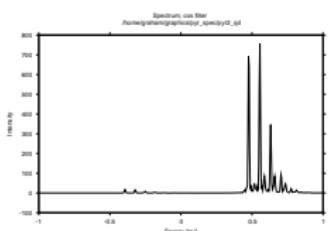
- More pictorial and obviously dynamical output
- dissociative states easily treated
- larger systems can be accessed by MCTDH
- time-dependent Hamiltonians can be treated

Effect of damping

$$H = \sum_{i=1,2} \frac{\omega_i}{2} \left(\frac{\partial^2}{\partial Q_i^2} + Q_i^2 \right) + \begin{pmatrix} E_1 + \kappa^{(1)} Q_1 & \lambda Q_2 \\ \lambda Q_2 & E_2 + \kappa^{(2)} Q_1 \end{pmatrix} \quad (26)$$



Eigenvalues

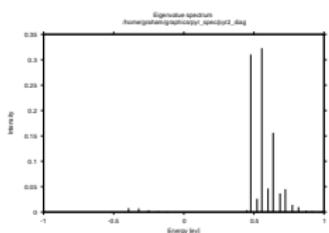


Dynamics

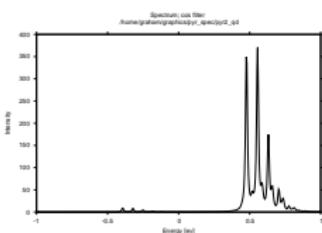
$\tau = 400$ fs

Effect of damping

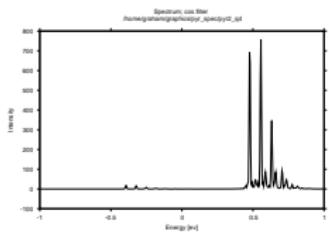
$$H = \sum_{i=1,2} \frac{\omega_i}{2} \left(\frac{\partial^2}{\partial Q_i^2} + Q_i^2 \right) + \begin{pmatrix} E_1 + \kappa^{(1)} Q_1 & \lambda Q_2 \\ \lambda Q_2 & E_2 + \kappa^{(2)} Q_1 \end{pmatrix} \quad (26)$$



Eigenvalues



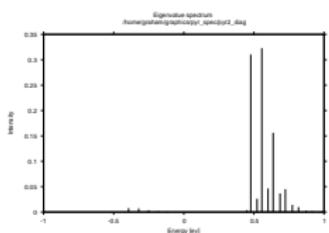
Dynamics
 $\tau = 100 \text{ fs}$



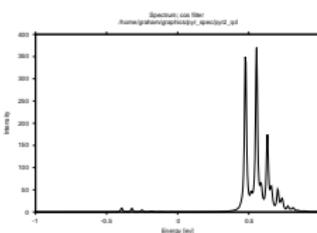
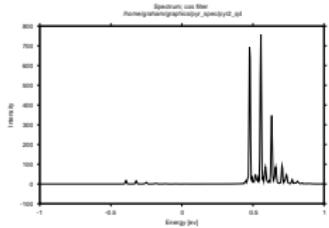
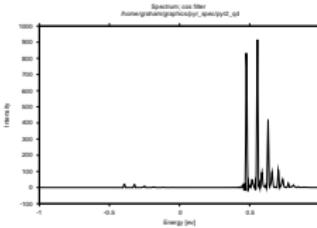
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Eigenvalues

Dynamics
 $\tau = 100 \text{ fs}$ Dynamics
 $\tau = 400 \text{ fs}$ Dynamics
 $\tau = 1000 \text{ fs}$

Time-resolved spectra

Add light field to Hamiltonian

$$\hat{H} = \hat{H}_M + \hat{H}_{ML} \quad \text{where} \quad \sum_{ij} | \psi_i \rangle \mu_{ij} E(t) \langle \psi_j | \quad (27)$$

Time-resolved spectra

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Time-resolved photo-electron spectrum:

Need to describe free-electron continuum, e.g.

$$| \Psi(R, t) \rangle = | \tilde{X} \rangle + | \tilde{A} \rangle + \sum_{i=1,2} \int_0^{\infty} dE | \tilde{X}_i^l(E) \rangle \quad (28)$$

Spectrum is long-time population of continuum states

$$I(\omega) \propto \sum_{i=1,2} \int_0^{\infty} dE | \langle \Psi(t \rightarrow \infty) | \tilde{X}_i^l(E) \rangle |^2 \quad (29)$$

Domcke and Stock Adv. Chem. Phys. (1997) **100**: 1

Seel and Domcke J. Chem. Phys. (1991) **95**: 7806

Time-resolved Photo-electron Spectrum: Toluene

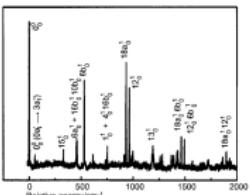


FIG. 1. The S_0 - S_1 excitation spectrum of toluene. Adapted from Hickman et al. (Ref. 2), with thanks to W. B. Lawrence.

Create Resonance ν_{6a} / ν_{10b16b}

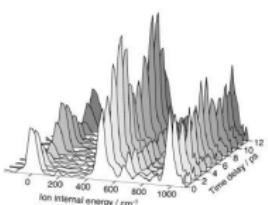


Fig. 3 3D plot of time-resolved photoelectron spectra from 0 to 12 ps.

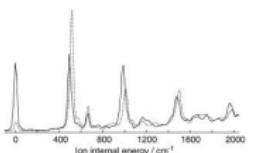


Fig. 4 Slow electron velocity-map imaging (SEVI) spectra at time delays of 0 ms (solid line) and 3 ns (dotted line).

Davies et al PCCP (10) 12: 9872

Time-resolved Photo-electron Spectrum: Toluene

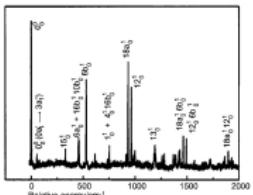


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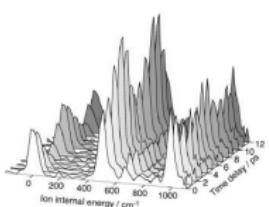


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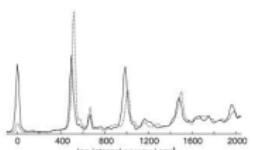
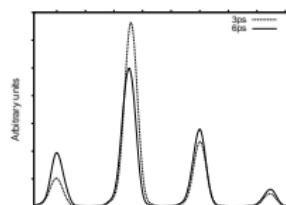
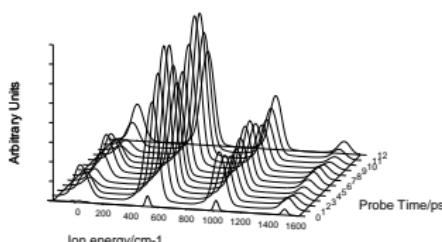


Fig. 4 Slow electron velocity-map imaging (SEVI) spectra at time delays of 0 ps (solid line) and 7 ps (dashed line).

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$$I(\omega) = \lim_{t \rightarrow \infty} \sum_{i \in \tilde{X}^+} |C_i^{\tilde{X}^+}(\omega, t)|^2 \quad (30)$$



Computationally expensive

Richings and Worth JCP (14) 141: 244115