Multidimensional Photochemistry and Non-adiabatic Dynamics

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- The Time-Dependent Schrödinger Equation
    - The Born-Oppenheimer Approximation
    - Adiabatic and Diabatic Pictures
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- The Hamiltonian
    - The Vibronic Coupling Model
    - Direct Dynamics

Köppel, Domcke and Cederbaum Adv. Chem. Phys. (84) 57: 59
Domcke, Yarkony, Köppel "Conical Intersections" World Scientific (04)
Klessinger and Michl "Excited-states and Photochemistry", VCH (94)
many reviews

The Time-Dependent Schrödinger Equation

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{q},\mathbf{r},t) = \hat{H}\Psi(\mathbf{q},\mathbf{r},t)} \tag{1}$$

If the Hamiltonian is time-independent, formal solution

$$\Psi(t) = \exp\left(-i\hat{H}t\right)\Psi(0) \tag{2}$$

Further, if $\hat{H}$ is time-independent we can write

Phase factor

$$\Psi(x,t) = \Psi_i(x)e^{-i\omega_i t} \tag{3}$$

and

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hbar\omega_i\Psi_i(x)e^{-i\omega_i t} \tag{4}$$

By comparison with the TDSE, Ψ_i are solutions to the time-independent Schrödinger equation

$$\hat{H}\Psi_i = E_i\Psi_i = \hbar\omega_i\Psi_i \tag{5}$$

Ψ_i is a Stationary State as expectation values (properties) are time-independent

$$\langle \hat{O} \rangle = \langle \Psi_i | \hat{O} | \Psi_i \rangle e^{i\omega_i t} e^{-i\omega_i t} = \langle \Psi_i | \hat{O} | \Psi_i \rangle \tag{6}$$

If wavefunction is a superposition of stationary states,

$$\chi(x, t) = \sum_i c_i \Psi_i(x) e^{-i\omega_i t} \tag{7}$$

now,

$$\langle \hat{O} \rangle (t) = -i\hbar \sum_i \sum_j c_i^* c_j \langle \Psi_i | O | \Psi_j \rangle e^{i(\omega_i - \omega_j)t} \tag{8}$$

An expectation value changes with time and depends on the initial function (c_i coefficients).

A non-stationary wavefunction is called a WAVEPACKET.

The Clamped Nucleus Hamiltonian

For a given nuclear configuration **q**, if we clamp the nuclei in place then the electronic Hamiltonian can be written:

$$\hat{H}_{\text{el}} = \sum_{i=1}^{N_e} -\frac{1}{2m_e}\nabla_i^2 - \sum_{i=1}^{N_e}\sum_{a=1}^{N_n}\frac{Z_a e}{4\pi\epsilon_0 r_{ia}} + \sum_{i,j=1}^{N_e}\frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{a,b=1}^{N_n}\frac{Z_a Z_b e^2}{4\pi\epsilon_0 R_{ab}} \quad (9)$$

eKE V_{eN} V_{ee} V_{NN}

In atomic units

Length: 1 Bohr = 0.529 Å $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$

Energy: 1 Hartree = 2625.5 kJ mol^{-1} $E_h = \frac{e^2}{4\pi\epsilon_0 a_0}$

= 27.21 eV

$$\hat{H}_{\text{el}} = \sum_{i=1}^{N_e} -\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N_e}\sum_{a=1}^{N_n}\frac{Z_a}{r_{ia}} + \sum_{i,j=1}^{N_e}\frac{1}{r_{ij}} + \sum_{a,b=1}^{N_n}\frac{Z_a Z_b}{R_{ab}} \quad (10)$$

The clamped nucleus Hamiltonian can be solved to provide the electronic wavefunctions at a specific nuclear configuration. This is what is done in quantum chemistry.

$$\hat{H}_{\mathrm{el}}\psi_i(\mathbf{r};\mathbf{q}) = E_i\psi_i(\mathbf{r};\mathbf{q}) \tag{11}$$

i.e. the wavefunction is a function of electronic coordinates but depends *parametrically* on the nuclear coordinates.

Return to full TDSE with Hamiltonian

$$\hat{H} = \hat{T}_N + \hat{H}_{\mathrm{el}} \tag{12}$$

and write the full wavefunction as a product of nuclear and electronic parts where the electronic function is a solution of the clamped nucleus Hamiltonian:

$$\Psi(\mathbf{q},\mathbf{r},\mathbf{t}) = \chi(\mathbf{q},\mathbf{t})\psi(\mathbf{r};\mathbf{q}) \tag{13}$$

This is an *adiabatic* separation of variables

The Nuclear Schrödinger Equation

First remove the electronic motion from the TDSE.

$$i\hbar\frac{\partial}{\partial t} \mid \Psi\rangle = \hat{H} \mid \Psi\rangle \tag{14}$$

$$i\hbar \mid \psi\rangle\frac{\partial \mid \chi\rangle}{\partial t} = \left(\hat{T}_N + \hat{H}_{\mathrm{el}}\right) \mid \chi\rangle \mid \psi\rangle \tag{15}$$

Multiply by $\langle\psi \mid$ and integrate over the electronic coordinates

$$i\hbar\frac{\partial}{\partial t} \mid \chi\rangle = (\langle\psi|T_N|\psi\rangle + V(q)) \mid \chi\rangle \tag{16}$$

using the potential function

$$\langle\psi|H_{\mathrm{el}}(q)|\psi\rangle = V(q) \tag{17}$$

To analyse KE function, use a simple form of the KEO

$$\hat{T}_N = \sum_\alpha -\frac{1}{2M_\alpha}\frac{\partial^2}{\partial q_\alpha^2} \tag{18}$$

with M_α the nuclear mass. Remembering that the electronic functions depend on the nuclear coordinate, a single term of this KEO can be written

$$\langle\psi|T_N|\psi\rangle = -\frac{1}{2M}\left(\langle\psi|\frac{\partial^2}{\partial q^2}\psi\rangle + 2\langle\psi|\frac{\partial}{\partial q}\psi\rangle\frac{\partial}{\partial q} + \frac{\partial^2}{\partial q^2}\right) \tag{19}$$

And as the *derivative operator* $\partial/\partial q$ is anti-hermitian

$$\langle\psi|\frac{\partial}{\partial q}\psi\rangle = 0 \tag{20}$$

we obtain

$$\langle\psi|T_N|\psi\rangle = -\frac{1}{2M}\left(\langle\psi|\frac{\partial^2}{\partial q^2}\psi\rangle + \frac{\partial^2}{\partial q^2}\right) \tag{21}$$

Ignoring the first term on the RHS, which is (hopefully) small

$$\langle\psi|T_N|\psi\rangle \approx T_N \tag{22}$$

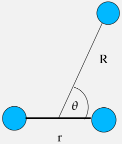
we obtain the TDSE in the *Adiabatic Approximation*:

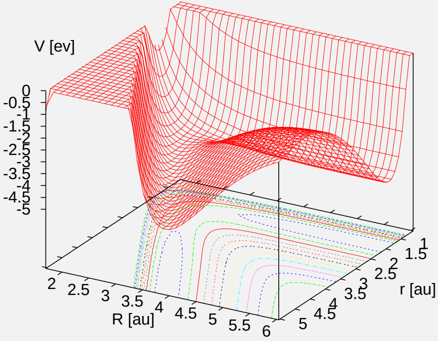
$$i\hbar\frac{\partial}{\partial t}\mid\chi\rangle = (T_N + V(q))\mid\chi\rangle \tag{23}$$

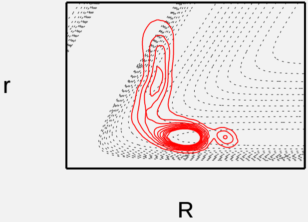
This is the basic picture used in chemistry that the nuclear and electronic motions can be separated. The nuclei then move over a potential surface provided by the electrons that do not depend on the electronic motion, but only on their position.

This is usually referred to as the Born-Oppenheimer Approximation. Sometimes, however, B-O Approx is used when the scalar term $\langle\psi|\frac{\partial^2}{\partial q^2}\psi\rangle$ is included. Most authors call this latter approximation the Born-Huang Approximation.

Wavepacket Dynamics







To solve the TDSE require:

- Potential surfaces
- Algorithm to propagate wavepacket

TDSE: The Complete Solution

A full solution requires a multi-configurational ansatz. Start by using Born representation

$$\Psi(\mathbf{q},\mathbf{r}) = \sum_i \chi_i(\mathbf{q})\psi_i(\mathbf{r};\mathbf{q}) \quad , \tag{24}$$

where electronic functions are all the solutions to clamped nucleus Hamiltonian Eq. (11). The TDSE is now

$$i\hbar \sum_i \mid \psi_i\rangle \frac{\partial \mid \chi_i\rangle}{\partial t} = \sum_i \left(\hat{T}_N + \hat{H}_{\mathrm{el}}\right) \mid \chi_i\rangle \mid \psi_i\rangle \tag{25}$$

Now multiply by one electronic function $\langle\psi_j\mid$ and again integrate

$$i\hbar \frac{\partial}{\partial t} \mid \chi_j\rangle = \sum_i \left[\langle\psi_j|T_N|\psi_i\rangle + V_j(q)\delta_{ji}\right] \mid \chi_i\rangle \tag{26}$$

using the full set of potential functions

$$\langle\psi_j|H_{\mathrm{el}}(q)|\psi_j\rangle = V_j(q) \tag{27}$$

One term of the KE operator in the electronic basis is now

$$\langle\psi_j|T_N|\psi_i\rangle = -\frac{1}{2M}\left(\langle\psi_j|\frac{\partial^2}{\partial q^2}\psi_i\rangle + 2\langle\psi_j|\frac{\partial}{\partial q}\psi_i\rangle\frac{\partial}{\partial q} + \frac{\partial^2}{\partial q^2}\right) \tag{28}$$

which can be written in terms of the *scalar* and *vector* derivative couplings, **G** and **F**

$$\langle\psi_j|T_N|\psi_i\rangle = -\frac{1}{2M}\left(G_{ji} - 2\vec{F}_{ji}.\nabla\right) + \hat{T}_N \tag{29}$$

where

$$G_{ji} = \sum_\alpha \langle\psi_j|\frac{\partial^2}{\partial q_\alpha^2}\psi_i\rangle \tag{30}$$

$$F_{ji}^\alpha = \langle\psi_j|\frac{\partial}{\partial q_\alpha}\psi_i\rangle \tag{31}$$

Defining the *non-adiabatic operator*

$$\Lambda_{ji} = \frac{1}{2M}\left(G_{ji} + 2\vec{F}_{ji}.\nabla\right) \tag{32}$$

the TDSE in the *adiabatic picture* is therefore

$$i\hbar\frac{\partial}{\partial t} \mid \chi_j\rangle = \sum_i \left[\left(T_N + V_j\right)\delta_{ji} - \Lambda_{ji}\right] \mid \chi_i\rangle \tag{33}$$

Finally, using the fact that

$$\mathbf{G} = (\nabla \cdot \mathbf{F}) + \mathbf{F} \cdot \mathbf{F} \tag{34}$$

Eq. (33) can be written:

$$\left[-\frac{1}{2M}(\nabla\mathbf{1} + \mathbf{F})^2 + \mathbf{V}\right]\boldsymbol{\chi} = i\hbar\frac{\partial\boldsymbol{\chi}}{\partial t} \quad , \tag{35}$$

The Adiabatic Picture

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

$$\left[\hat{T}_n + V\right]\chi = i\hbar\frac{\partial\chi}{\partial t} \tag{36}$$

and we recover the adiabatic TDSE where the nuclei move over a single potential energy surface, V, which can be obtained from quantum chemistry calculations.

An expression for the derivative coupling in terms of the energy of the states involved can be obtained from

$$\nabla\langle\psi_i|H_{el}|\psi_j\rangle = \langle\nabla\psi_i|H_{el}|\psi_j\rangle + \langle\psi_i|\nabla H_{el}|\psi_j\rangle + \langle\psi_i|H_{el}|\nabla\psi_j\rangle \tag{37}$$

As we are using the adiabatic basis,

$$\nabla\langle\psi_i|H_{el}|\psi_j\rangle = 0 \tag{38}$$

And as $H\psi_i = V_i\psi_i$, we obtain

$$\mathbf{F}_{ij} = \frac{\langle\psi_i \mid \left(\boldsymbol{\nabla}\hat{H}_{\mathrm{el}}\right) \mid \psi_j\rangle}{V_j - V_i} \quad \text{for } i \neq j \quad . \tag{39}$$

Compare this to the Hellman-Feymann expression to the derivative of a potential

$$\nabla\langle\psi_i|H_{el}|\psi_i\rangle = \langle\psi_i|\nabla H_{el}|\psi_i\rangle \tag{40}$$

and we see this is a “coupling force”.

The derivative coupling is singular if 2 potential surfaces become degenerate.

The Diabatic Picture

To remove these singularities, we first separate out a group of coupled states from the rest (group B.O. approximation).

$$\left[-\frac{1}{2M}(\nabla \mathbf{1}^{(g)} + \mathbf{F}^{(g)})^2 + \mathbf{V}^{(g)}\right] \boldsymbol{\chi}^{(g)} = i\hbar \frac{\partial \boldsymbol{\chi}^{(g)}}{\partial t} \quad , \tag{41}$$

If we rotate the adiabatic electronic basis via a unitary transformation

$$\psi^{(\boldsymbol{d})} = \mathbf{S}(\mathbf{q})\psi^{(\boldsymbol{a})} \tag{42}$$

then (dropping (g) superscript)

$$\mathbf{S}^{\dagger}\left[-\frac{1}{2M}\left(\nabla \mathbf{1} + \mathbf{F}\right)^2 + \mathbf{V}\right] \mathbf{S}\mathbf{S}^{\dagger} \boldsymbol{\chi} = i\hbar \mathbf{S}^{\dagger} \dot{\boldsymbol{\chi}} \quad , \tag{43}$$

such that the Hamiltonian can be written

$$[T_N \mathbf{1} + \mathbf{W}]\, \chi^{(d)} = i\hbar \frac{\partial \chi^{(d)}}{\partial t} \quad , \tag{44}$$

where all elements of **W** are potential-like terms

$$\begin{aligned} \mathbf{W} &= \mathbf{S}^{\dagger}\mathbf{V}\mathbf{S} && (45) \\ \chi^{(d)} &= \mathbf{S}^{\dagger}\chi^{(a)} && (46) \\ -\frac{1}{2M}\mathbf{S}^{\dagger}\left(\nabla\mathbf{1} + \mathbf{F}\right)^{2}\mathbf{S} &= T_N \mathbf{1} && (47) \end{aligned}$$

The last relationship can be shown to be correct if

$$\nabla \mathbf{S} = -\mathbf{F}\mathbf{S} \tag{48}$$

Baer Chem. Phys. Lett. (1975) **35**: 112

Worth and Cederbaum Ann. Rev. Phys. Chem. (2004) **55**: 127

Surface Crossings

For a 2-state system, the diabatic potentials are

$$\mathbf{W} = \begin{pmatrix} W_{11} & W_{12} \\ W_{12} & W_{22} \end{pmatrix} \tag{49}$$

Eigenvalues of diabatic potential matrix are adiabatic PES:

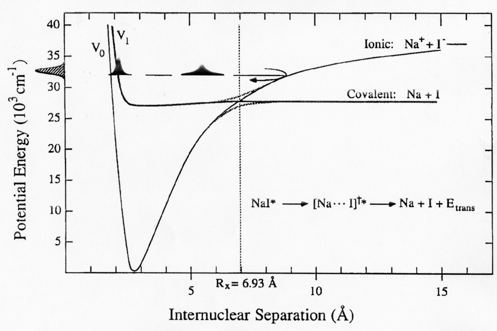
$$V_{\pm} = \frac{1}{2}(W_{11} + W_{22}) \pm \frac{1}{2}\sqrt{\Delta W^2 + 4W_{12}^2} \tag{50}$$

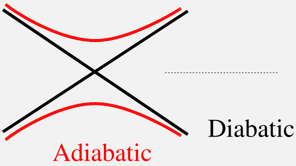
Surfaces degenerate at $\mathbf{q}_0$ if

$$\begin{aligned} \Delta W &= W_{22} - W_{11} = 0 \qquad (51) \\ W_{12} &= 0 \qquad (52) \end{aligned}$$

Avoided Crossing

Two conditions need to be met for degeneracy. Impossible if only 1 coordninate. Hence in a 1D system states that have non-zero coupling do not meet and form an *avoided crossing*.





NaI Potential Surfaces

In multi-dimensional systems, Eqs. (51,52) can be satisfied.

Diabatic potential matrix elements are all potential like functions so can be represented by a Taylor expansion around a point such as q_0

$$W_{ij} = W_{ij}(q_0) + \sum_{\alpha} \left. \frac{\partial W_{ij}}{\partial q_\alpha} \right|_{q=q_0} (q_\alpha - q_0) + \sum_{\alpha,\beta} \frac{1}{2} \left. \frac{\partial^2 W_{ij}}{\partial q_\alpha q_\beta} \right|_{q=q_0} (q_\alpha - q_0)(q_\beta - q_0) + \dots \tag{53}$$

Move to q_0 where the states $|1\rangle$ and $|2\rangle$ are degenerate. If at this point we take $\psi_i^{(d)} = \psi_i^{(a)}$ then

$$\begin{aligned} W_{ij} = \langle \psi_i^{(d)} | H_{el} | \psi_j^{(d)} \rangle &= E_i \quad ; \quad i = j && (54) \\ &= 0 \quad ; \quad i \neq j && (55) \end{aligned}$$

At q_0, $E_1 = E_2 = E$ and so expanding to first order:

$$\mathbf{W} = \begin{pmatrix} E & 0 \\ 0 & E \end{pmatrix} + \begin{pmatrix} \vec{\kappa}_1 \cdot \vec{r} & \vec{\lambda} \cdot \vec{r} \\ \vec{\lambda} \cdot \vec{r} & \vec{\kappa}_2 \cdot \vec{r} \end{pmatrix} \tag{56}$$

where $r_\alpha = q_\alpha - q_{0,\alpha}$ and λ, κ_i vectors of potential derivatives. As the diabatic and adiabatic electronic functions are equal at q_0, the on-diagonal derivative is the gradient of the potential

$$\kappa_{\alpha,i} = \frac{\partial}{\partial q_\alpha} \langle \psi_i^{(d)} | H_{el} | \psi_i^{(d)} \rangle = \frac{\partial}{\partial q_\alpha} V_i = \langle \psi_i^{(a)} | \frac{\partial H_{el}}{\partial q_\alpha} | \psi_i^{(a)} \rangle \tag{57}$$

and the off-diagonal derivative is the derivative coupling (See Eq. (37) and use the fact that thje derivative coupling is 0 in the diabatic basis).

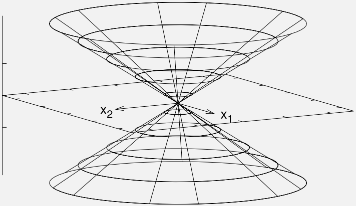
$$\lambda_\alpha = \frac{\partial}{\partial q_\alpha} \langle \psi_1^{(d)} | H_{el} | \psi_2^{(d)} \rangle = \langle \psi_1^{(a)} | \frac{\partial H_{el}}{\partial q_\alpha} | \psi_2^{(a)} \rangle \tag{58}$$

Thus

$$\begin{aligned} \Delta W = (\vec{\kappa}_2 - \vec{\kappa}_1) \cdot \vec{r} &= \vec{g} \cdot \vec{r} && \text{gradient difference} \\ W_{12} = \vec{\lambda} \cdot \vec{r} &= \vec{h} \cdot \vec{r} && \text{derivative coupling} \end{aligned}$$

If we move so that $\vec{r}$ is orthogonal to g, h, the states remain degenerate. If we move so that $\vec{r}$ is in the plane g, h, the degeneracy is lifted.

The plane defined by $\{g, h\}$ is called the *branching plane*. And the shape of the surfaces in the branching space have the topography of a double cone. This is a *conical intersection*



The Importance of Symmetry

Symmetry plays an important role as conical intersections often occur at nuclear configurations with high symmetry. When this happens, the matrix elements

$$\langle\psi_i|H_{el}|\psi_j\rangle \quad \text{and} \quad \langle\psi_i|\frac{\partial H_{el}}{\partial q_\alpha}|\psi_j\rangle$$

will be zero if the integrand is not totally symmetric wrt the point group of the molecule. As the H is always totally symmetric,

$$\langle\psi_i|H_{el}|\psi_j\rangle \neq 0 \quad \text{if} \quad \Gamma_i \otimes \Gamma_j \supset A_1 \tag{59}$$

$$\langle\psi_i|\frac{\partial H_{el}}{\partial q_\alpha}|\psi_j\rangle \neq 0 \quad \text{if} \quad \Gamma_i \otimes \Gamma_j \otimes \Gamma_\alpha \supset A_1 \tag{60}$$

where A_1 represents the totally symmetric irrep

In all cases

- $\kappa_{\alpha,i} \neq 0$ only for $\Gamma_\alpha \supset A_1$

If the electronic states have different symmetries

- $\lambda_\alpha \neq 0$ only for $\Gamma_\alpha = \Gamma_i \otimes \Gamma_j$

For example in pyrazine, molecule is D_{2h}, states $S_1(B_{3u}), S_2(B_{2u})$ and as $B_{2u} \otimes B_{3u} = B_{1g}$ only modes of this symmetry can couple the states (there is only 1 of these ν_{10a}). There are four modes with A_g symmetry that have non-zero κ values.

The GD and DCP are thus independent and a conical intersection must occur.

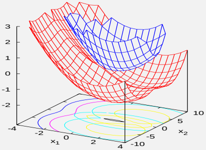
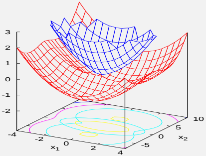
Some point groups (non-Abelian) have degenerate representations. These impose further constraints on relationships between the values of κ and λ.

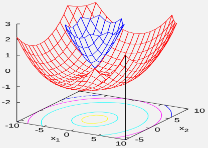
For example, in many point groups with an E irrep, $E \otimes e \supset A_1$ and the doubly degenerate electronic states are coupled by doubly degenerate vibrations. This is the $E \otimes e$ Jahn-Teller case and $\kappa_1 = -\kappa_2 = \lambda$.

Higher order terms are goverened by similar relationships. For a complete analysis of the JT problem see Viel and Eisfeld JCP (04) 120: 4603.

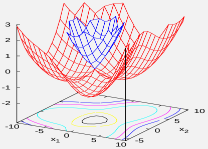
If no symmetry is present a CoIn can form if the modes involved in the $\vec{\kappa}$ and $\vec{\lambda}$ happen to be independent. These are called *accidental* CoIn in contrast to *symmetry induced* CoIn.

Types of Conical Intersections

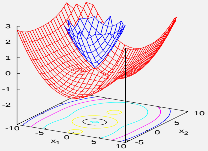
	- Sloped conical intersection - κ_2, κ_1 same sign
	- Peaked conical intersection - κ_2, κ_1 opposite signs



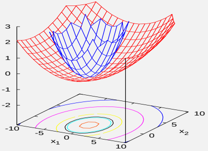
- E⊗*e* Jahn-Teller
- $\kappa_2 = -\kappa_1 = \lambda$
- Non-Abelian groups with *E* irrep



- Jahn-Teller
- $\kappa_2 = -\kappa_1 = \lambda$
- second-order couplings included



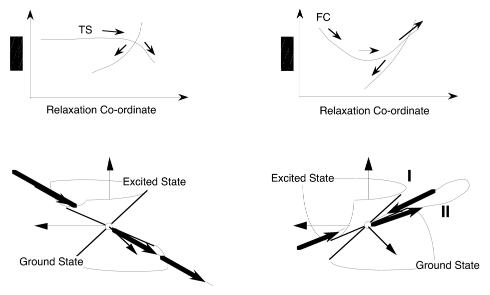
- $E \times b$ Jahn-Teller
- $\kappa_2 = -\kappa_1 \neq \lambda$
- D_2d



- Renner-Teller Intersection
- $\kappa_2, \kappa_1, \lambda = 0$
- Second-order Terms highest order

Peaked v Sloped

For dynamics, 2 main classifications

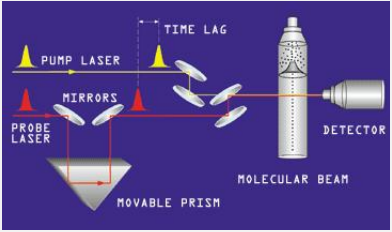


Peaked Sloped

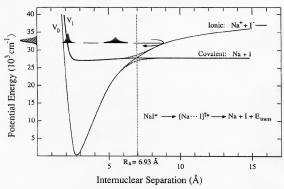
Atchity, Xantheas and Ruedenberg JCP (91) 95: 1862

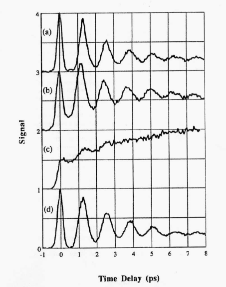
Non-adiabatic Crossing in NaI

Pump-probe Spectroscopy



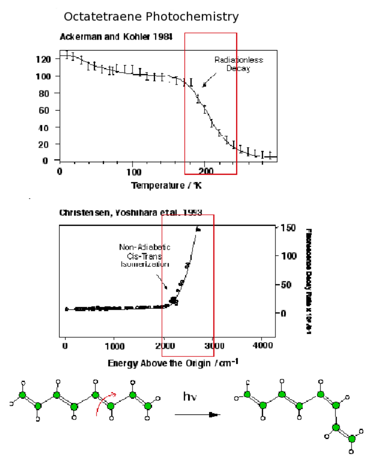
- pump pulse inititiates reaction
- probe pulse provides signal related to dynamics





Signature of Conical Intersections

Octatetraene



Pyrazine

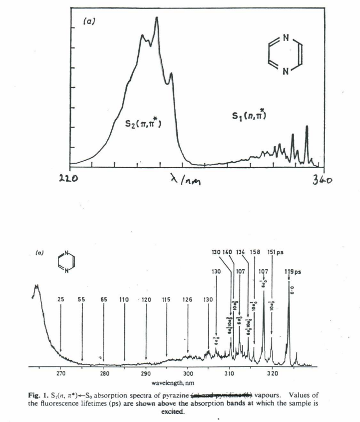


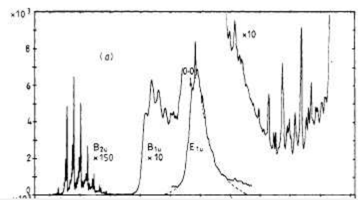
Fig. 1. $S_1(n,\pi^*)\leftarrow S_0$ absorption spectra of pyrazine ~~(a) and pyridine (b)~~ vapours. Values of the fluorescence lifetimes (ps) are shown above the absorption bands at which the sample is excited.

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

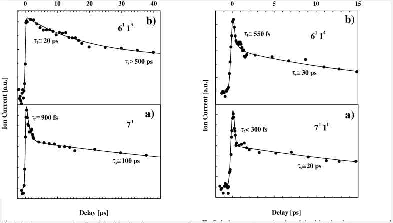
Benzene: Photophysics

	Quantum yield			
Process	253 nm	248 nm	242 nm	237 nm
Formation of photoproducts	0.016	0.022	0.024	0.037
Fluorescence	0.18	0.10	0	0
Formation of triplet (ISC)	0.6	0.6	0	0

Absorption Spectrum

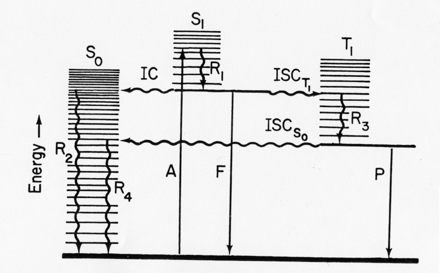


"Channel 3"

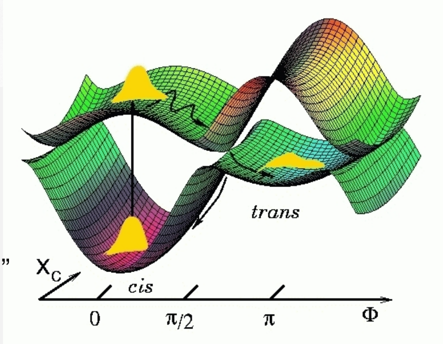


Clara *et al* Appl. Phys. B (00)71: 431

Photochemistry



Jablonski Diagram



Evolution over Potential Surfaces

Conical Intersections =
"Photochemical Funnels"

Other Conical Intersections

Intersections can also occur in higher dimensions:

- 3-states (Matsika and Yarkony JACS (03) 125: 10672)
- 2-states v 3-states (Coe and Matinez JACS (05) 127: 4560)
- 4-states (Assmann, Worth and Gonzalez JCP (12) 137: 22A524)

3-state CoIns have a 5-dimensional branching space etc.

And can also be formed in diatomics when

- Light-Induced (Halasz, Vibok and Cederbaum JPCL (15) 6: 348)

The Adiabatic-Diabatic Transformation matrix

The ADT matrix, **S** is defined vy Eq. (48) only through a derivative wrt q. To completely define it specify that the diabatic and adiabatic basis are identical at a particular point, q_0. This may be the CoIn minimum (as above) or the FC point, or some other suitable point such as a dissociation assymptote.

$$\mathbf{S}(q_0) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{61}$$

This is referred to as fixing the *global gauge*.

NB the ADT is a global function $\mathbf{S}(q)$

For a 2-state CoIn it is possible to get an analytic expression for **S**. First write the diabatic potential matrix

$$\mathbf{W} = \begin{pmatrix} \Sigma - \Delta & W_{12} \\ W_{12} & \Sigma + \Delta \end{pmatrix} \tag{62}$$

with

$$\Sigma = \frac{1}{2}(W_{11} + W_{22}) \quad ; \quad \Delta = \frac{1}{2}(W_{22} - W_{11}) \tag{63}$$

Express the unitary ADT matrix in terms of an angle

$$\mathbf{S} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \tag{64}$$

Now choose θ to diagonalise **W**

$$\mathbf{SWS}^T = \mathbf{V} \tag{65}$$

$$\begin{aligned} \left(\cos^2\theta - \sin^2\theta\right) W_{12} + 2\cos\theta\sin\theta\Delta &= 0 && (66) \\ \Sigma \pm \left(\cos^2\theta - \sin^2\theta\right)\Delta - 2\cos\theta\sin\theta W_{12} &= V_{\pm} && (67) \end{aligned}$$

where

$$V_{\pm} = \Sigma \pm \sqrt{\Delta^2 + W_{12}^2} \qquad (68)$$

are the eigenvalues (see Eq. (50)). These equations can be re-arranged to give

$$\begin{aligned} \tan 2\theta &= \frac{W_{12}}{\Delta} && (69) \\ \cos\theta &= \frac{1}{\sqrt{2}}\left(1 + \frac{\Delta}{d}\right)^{\frac{1}{2}} \quad ; \quad \sin\theta = \frac{1}{\sqrt{2}}\left(1 - \frac{\Delta}{d}\right)^{\frac{1}{2}} && (70) \end{aligned}$$

with

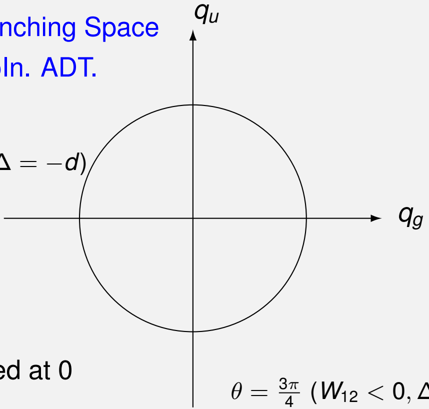
$$d = \frac{1}{2}(V_+ - V_-) = \sqrt{\Delta^2 + W_{12}^2} \qquad (71)$$

$$\theta = \tfrac{\pi}{4}\ (W_{12} > 0, \Delta = 0)$$

$$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$$

Travel in Branching Space

Around a CoIn. ADT.



$$\theta = 0\ (W_{12} = 0, \Delta = d)$$

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\theta = \tfrac{\pi}{2}\ (W_{12} = 0, \Delta = -d)$$

$$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

$$\theta = \pi\ (W_{12} = 0, \Delta = d)$$

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \times -1$$

S is undefined at 0

$$\theta = \tfrac{3\pi}{4}\ (W_{12} < 0, \Delta = 0)$$

$$-\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$$

Geometric Phase

It is known that an adiabatic wavefunction, ψ undergoing transport has a phase factor

$$\gamma(C) = i \oint_C \langle\psi|\frac{\partial}{\partial q}\psi\rangle dq \qquad (72)$$

which means that the wavefunction changes sign on travelling a closed loop around a conical intersection.

This is the *Berry Phase*. Berry, Proc. Roy. Soc. A (84) 392: 45.

Note that the sign change is cancelled by the sign change in S.

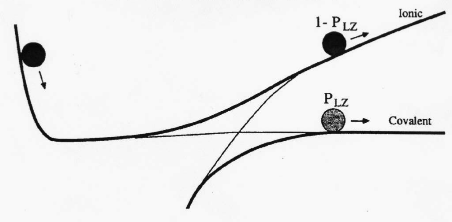
Importance in scattering: Juanes-Marcos *et al* Science (05) 309: 1227

Landau-Zener Model

For a particle on adiabatic surface 2 in the “non-adiabatic region”, the probability of moving to surface 1 is

$$P_{2\to 1} = \exp\left(-\frac{2\pi}{\hbar}\frac{F_{12}^2}{\dot{q}|F_1 - F_2|}\right) \tag{73}$$

If $P_{2\to 1} \longrightarrow 1$ particle changes adiabatic (stays on diabatic) state.



Propagating wavepacket: The Standard Method

Nuclear wavefunction expanded in primitive basis set:

$$\Psi(q_1, \ldots q_f, t) = \sum_{j_1=1}^{N_1} \cdots \sum_{j_p=1}^{N_f} A_{j_1 \ldots j_f}(t)\, \chi_{j_1}^{(1)}(q_1) \cdots \chi_{j_f}^{(f)}(q_f)$$

Use Dirac-Frenkel Variational Principle:

$$\left\langle \delta\Psi \middle| H - i\frac{\partial}{\partial t} \middle| \Psi \right\rangle = 0$$

to obtain equations of motion for *A*:

$$i\dot{A}_{j_1 \ldots j_f} = \sum_L \langle \chi_{j_1}^{(1)}(q_1) \cdots \chi_{j_f}^{(f)}(q_f) | H | \chi_{l_1}^{(1)}(q_1) \cdots \chi_{l_f}^{(f)}(q_f) \rangle A_{l_1 \ldots l_f}$$

$$i\dot{A}_J = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L$$

Kulander “Time-dependent methods for quantum dynamics”, Elsevier, 1991

Kosloff, Ann. Rev. Phys. Chem. (94) **45**: 145

The Hamiltonian matrix elements

Need to evaluate matrix elements (integrals)

$$\begin{aligned} H_{JL} &= \sum_{\ell_1,\ldots\ell_f} \langle \chi^{(1)}_{j_1} \cdots \chi^{(f)}_{j_f} | H | \chi^{(1)}_{\ell_1} \cdots \chi^{(f)}_{\ell_f} \rangle \\ &= \sum_{\ell_1,\ldots\ell_f} \langle \chi^{(1)}_{j_1} \cdots \chi^{(f)}_{j_f} | T + V | \chi^{(1)}_{\ell_1} \cdots \chi^{(f)}_{\ell_f} \rangle \end{aligned}$$

As written an $N^f \times N^f$ matrix of multi-dimensional integrals!

I. Usually

$$T = \sum_{\kappa} T_{\kappa}$$

$$T_{JL} = \sum_{\kappa} \langle \chi^{(\kappa)}_{j_\kappa} | T_{\kappa} | \chi^{(\kappa)}_{\ell_\kappa} \rangle \delta_{J^\kappa L^\kappa}$$

$N \times N$ matrices, which by a suitable choice of basis functions can be solved analytically

II. The potential is a local operator $V(\mathbf{q})$. Thus if basis functions are localised, $\chi_j^{(\kappa)} \approx \delta(q - q_j)$ then

$$\begin{aligned} V_{JL} &= \langle \chi_{j_1}^{(1)} \cdots \chi_{j_f}^{(f)} | V | \chi_{\ell_1}^{(1)} \cdots \chi_{\ell_f}^{(f)} \rangle \\ &= V(q_{j_1} \ldots q_{j_f}) \delta_{JL} \end{aligned}$$

To enable I and II, use a DVR basis set in which

$$\begin{aligned} X_{ij} &= \langle \phi_i | \hat{x} | \phi_j \rangle \\ \mathbf{UXU}^T &= \mathbf{x} \end{aligned}$$

where ϕ_i are an analytically known FBR. And so

$$\chi_\alpha = \sum_i U_{\alpha i} \phi_i$$

are the DVR, $\chi_\alpha \sim \delta(x - x_\alpha)$. Various DVRs possible.

Beck *et al* Phys. Rep. (2000) **324**: 1

Integrating the TDSE

Full solution is

$$\Psi(t) = e^{-\frac{i}{\hbar}\hat{H}t}\Psi(0)$$

Split-operator method.

$$e^{-\frac{i}{\hbar}\hat{H}t} \neq e^{-\frac{i}{\hbar}Tt}e^{-\frac{i}{\hbar}Vt}$$

so divide propagation into short steps and approximate

$$\Psi(t+\delta t) = e^{-\frac{i}{2\hbar}V\delta t}e^{-\frac{i}{\hbar}T\delta t}e^{-\frac{i}{2\hbar}\hat{V}\delta t}\Psi(t)$$

Chebyshev Propagation Represent propagator by polynomial expansion:

$$e^{-\frac{i}{\hbar}\hat{H}t}\Psi = \sum_n a_n P_n(H)\Psi$$

where $P_n(H)$ are generated by a recurrence relationship

Great but limited due to exponential increase in computer resources $\sim N^f$ .....

The Multiconfigurational Time-Dependent Hartree (MCTDH) Method

$$\Psi(q_1,\ldots,q_f,t)=\sum_{j_1=1}^{n_1}\cdots\sum_{j_f=1}^{n_f}A_{j_1\ldots j_f}(t)\prod_{\kappa=1}^{f}\varphi_{j_\kappa}^{(\kappa)}(q_\kappa,t)$$

Variational equations of motion for A and φ.

$$\begin{aligned} i\dot{A}_J &= \sum_L \langle\Phi_J|H|\Phi_L\rangle A_L \\ i\dot{\varphi}^{(\kappa)} &= \left(1-P^{(\kappa)}\right)\left(\rho^{(\kappa)}\right)^{-1}\langle\mathbf{H}\rangle^{(\kappa)}\varphi^{(\kappa)} \end{aligned}$$

- non-linear equations of motion
- Computer memory $n^f + fnN$

SPFs expanded in *primitive grid*

$$\varphi_j=\sum_{i=1}^{N}a_{ij}\chi_i$$

Beck *et al* Phys. Rep. (00) 324:1

Meyer, Gatti and Worth “Multidimensional quantum dynamics”, Wiley-VCH, 2009

Where we have *single-hole functions*,

$$\psi_{k_f}^{(f)} = \sum_{j_1=1}^{n_1} \cdots \sum_{j_{f-1}=1}^{n_{f-1}} A_{j_1 \ldots j_{f-1} k_f}(t) \prod_{\kappa=1}^{f-1} \varphi_{j_\kappa}^{(\kappa)}(q_\kappa, t)$$

mean-field operators and density matrices

$$\langle H \rangle_{ij}^{(\kappa)} = \langle \psi_{i_\kappa}^{(\kappa)} | H | \psi_{j_\kappa}^{(\kappa)} \rangle \qquad \rho_{ij}^{(\kappa)} = \langle \psi_{i_\kappa}^{(\kappa)} | \psi_{j_\kappa}^{(\kappa)} \rangle = \textstyle\sum_J A^*_{J_i^\kappa} A_{J_j^\kappa}$$

and

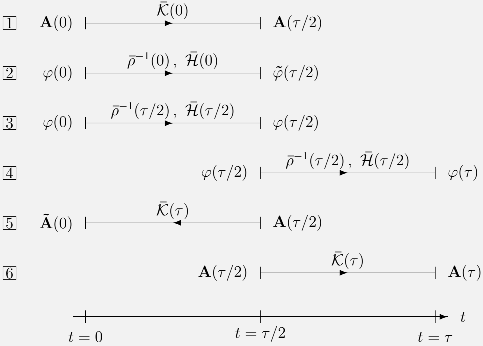
time-dependent matrix elements

$$H_{JL} = \langle \Phi_J | H | \Phi_L \rangle = \langle \phi_{j_1}^{(1)} \ldots \phi_{j_f}^{(f)} | H | \phi_{l_1}^{(1)} \ldots \phi_{l_f}^{(f)} \rangle$$

- for efficiency need product potential $V = \sum_s c_s h_s^{(1)} h_s^{(2)} \ldots$

$$\langle \Phi_I | H | \Phi_J \rangle = \textstyle\sum_s c_s \langle \varphi_{i_1}^{(1)} | h^{(1)} | \varphi_{j_1}^{(1)} \rangle \langle \varphi_{i_2}^{(2)} | h^{(2)} | \varphi_{j_2}^{(2)} \rangle \ldots$$

The Constant Mean Field Integration Scheme



$\boxed{1}$ $\mathbf{A}(0) \xrightarrow{\bar{\mathcal{K}}(0)} \mathbf{A}(\tau/2)$

$\boxed{2}$ $\varphi(0) \xrightarrow{\bar{\rho}^{-1}(0)\,,\ \bar{\mathcal{H}}(0)} \tilde{\varphi}(\tau/2)$

$\boxed{3}$ $\varphi(0) \xrightarrow{\bar{\rho}^{-1}(\tau/2)\,,\ \bar{\mathcal{H}}(\tau/2)} \varphi(\tau/2)$

$\boxed{4}$ $\varphi(\tau/2) \xrightarrow{\bar{\rho}^{-1}(\tau/2)\,,\ \bar{\mathcal{H}}(\tau/2)} \varphi(\tau)$

$\boxed{5}$ $\tilde{\mathbf{A}}(0) \xleftarrow{\bar{\mathcal{K}}(\tau)} \mathbf{A}(\tau/2)$

$\boxed{6}$ $\mathbf{A}(\tau/2) \xrightarrow{\bar{\mathcal{K}}(\tau)} \mathbf{A}(\tau)$

$$i\dot{A}_J(t) = \sum_L \bar{\mathcal{K}}_{JL} A_L(t)$$

$$i\dot{\varphi}_j^{(1)}(t) = \left(1 - P^{(1)}\right)\left(h^{(1)}\varphi_j^{(1)}(t) + \sum_{k,l=1}^{n_1}\left(\bar{\rho}^{(1)\ -1}\right)_{jk}\sum_{r=1}^{s}\bar{\mathcal{H}}_{rkl}^{(1)}\, h_r^{(1)}\,\varphi_l^{(1)}(t)\right)$$

$$\vdots \qquad\qquad \vdots$$

Note on Treating Non-Adiabatic Systems

$$\mathbf{H} = T\mathbf{1} + \mathbf{W}$$

To include the electronic degree of freedom use either:

Multi-set

$$\Psi(q_1,\ldots,q_f,t) = \sum_{s=1}^{n_s} \sum_{j_1=1}^{n_1} \ldots \sum_{j_f=1}^{n_f} A^{(s)}_{j_1\ldots j_f}(t) \prod_{\kappa=1}^{f} \varphi^{(s,\kappa)}_{j_\kappa}(q_\kappa,t)$$

Or Single-Set:

$$\Psi(q_1,\ldots,q_f,t) = \sum_{j_1=1}^{n_1} \ldots \sum_{j_f=1}^{n_f} \sum_{s=1}^{n_s} A_{j_1\ldots j_f,s}(t) \prod_{\kappa=1}^{f} \varphi^{(\kappa)}_{j_\kappa}(q_\kappa,t)|s\rangle$$

$$H = \sum_{s=1}^{n_s} |s\rangle T \langle s| + \sum_{s=1}^{n_s} \sum_{t=1}^{n_s} |s\rangle W_{st} \langle t|$$

Combined Mode Particles

Re-write MCTDH ansatz

$$\Psi(q_1,\ldots,q_f,t) = \sum_{j_1=1}^{n_1}\cdots\sum_{j_p=1}^{n_p} A_{j_1\ldots j_p}(t)\prod_{\kappa=1}^{p}\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t)$$

A “particle” may contain more than one coordinate,
$Q_i = (q_a, q_b, \ldots, q_w)$

e.g.

$$\begin{aligned}\Psi(q_1,q_2,q_3,t) &= \sum_{j_1}\sum_{j_2} A_{j_1 j_2}(t)\,\varphi_{j_1}^{(1)}(q_1,t)\,\varphi_{j_2}^{(2)}(q_2,q_3,t)\\ &= \sum_{j_1}\sum_{j_2} A_{j_1 j_2}(t)\,\varphi_{j_1}^{(1)}(Q_1,t)\,\varphi_{j_2}^{(2)}(Q_2,t)\end{aligned}$$

Saving in memory

All 1D functions

$$Mem \sim n^f + fnN$$

Now combine d modes in each particle.
$p = \frac{f}{d}$ particles with grid lengths of N^d
If $\tilde{n} \leq n^d$ save memory.

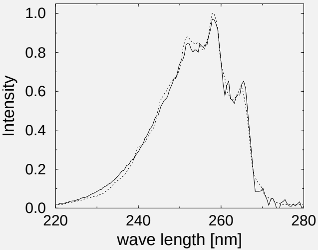
$$Mem \sim \tilde{n}^p + p\tilde{n}N^d$$

If $d = f$, then full-grid used and $\tilde{n} = 1$

$$Mem \sim N^f$$

Result: MCTDH can treat ca 30 modes

Bench Mark: Pyrazine Spectrum



- full 24D QD
- 650 MB
  (205 MB good result)
- ca 2×10^{22} MB for "standard"

Raab *et al* JCP (99) 110: 936

Multi-Layer MCTDH (ML-MCTDH)

Expand a multi-mode SPF in an MCTDH expansion to create layers:

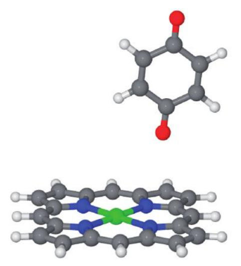
$$
\begin{aligned}
\Psi(q_1,\ldots,q_f,t) &= \sum_{j_1=1}^{n_1}\ldots\sum_{j_p=1}^{n_p} A_{j_1\ldots j_p}(t)\prod_{\kappa=1}^{p}\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t) && \text{Layer 1}\\
\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t) &= \sum_{k_1=1}^{n_1}\ldots\sum_{k_Q=1}^{n_Q} B_{k_1\ldots k_Q}^{\kappa,j_\kappa}(t)\prod_{\nu=1}^{Q}\nu_{k_\nu}^{(\nu)}(R_\nu,t) && \text{Layer 2}\\
\nu_{k_\nu}^{(\nu)}(R_\nu,t) &= \sum_{l_1=1}^{n_1}\ldots\sum_{l_R=1}^{n_R} C_{l_1\ldots l_R}^{\nu,k_\nu}(t)\prod_{\xi=1}^{R}\xi_{l_\xi}^{(\xi)}(S_\xi,t) && \text{Layer 3}\\
\ldots &= \ldots
\end{aligned}
$$

Each layer acts as a set of SPFs for the layer above and a set of coeficients for the layer below.

Leads to a recursive sets of variational equations of motion:

Wang and Thoss JCP (2003) **119**; 1289

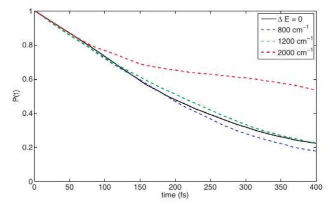
$$\begin{aligned}
i\dot{A}_J &= \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L \\
i\dot{\varphi}^{(\kappa)} &= \left(1 - P^{(\kappa)}\right) \left(\rho^{(\kappa)}\right)^{-1} \langle \mathbf{H} \rangle^{(\kappa)} \varphi^{(\kappa)} \\
i\dot{\nu}^{(\nu)} &= \left(1 - P^{(\nu)}\right) \left(\rho^{(\nu)}\right)^{-1} \langle \mathbf{H} \rangle^{(\nu)} \nu^{(\nu)} \\
\ldots &= \ldots
\end{aligned}$$



Borelli *et al* Mol. Phys. (2012) 110: 751

135 Mode Quantum Dynamics

Photo-induced ET. Spin-Boson Model.



Parametrized Spfs (G-MCTDH)

$$\Psi(Q_1,\ldots,Q_f,t)=\sum_{j_1=1}^{n_1}\cdots\sum_{j_p=1}^{n_f}A_{j_1\ldots j_p}(t)\prod_{\kappa=1}^{p-n}\varphi_{j_\kappa}^{(\kappa)}\prod_{\kappa=n+1}^{p}g_{j_\kappa}^{(\kappa)}$$

Replace single-particle functions with Gaussian functions

$$g_j(\mathbf{Q},t)=\exp\left(\mathbf{Q}^T\zeta_j\mathbf{Q}+\mathbf{Q}^T\boldsymbol{\xi}_j+\eta_j\right)$$

Propagate parameters $\lambda=\{\zeta,\boldsymbol{\xi},\eta\}$

$$\begin{aligned} i\dot{A}_j &= \sum_{lk}\mathcal{S}_{jk}^{-1}\langle\Phi_k|H|\Phi_l\rangle A_l-\sum_{\kappa=1}^{p}\sum_{l=1}^{n_\kappa}iS_{jk}^{-1}\langle g_k|\frac{\partial}{\partial t}g_l\rangle A_{J_l^\kappa}\\ &= \sum_{lk}\mathcal{S}_{jk}^{-1}H_{kl}A_l-\sum_{\kappa=1}^{p}\sum_{l=1}^{n_\kappa}iS_{jk}^{-1}\tau_{kl}A_{J_l^\kappa}\\ i\dot{\boldsymbol{\Lambda}} &= \mathbf{C}^{-1}\mathbf{Y}\end{aligned}$$

Burghardt *et al* JCP (99) 99:2927 ; Burghardt *et al* JCP (08) 129:174104

ADVANTAGES

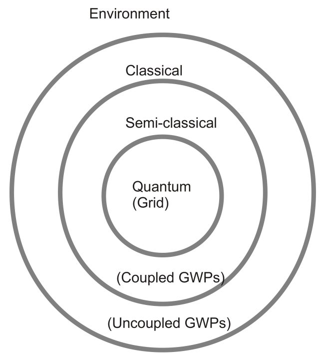
- Need more GFs than SPFs,
- **BUT** set of parameters smaller than no. of grid points
- spatially unrestricted

DISADVANTAGES

- Non-orthogonal basis set - numerically difficult
- Efficiency requires approximate integral evaluation
  LHA $V = V(x_0) + V'(x - x_0) + V''(x - x_0)^2$
  - convergence on exact result depends on accuraccy of integrals

General Scheme

G-MCTDH gives general framework for Quantum — semi-classical — classical dynamics. Can also treat open systems using density matrix formalism.



Alternative Ansatz: MCTDH/G

Return to original MCTDH equation and variational derivation:

$$\Psi(Q_1,\ldots,Q_f,t)=\sum_{j_1=1}^{n_1}\cdots\sum_{j_f=1}^{n_p}A_{j_1\ldots j_p}(t)\prod_{\kappa=1}^{p}\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t)$$

and now using

$$|\,\varphi_r\rangle=\sum_{\alpha=1}^{m}|\,g_\alpha\rangle D_{\alpha r}\quad;\quad r=1,n$$

obtain EOMs for the A_J, φ_j and $\lambda_{a\alpha}$ as before, but for SPFs

$$i\dot{D}_{\gamma i}=\sum_{lj\alpha}S^{-1}_{\gamma\alpha}\rho^{-1}_{ij}\langle g_\alpha|(1-P)\langle H\rangle_{jl}|\varphi_l\rangle+\sum_m f_{mi}D_{\gamma m}-\sum_{\alpha\beta}S^{-1}_{\gamma\alpha}\tau_{\alpha\beta}D_{\beta i}$$

with $P=\sum_r|\varphi_r\rangle\langle\varphi_r|$. GWPs are TD basis for SPFs.

First layer of “Multi-layer G-MCTDH”

Römer, Ruckenbauer and Burghardt JCP (13) **138**: 064106

Grid-based QD $\longrightarrow$ Gaussian Wavepackets

In limit of only GWP basis functions G-MCTDH becomes the Variational Multi-configurational GWP Method: vMCG

$$\Psi(\mathbf{x}, t) = \sum_J A_J g_J(\mathbf{x}, t)$$

GWPs long-tradition in time-dependent QD.

- Conceptually simple
- Can be related to semi-classical dynamics
- possible to use for *direct dynamics*

BUT

- numerically unstable
- convergence properties not clear
- limited to rectilinear coordinates

vMCG Equations of Motion

$$\Psi(Q_1, \ldots, Q_f, t) = \sum_{j=1}^{n_1} A_j(t) g_j$$

EOMs are as for G-MCTDH (above). For *frozen* GWP basis, the EOMS can be written in terms of the centre coordinate and momentum as

$$\begin{aligned} \dot{q}_{l\beta} &= \frac{p_{l\beta}}{m_\beta} + \frac{1}{2\zeta_{l\beta}} \mathrm{Im} \sum_{m\alpha} C^{-1}_{l\beta m\alpha} \tilde{Y}_{m\alpha} \\ \dot{p}_{l\beta} &= -V'_{l\beta} + \mathrm{Re} \sum_{m\alpha} C^{-1}_{l\beta m\alpha} \tilde{Y}_{m\alpha} \end{aligned}$$

Most other GWP based methods use basis functions that follow classical trajectories.

Multiple Spawning

Martinez and Ben-Nun have developed GWP propagation for non-adiabatic systems. Basic ansatz:

$$\Psi(q,t) = \sum_s \sum_j A_j^{(s)}(t) g_j^{(s)}(g,t)$$

Variational solution of TDSE for expansion coefficients

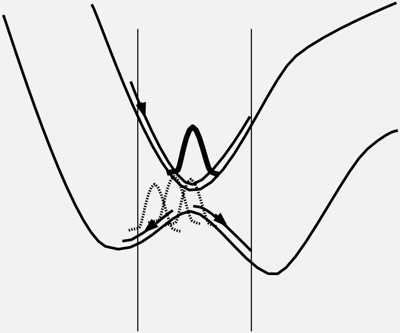
$$i\dot{A}_j = \sum_{lk} \mathcal{S}_{jk}^{-1} \langle \Phi_k \,|\, H \,|\, \Phi_l \rangle A_l - \sum_{\kappa=1}^{p} \sum_{l=1}^{n_\kappa} i S_{jk}^{-1} \langle g_k | \frac{\partial}{\partial t} g_l \rangle A_{J_l^\kappa}$$

- A_J as vMCG.
- GWPs follow classical trajectories as Heller.

If basis set complete, and integrals exact, full solution.

Basis set expanded in non-adiabatic region

- Identify region
- Propagate GWPs though region
- “Spawn” GWPs on other surface
- Rewind time
- Propagate coupled functions

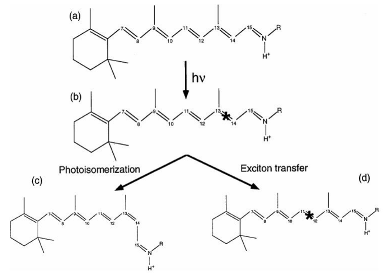


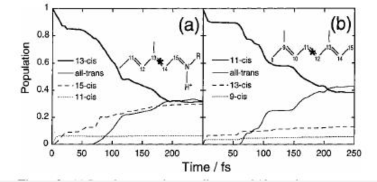
Different criteria to place functions so as to conserve energy etc.

Very efficient

Martinez et al JPC (96) 100: 7884
Ben-Nun and Martinez JCP (98) 108: 7244

E.g. **Retinal Isomerisation**





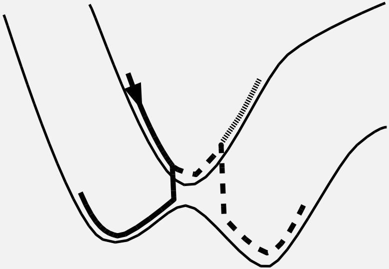
6 diabatic states all DOFs. 3 runs with 10 starting GWPs

(Ben-Nun and Martinez JPCA (98) 102: 9607)

Tunneling can also be simulated but only if barrier position known
(Ben-Nun and Martinez JCP (00) 112: 6113)

Trajectory Surface Hopping

Classical trajectory swarm sampling surfaces. Non-adiabatic term as hop. $P_{2\rightarrow 1} = -\frac{d}{dt}\log|c_2|^2$. (Tully)



Advantages:
Computationally simple. Good scaling.

Disadvantages:
Can converge slowly (ensemble of emsemble).
Looses nuclear coherence during conical intersection crossing.

Ehrenfest Dynamics

Assume a single configuration and a TD electronic function

$$\Psi(\mathbf{q},\mathbf{r},t)=\sum_i A(t)\chi(\mathbf{q},t)\psi(\mathbf{r},t) \quad . \tag{74}$$

Evaluating $[\hat{q},H]$ and $[\hat{p},H]$ leads to the Ehrenfest theorem

$$\frac{\partial}{\partial t}\langle\hat{q}\rangle=\frac{1}{m}\langle\hat{p}\rangle \quad ; \quad \frac{\partial}{\partial t}\langle\hat{p}\rangle=-\langle\frac{\partial V}{\partial q}\rangle \quad . \tag{75}$$

The localised nature of the nuclear functions means that the dynamics reduces to classical equations of motion:

$$\dot{q}_i=\frac{P_i}{m} \quad ; \quad \dot{p}_i=-\left.\frac{\partial V}{\partial q}\right|_{q=q_i} \tag{76}$$

with the potential averaged over electronic states

$$V=\langle\psi(t)|H_{el}|\psi(t)\rangle=\sum_{ij}c_i^*(t)\langle\psi_i|H_{el}|\psi_j\rangle c_j(t) \tag{77}$$

Coherent Coupled States / Multi-Configurational Ehrenfest

CCS is from the field of semi-classical dynamics. Superposition of trajectory-guided frozen Gaussians that follow Ehrenfest forces:

$$\begin{aligned} \dot{q} &= p \\ \dot{p} &= \langle -\frac{\partial V}{\partial q} \rangle \end{aligned}$$

hence some quantum effects in GWP propagation. Various tricks to help expand basis set and acheive good results.

Shalashilin and Child JCP (01) 115: 5637

Shalashilin JCP (10) 132; 244111

Compared to vMCG: Shalashilin and Burghardt JCP (08) 129: 084104

A Simple Hamiltonian: The Vibronic Coupling Model

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

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

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

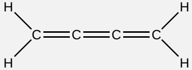
$$\begin{aligned} W_{\alpha\beta} &= \langle\psi_\alpha|H_{el}|\psi_\beta\rangle \\ W_{\alpha\beta} &\approx V^0_\alpha\delta_{\alpha\beta} + \varepsilon_\alpha + \sum_i \frac{\partial}{\partial Q_i}\langle\psi_\alpha|H_{el}|\psi_\beta\rangle \underbrace{\frac{\partial}{\partial Q_i}\langle\psi_\alpha|H_{el}|\psi_\beta\rangle}_{} Q_i + \ldots \end{aligned}$$

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

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

Worth *et al*, Int. Rev. Phys. Chem. (08) **27**: 569

Butatriene photoelectron spectrum



18 modes $\mathrm{D_{2h}}$

$X^2\mathrm{B_{2g}}$; $A^2\mathrm{B_{2u}}$

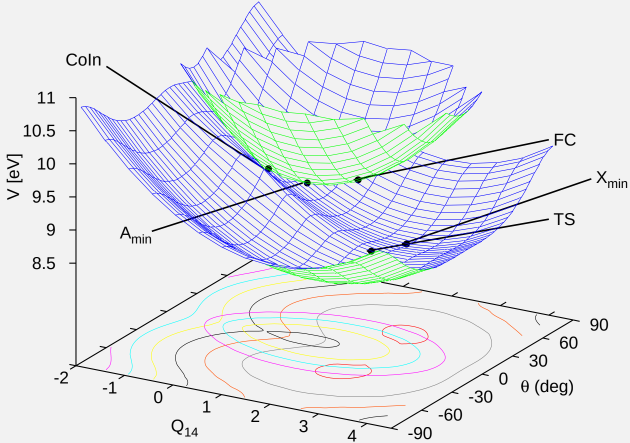
$$\begin{aligned}\mathbf{H} \;=\; & \sum_i \frac{\omega_i}{2}\left(-\frac{\partial^2}{\partial Q_i^2}+Q_i^2\right)\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}+\begin{pmatrix}\epsilon_1 & 0\\ 0 & \epsilon_2\end{pmatrix}\\ & +\sum_{i\in \mathrm{A_g}}^{4}\begin{pmatrix}\kappa_i^{(1)} & 0\\ 0 & \kappa_i^{(2)}\end{pmatrix}Q_i+\begin{pmatrix}0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

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

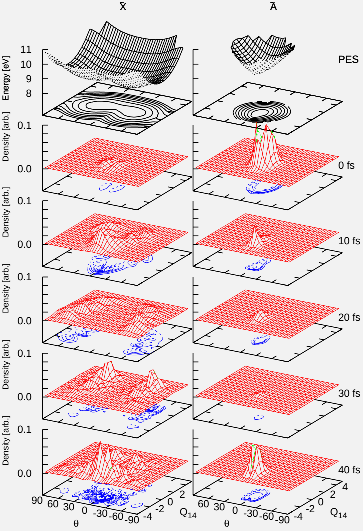
linear: 5 modes, 16 parameters
bilinear: 18 modes, 79 parameters

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

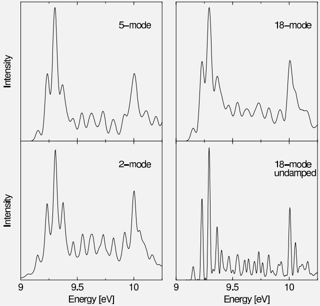
Butatriene Cation PES $\tilde{X}/\tilde{A}$



Butatriene Dynamics



N	MCTDH MB	standard MB
2	0.9	16.4
5	10.3	2.5×10^4
18	431.5	1.5×10^{17}



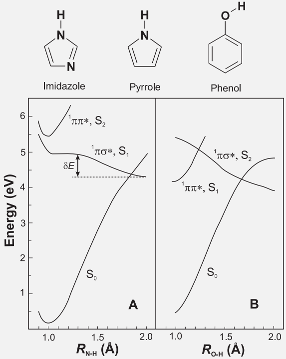
Diabatisation

The VC Hamiltonian is referred to as *diabatisation by ansatz*. A similar, but more powerful version using internal coordinates has been developed by Yarkony (Zhu and Yarkony JCP (16) 144: 044104).

Other procedures to provide diabatic states rely on using properties that are assumed to be smooth e.g.

- dipoles + quadrupoles (DQ Method Hoyer *et al* JCP (16) 144: 194101
- orbitals (Boys localisation Subotnik *et al* JCP (08) 129: 244101
- generalised Mulliken-Hush ET (Cave and Newton CPL (96) 249: 15)
- overlap wrt a reference MRCI wavefunction (Simah JCP (99) 45: 2193) - Molpro

Heteroaromatic Photodissociation



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

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

Photodissociation of Aniline

Vertical Excitation Energies at FC using aug-cc-pVDZ

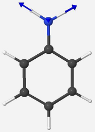
State		EOM-CCSD	EOM-CCSD(T)	Experimental
$\tilde{X}$	$A^{'}$	0.00	0.00	0.00
$\tilde{A}(\pi\pi^*)$	$A^{''}$	4.77	4.21	4.40^a
$\tilde{B}(\pi\sigma^*/3s)$	$A^{'}$	5.02	4.69	4.60^b
$\tilde{C}(3p_z)$	$A^{'}$	5.67	5.31	-
$\tilde{D}(3p_y)$	$A^{''}$	5.77	5.42	-
$\tilde{E}(\pi\pi^*)$	$A^{'}$	5.85	5.42	5.39^a
$\tilde{F}(3p_z)$	$A^{'}$	6.38	6.05	-
$\tilde{G}(3d_{yz})$	$A^{''}$	6.39	6.04	-

Wang *et al* JCPA (13) 117: 7298

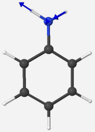
Model Hamiltonian

$$\mathbf{H} = \mathbf{T} + \mathbf{W} \quad \text{with} \quad \mathbf{W}(\mathbf{Q}) = \mathbf{W}^{(0)} + \mathbf{W}^{(1)}(\mathbf{Q}) + \mathbf{W}^{(2)}(\mathbf{Q}) + \cdots .$$

Usual Vibronic Coupling model in mass-frequency scaled normal modes except for N—H bonds: take mode combination



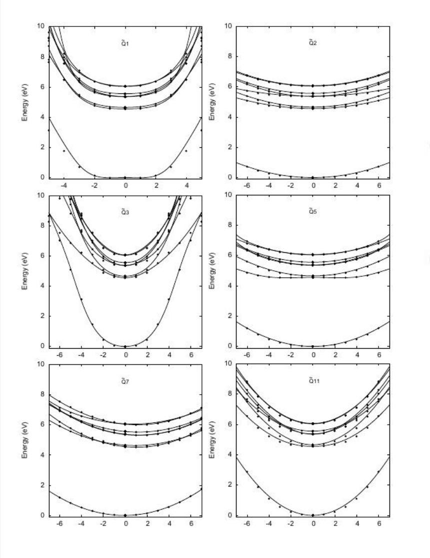
Q_{35}

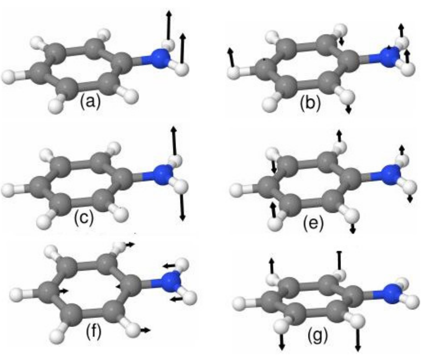


Q_{36}

$$W_{ii}^{(0)}(\tilde{\mathbf{Q}}) = E_i + \sum_{\alpha=1}^{34} \frac{\omega_\alpha}{2} \tilde{Q}_\alpha^2 + \frac{\omega^+}{2} \left[\tilde{Q}_{35}^2 + \tilde{Q}_{36}^2 \right] + \omega^- \tilde{Q}_{35} \tilde{Q}_{36}$$

Cuts through PES

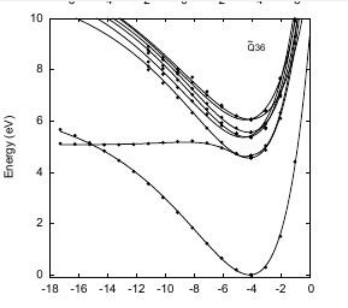




Cut through PES along N—H

Morse oscillators for bound states, avoided crossing for $\tilde{B}(\pi\sigma^*/3s)$

$$W_{22}(\tilde{Q}_{36}) = \frac{1}{2}\left\{\nu_b + \nu_d - \sqrt{(\nu_b - \nu_d)^2 + 4\left(\Delta \tanh\left[\rho\tilde{Q}_{36}\right]\right)^2}\right\},$$



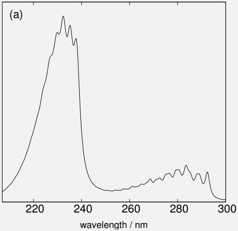
$$\nu_b = D_b\left[\exp(-\alpha_b(\tilde{Q}_{36} - \tilde{Q}^b_{36,0})) - 1\right]^2$$

$$\nu_d = A\exp(-\alpha_d(\tilde{Q}_{36} - \tilde{Q}^d_{36,0})) + D_d.$$

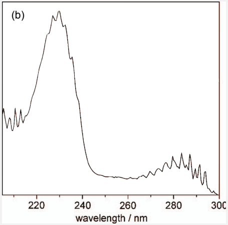
Topologies EOM-CCSD. Corrected at Q_0 using EOM-CCSD(T).

Aniline Spectrum

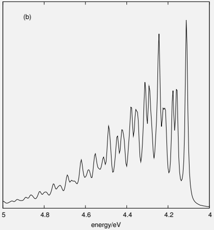
Calculated



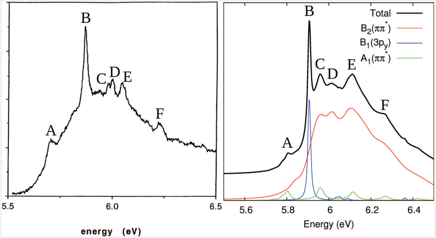
Experiment

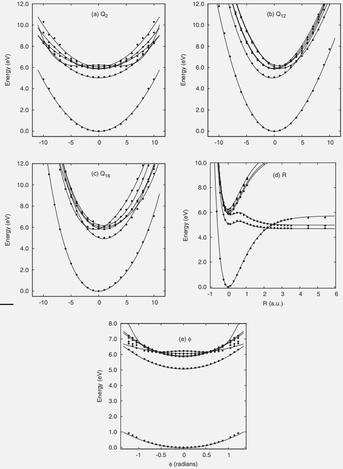


Lower band



Electronic Absorption Spectrum of Pyrrole





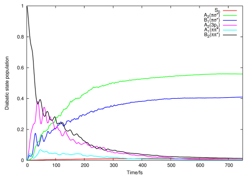
Symmetry	Character	CASSCF	CASPT2
A_1		0.00	0.00
A_2	$3s/\pi\sigma^*$	4.17	5.06
B_1	$3s/\pi\sigma^*$	4.87	5.86
A_2	$3p_z$	4.91	5.87
A_1	$\pi\pi^*$	6.47	6.01
B_2	$\pi\pi^*$	7.83	6.24
B_1	$3p_z$	5.67	6.69

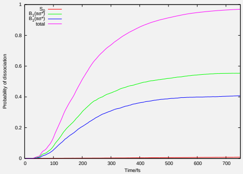
- 6-state, 9-mode model.

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

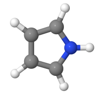
Ignoring ν_2

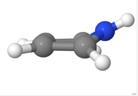
State populations





Flux



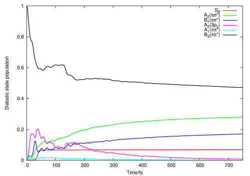


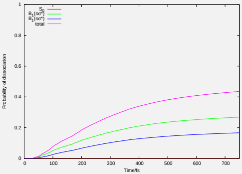
“Trapped”

“Geometry”

Including ν_2

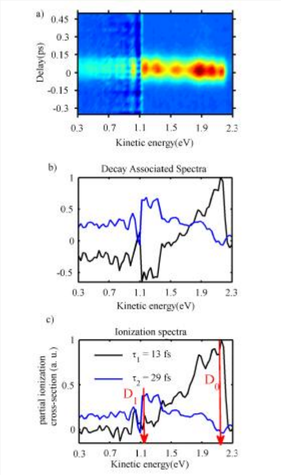
State populations

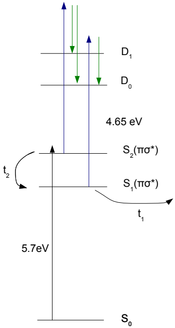


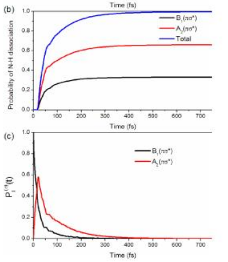


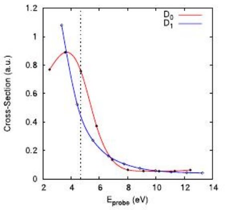
Flux

Pyrrole: Time-resolved Photo-electron spectroscopy









Pump-probe with 5.7 eV

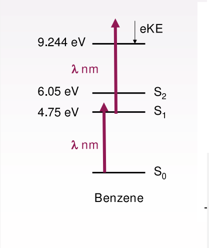
Wu *et al* JCP (15) 142: 074312

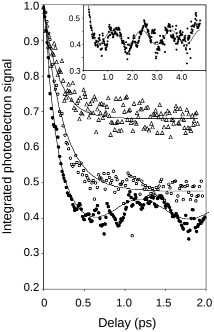
Benzene: Time-Resolved Spectra

Total Ion Count

Photo-electron spectra

Pump 243 nm
Probe:
260, 254, 235





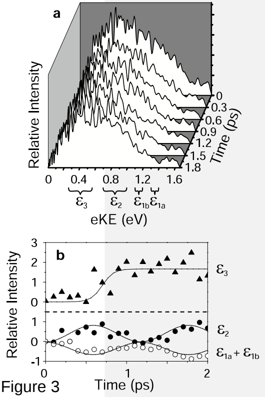


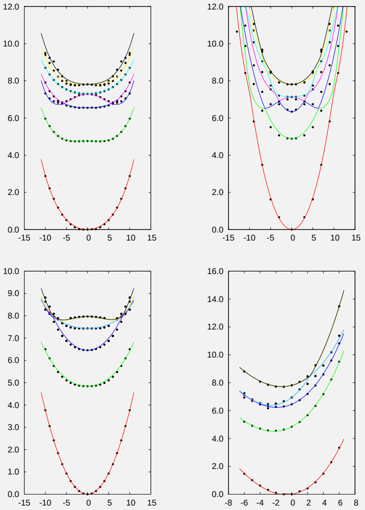
Figure 3

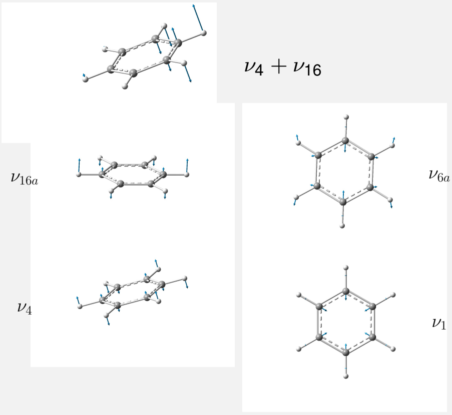
Decay 220 fs + 12 ps

Minns *et al* PCCP (10) **12**: 15607

Period 1.2 ps

Benzene Potential Energy Surface Cuts

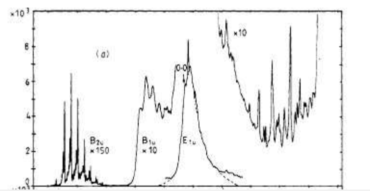


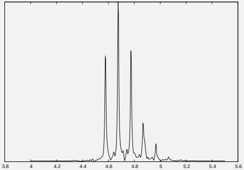


CASPT2 (6,6)/Roos

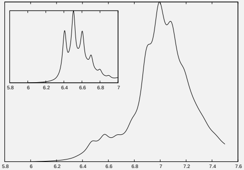
Simulated Absorption Spectra

5-state 8-mode model.





B_{2u}



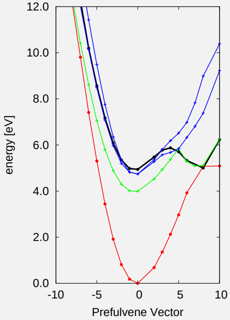
$B_{1u} + E_{1u}$

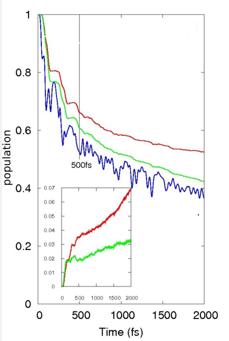
Penfold and Worth JCP (09) 131: 064303

Importance of Triplet States and ISC

Need SOC between states: $\langle {}^3\Psi | H_{SO} | {}^1\Psi \rangle$
At FC point, S_1/T_2 coupling zero. In general SOC small (< 5 cm^{-1})

5-state model (S_0, S_1, T_1, T_2)





$S + T$ (red)
S_1 (green)
$S_1 FC$ (blue)

T populations (inset)

Penfold *et al* JCP (12) 137: 22A548

Ab Initio Multiple Spawning: AIMS

Efficiency of spawning perfect for direct dynamics. Run in adiabatic picture.

- Review: Ben-Nun and Martinez Adv. Chem. Phys. (02) 141: 439
- QM/ MM: PYP / GFP Chromophores in solution Virchup et. al JPCB (09) 113: 3280
- Rydberg states in ethylene Mori *et al* JPCA (12) 116: 808
- TRPEspec of uracil Hudock *at al* JPCA (07) 111:8500

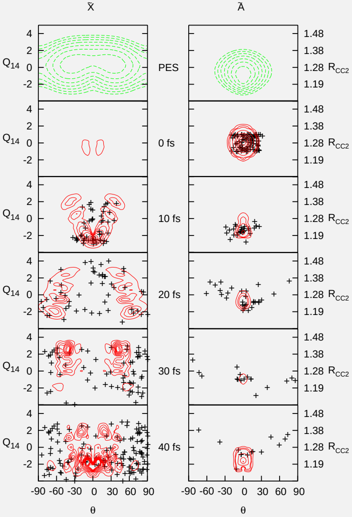
Surface Hopping

A number of programs / methods. E.g.

- Newton-X (Barbatti)
- SHARC (Gonzalez)
- CPMD (Tavernelli)

Simple, but difficult ot converge and loss of nuclear coherence.

Butatriene Dynamics From Ã



Surface Hopping

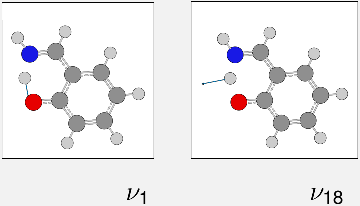
v

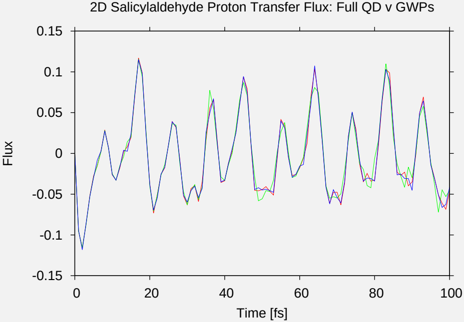
wavepacket dynamics

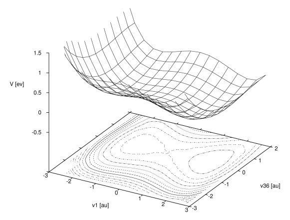
Salicylaldimine Test Case: 2D Proton transfer

Hamiltonian in normal modes fitted to RHF/3-21G*

$$
\begin{aligned}
H \quad = \quad & \sum_{\kappa=1,18} \frac{\omega_\kappa}{2} \left(\frac{\partial^2}{\partial q_\kappa^2} + q_\kappa^2 \right) + \sum_{n=1}^{4} A_n q_1^n \\
& + B_{11} q_1 q_{18} + B_{22} q_1^2 q_{18}^2 \\
& + B_{31} q_1^3 q_{18} + B_{13} q_1 q_{18}^3
\end{aligned}
$$



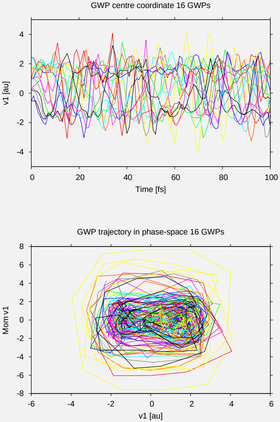




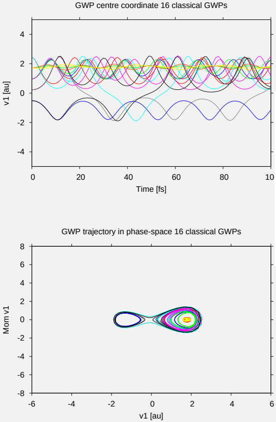
16 / 32 GWPs

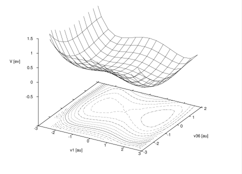
Trajectories with 16 GWPs

vMCG



Classical

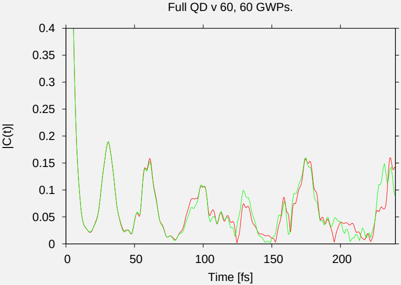




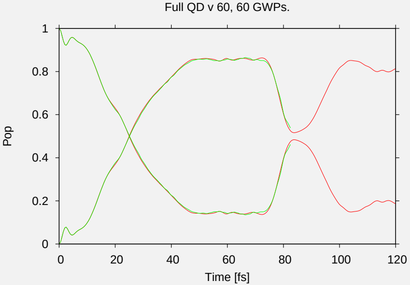
Richings *et al* Int. Rev. Phys. Chem. (15) 34: 269

4D model: Linear Coupling

Autocorrelation function:



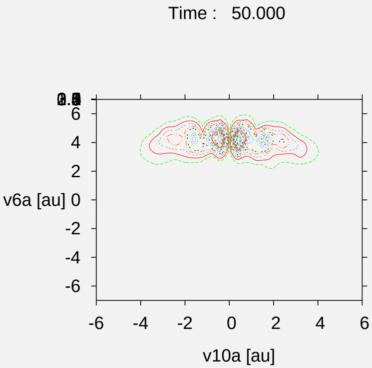
State Populations:



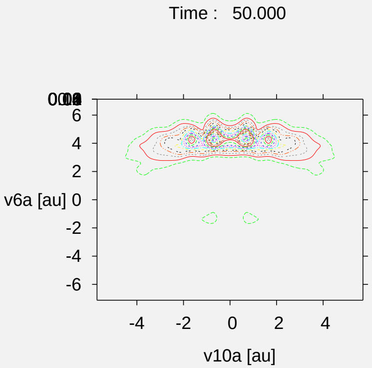
QD basis size: 4060 SPFs, 355,000 primitives

Pyrazine wavepacket on S_1

GWPs: 10,10



MCTDH



Direct Dynamics

- For integrals $\langle g_j|H|g_k\rangle$, Quantum chemistry to second order.
- Gradients and Hessians directly from quantum chemistry.
- Store results in a database (energy, gradient, Hessian)

Ideally use adiabatic PES in direct dynamics as they are readily available from quantum chemistry packages.

- States interact *via* the non-adiabatic coupling terms (NACT)

$$\mathbf{F}_{ab} = \frac{\langle\psi_a|\nabla \hat{H}_{\mathrm{el}}|\psi_b\rangle}{V_b - V_a}$$

- NACTs go to infinity at a conical intersection and adiabatic PES become non-differentiable at such points.

Problem for LHA. Avoid these problems by transforming to the diabatic picture. How can we define diabatic states on-the-fly?

Diabatisation by Propagation

Adiabatic - Diabatic transformation, **S**, defined by the differential equation

$$\nabla \mathbf{S} = -\mathbf{F}\mathbf{S}$$

where **F** is derivative coupling. Exact for complete set of states.

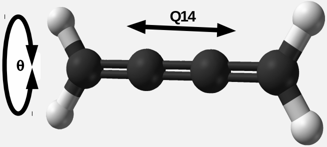
- At each GBF position evaluate **F**.
- Choose $\mathbf{S} = \mathbf{1}$ at the initial point of the propagation.
- Solve for **S** by propagating from the nearest, previously calculated, point.

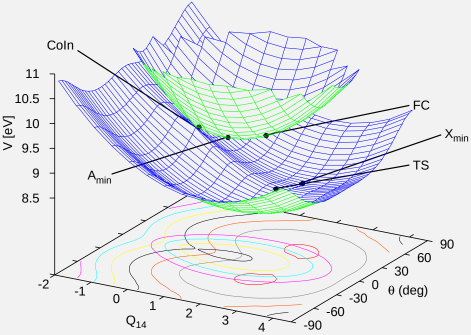
$$\mathbf{S}(\mathbf{q} + \Delta\mathbf{q}) = \left(\mathbf{I} + \frac{1}{2}\int \mathbf{F}.\Delta\mathbf{q}\right)^{-1} \left(\mathbf{I} - \frac{1}{2}\int \mathbf{F}.\Delta\mathbf{q}\right) \mathbf{S}(\mathbf{q})$$

- PES and gradients transformed by **S**.
- Applicable to any number of states.

Richings and Worth J. Phys. Chem. A (2015) 119: 12457

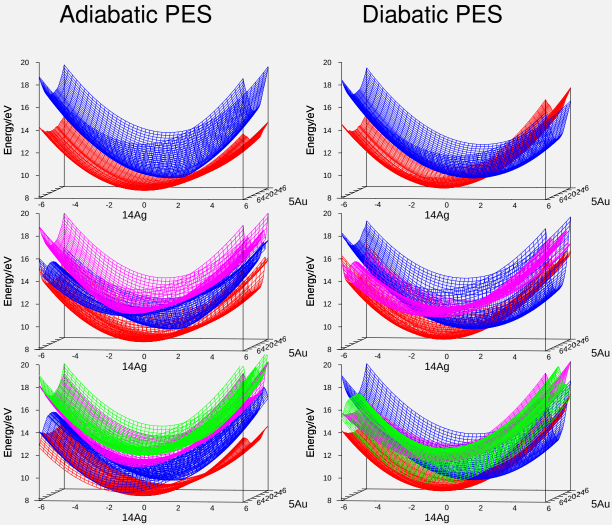
Butatriene Model





- Ground state normal modes from CAS(6,6)/3-21G* (G03).
- 2-mode model: torsion angle and symmetric central C-C stretch.
- Dynamics run on first-excited ion states.
    - DD-vMCG using 25 GWPs with propagated diabatisation.
    - Powell updated Hessian

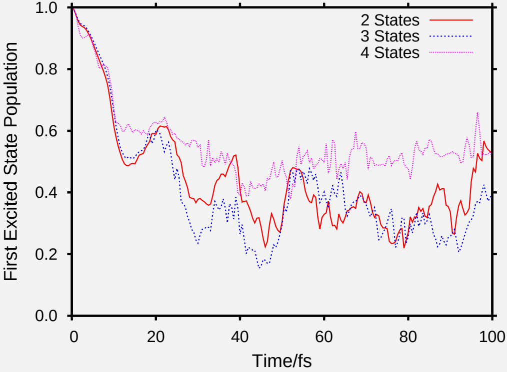
Butatriene Ion: Excited-State Manifold


Adiabatic PES

Diabatic PES

- CoIns found
- Smooth Diabatic PES
- Surfaces depend on Nstate

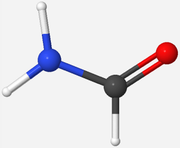
Butatriene Ion: Excited State Populations



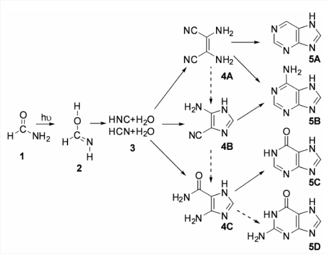
- Initial wavepacket at origin of the coordinate system on $\tilde{A}$-state.
- Rapid de-population of the $\tilde{A}$-state as the CoIn is encountered followed by partial re-population and oscillation.
- DD-vMCG results follow full grid-based dynamics.

Formamide

Formamide

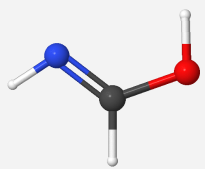


- Smallest, most stable molecule consisting of HCNO
- Prebiotic Earth
- Found, by spectral molecular survey, on Hale-Bopp[1]
- "Tentatively" found in IR-spectra of interstellar ices[2]
- Decomposition pathways studied [3]
- As yet, no excited state studies



[1]D. Bockelée-Morvan, et al, Astron. Astrophys. (2000) 353 1101-1114
[2]S. Raunier, et al., Astron. Astrophys. (2004) 416 165-169
[3]V. S. Nguyen, et al., J. Phys. Chem. A (2013) 117 2543-2555

Formamidic Acid: Electronic Structure



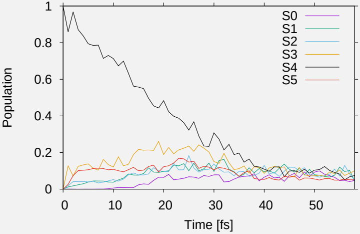
- SA-CAS(10,7)/6-31++G*
- 6 states

State	VEE/eV	Transition Dipole/au	Character
S_1	6.761	0.234	$n\pi^*$
S_2	7.082	0.010	$\pi\sigma^*$
S_3	7.747	0.535	$n\pi^*$
S_4	10.245	1.482	$\pi\pi^*$
S_5	10.781	0.351	$\pi\sigma^*$

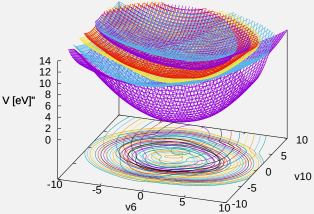
Formamidic Acid: Direct Dynamics

Initial Vertical Excitation to bright $S_5(\pi\pi^*)$. 60fs 24 GWPs.

Diabatic Populations



Potential Surfaces



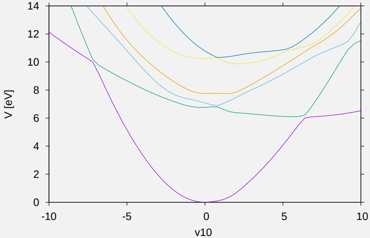
Trajectory Analysis

Product	No.
O-H break	14
HN-CO	6
N-CH-O	2
NH + CO	1
HNC-H-O	1

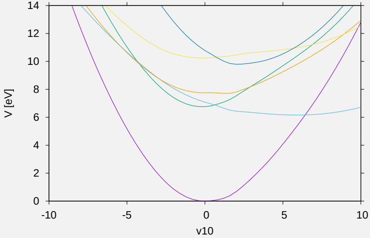
Potential Surfaces

Cut along O–H bond

Adiabatic

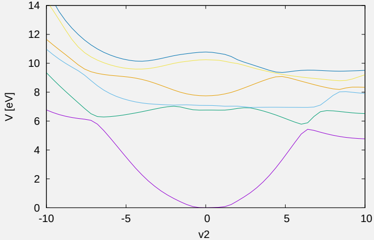


Diabatic

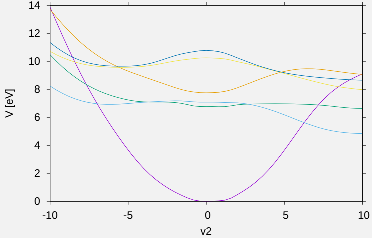


Cut along O–H OOP

Adiabatic



Diabatic



Ozone Photodissociation

Two dissociation pathways

$$\begin{array}{lcl} \mathrm{O}_3(X^1A_1) & \longrightarrow & \mathrm{O}(2p\,^1D_2) + \mathrm{O}_2(A^1\Delta_g) \\ \mathrm{O}_3(X^1A_1) & \longrightarrow & \mathrm{O}(2p\,^3P_2) + \mathrm{O}_2(X^3\Sigma_g^-) \end{array}$$

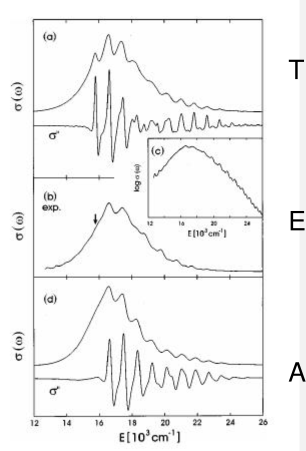
Chappuis Band:

- 400 - 750 nm
- Coupled $1^1A_2/1^1B_1$

Detailed QD study.
Full valence CASPT2/DZP.

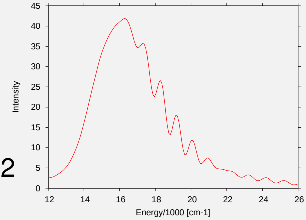
Woywod *et al* JCP (97) 107:7282

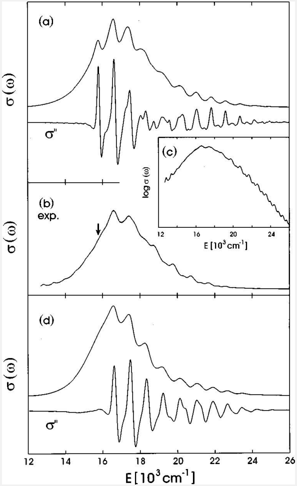
Flöhtmann *et al* JCP (97) 107: 7296



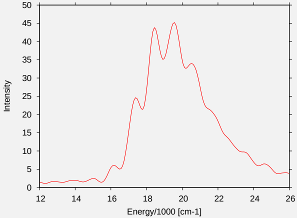
DD-vMCG of Ozone: Spectrum

CASPT2



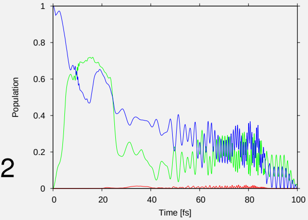


CAS

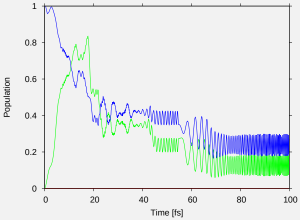


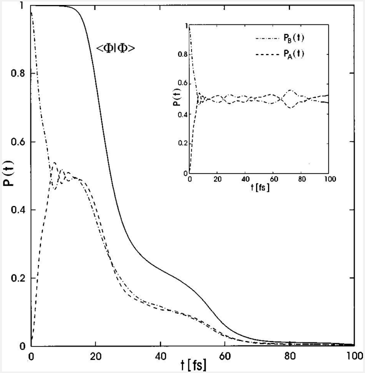
DD-vMCG of Ozone: State Populations

CASPT2



CAS





Conclusions

Variational time-dependent basis sets are a powerful way of obtaining the full solution to the TDSE including non-adiabatic effects.

- MCTDH provides a complete framework.
  - ML-MCTDH grid-based for truly large systems - simple PES
  - G-MCTDH flexible route to approximate dynamics - any PES but restricted coordinates
- G-MCTDH $\longrightarrow$ vMCG $\longrightarrow$ GWP methods
  - still complete solution possible
  - numerically difficult

- Vibronic Coupling Model good for short-time dynamics
- More flexibility required for complete description of photochemistry
- Direct Dynamics present state-of-the art: DD-vMCG, AIMS, ...

Present bottleneck: Electronic Structure theory!