# From Grids to Gaussians. Non-adiabatic Simulations with the Quantics Package

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# Quantum Dynamics Simulations

Dynamical phenomena are described by the
**Time-Dependent Schrödinger Equation**

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{R},t) = (\hat{T}\mathbf{1} + \mathbf{W}(R))\Psi(\mathbf{R},t)$$

1. Grid-based Solutions: MCTDH, ML-MCTDH

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

- Variational equations of motion for $A$ and $\varphi$.
- Up to 1000 DOF
- Needs analytic potential functions

Meyer, Gatti, F. and Worth, MCTDH, (09) VCH

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## 2. Gaussian Wavepacket Methods: vMCG

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

with GWP basis

$$g(\mathbf{x}, \mathbf{t}) = \exp[-(\mathbf{x} - \mathbf{x_0})^\mathbf{T} \alpha (\mathbf{x} - \mathbf{x_0}) + \mathbf{i}\mathbf{p}^\mathbf{T}(\mathbf{x} - \mathbf{x_0}) + \mathbf{i}\gamma]$$

- Variational equations of motion for $A$ and $\lambda = (\mathbf{x_0}, \mathbf{p_0})$
- Up to 50 DOF at present
- Can calculate potentials *on-the-fly* using quantum chemistry

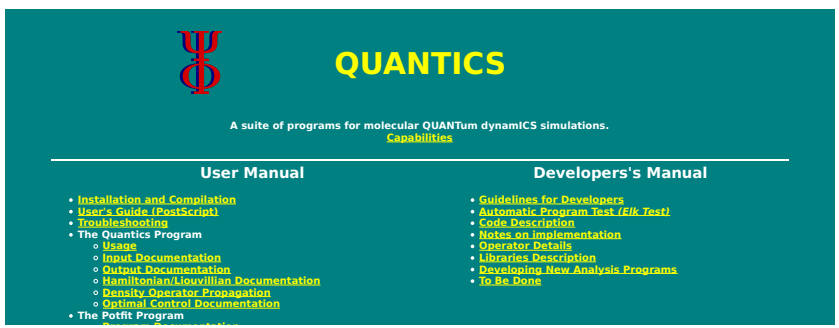
Burghardt *et al* JCP (99) 99:2927 Richings *et al* IRPC. (15) **34**: 269

## The QUANTICS Package

Worth Comp. Phys. Comm. (20) **248**: 107040

https://www.chem.ucl.ac.uk/quantics/

QUANTICS Documentation



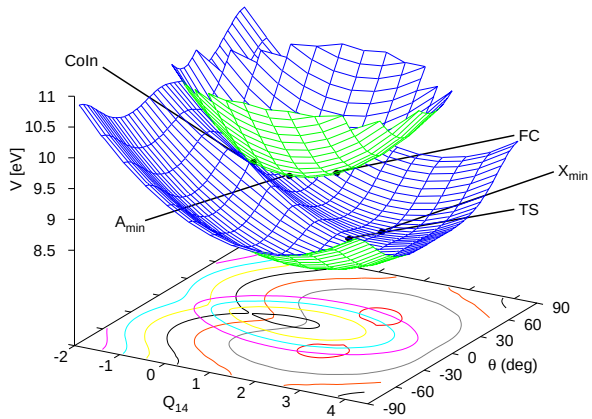
# Describing photo-excitation

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

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

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



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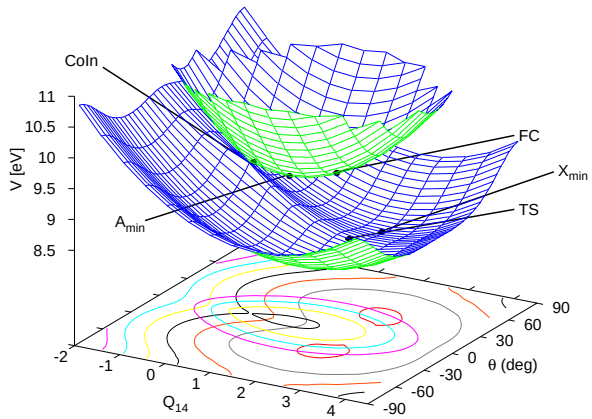

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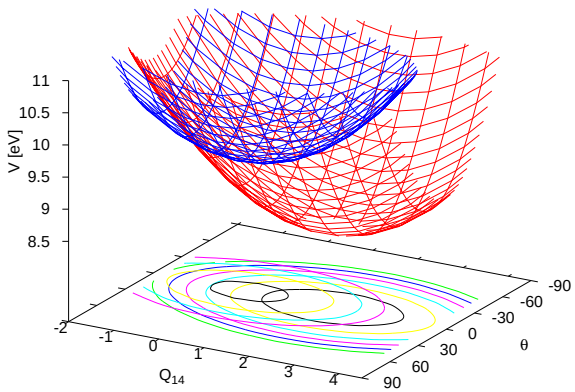



In the diabatic picture

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

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

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

# The Multiconfiguration Time-Dependent Hartree (MCTDH) Method

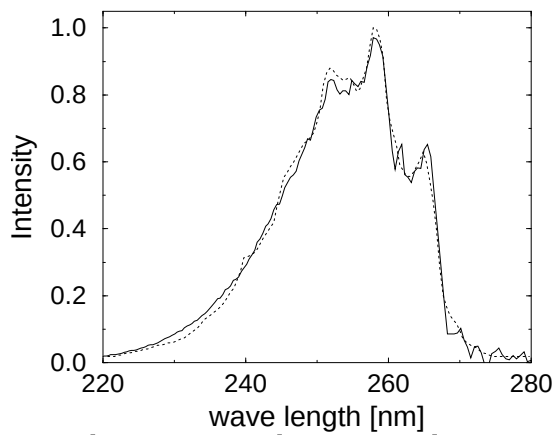
$$\Psi(q_1,\ldots,q_f,t)=\sum_{j_1=1}^{n_1}\ldots\sum_{j_p=1}^{n_p}A_{j_1\ldots j_p}(t)\prod_{\kappa=1}^{p}\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t)$$

Variational equations for $A$ and *single-particle functions* (SPFs) $\varphi$.

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

$$i\dot{\varphi}^{(\kappa)} = \left(1-P^{(\kappa)}\right)\left(\rho^{(\kappa)}\right)^{-1}\langle\mathbf{H}\rangle^{(\kappa)}\varphi^{(\kappa)}$$

- $\varphi_i(x,t)=\sum_\alpha c_{i\alpha}(t)\chi_\alpha(x)$
- non-linear equations of motion
- Computer memory $n^p+pnN$




pyrazine absorption Spectrum: 24D

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

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

# Multi-Layer MCTDH (ML-MCTDH)

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

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

$$\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t) = \sum_{k_1=1}^{n_1}\cdots\sum_{k_Q=1}^{n_Q} B_{k_1\ldots k_Q}^{\kappa,j_\kappa}(t)\prod_{\nu=1}^{Q}\nu_{k_\nu}^{(\nu)}(R_\nu,t) \qquad \text{Layer 2}$$

$$\nu_{k_\nu}^{(\nu)}(R_\nu,t) = \sum_{l_1=1}^{n_1}\cdots\sum_{l_R=1}^{n_R} C_{l_1\ldots l_R}^{\nu,k_\nu}(t)\prod_{\xi=1}^{R}\xi_{l_\xi}^{(\xi)}(S_\xi,t) \qquad \text{Layer 3}$$

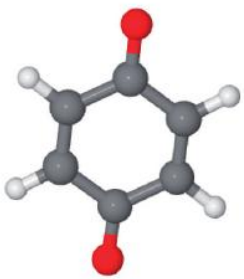
$$\ldots = \ldots$$

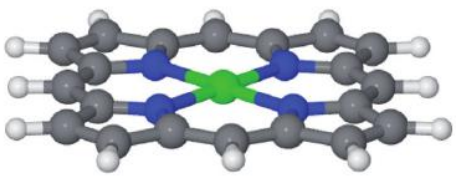
Each layer acts as a set of SPFs for the layer above and a set of coeficients for the layer below.

Leads to a recursive sets of variational equations of motion:

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

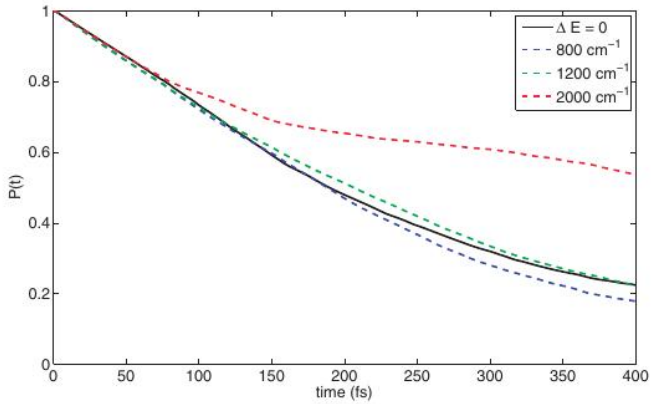
$$
\begin{aligned}
i\dot{A}_J &= \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L \\
i\dot{\varphi}^{(\kappa)} &= \left(1 - P^{(\kappa)}\right) \left(\rho^{(\kappa)}\right)^{-1} \langle \mathbf{H} \rangle^{(\kappa)} \varphi^{(\kappa)} \\
i\dot{\nu}^{(\nu)} &= \left(1 - P^{(\nu)}\right) \left(\rho^{(\nu)}\right)^{-1}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





## 135 Mode Quantum Dynamics

Photo-induced ET. Spin-Boson Model.




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

# A Simple Hamiltonian: The Vibronic Coupling Model

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

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

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

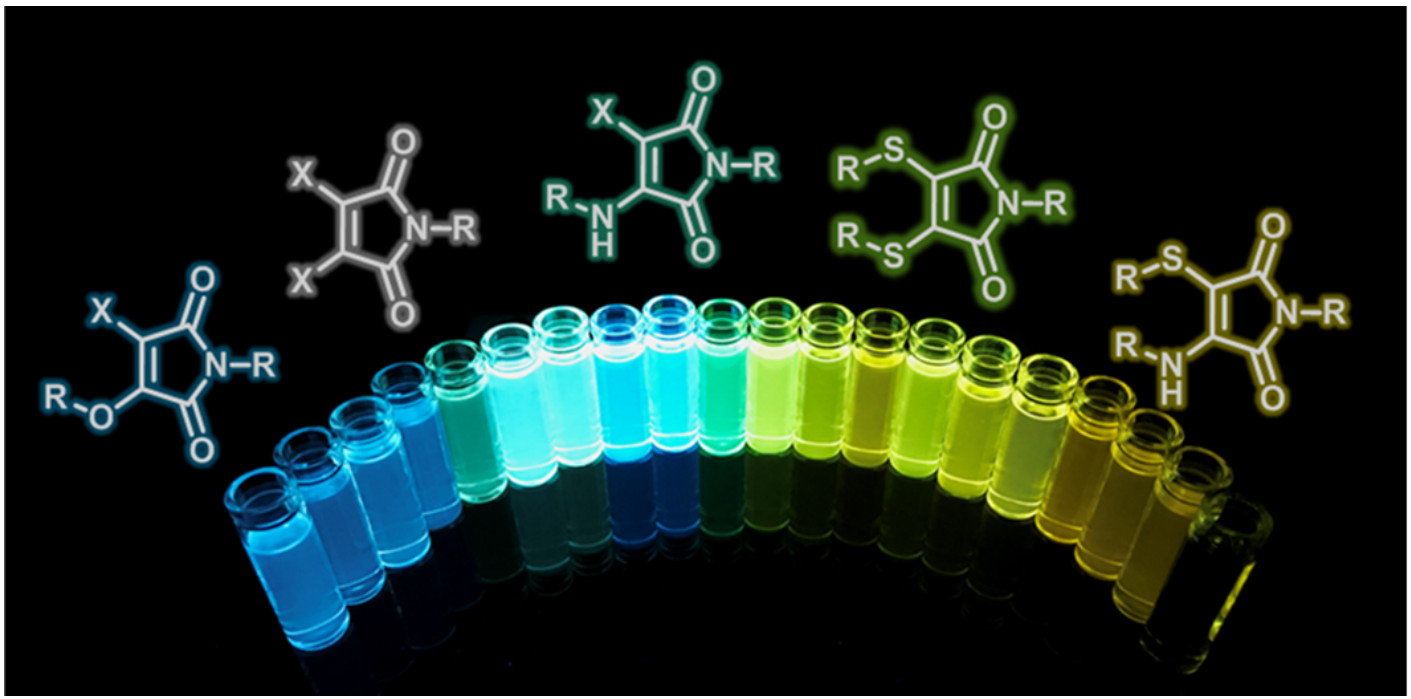
$$\begin{aligned} W_{\alpha\beta} &= \langle\psi_\alpha|H_{el}|\psi_\beta\rangle \\ W_{\alpha\beta} &\approx V^0_\alpha\delta_{\alpha\beta} + \varepsilon_\alpha + \sum_i \underbrace{\frac{\partial}{\partial Q_i}\langle\psi_\alpha|H_{el}|\psi_\beta\rangle}\, Q_i + \ldots \end{aligned}$$

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

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

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

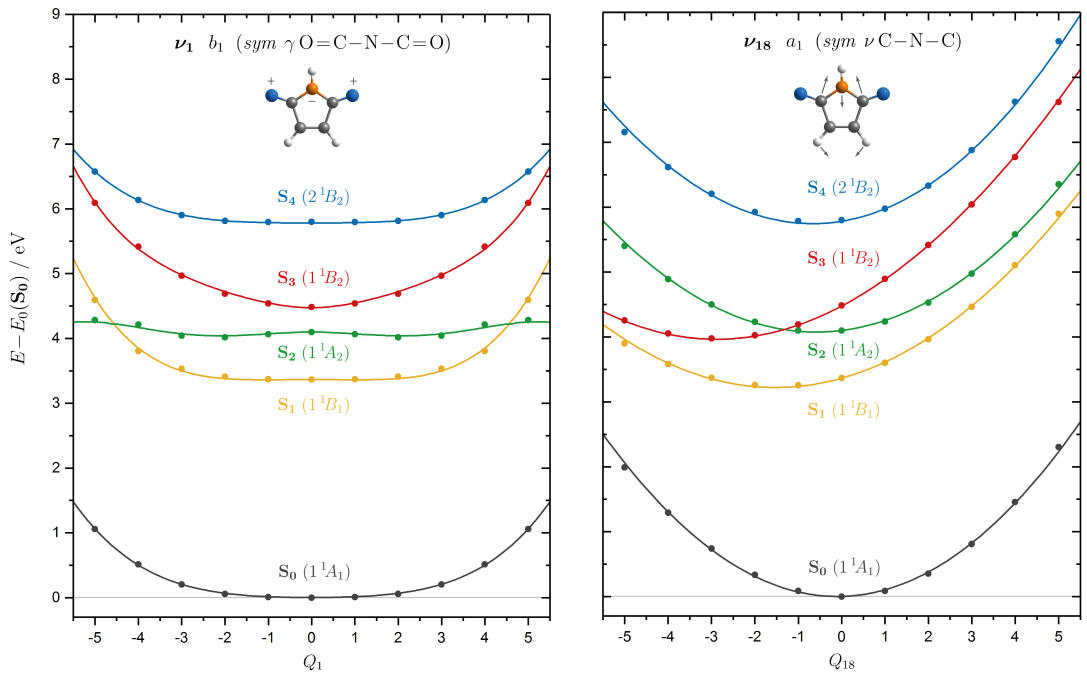
# Maleimide: A small, versatile fluorophore




Experimental Group of Rachel O'Reilly, Birmingham

# Maleimide Potential Energy Surfaces

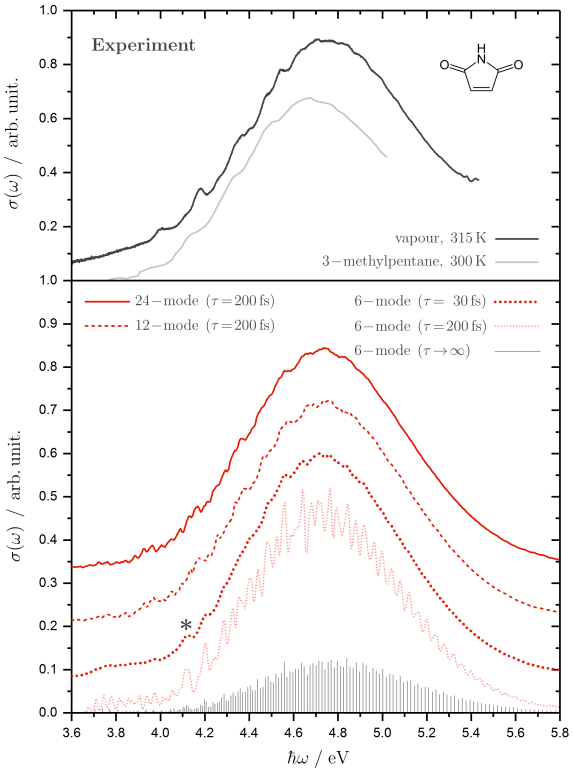
| state | sym | CASPT2(12,9) cc-pVDZ $E/\mathrm{eV}$ | Experiment $E/\mathrm{eV}\,(f)$ |
|---|---|---|---|
| $\mathbf{S_0}(n_2^2)$ | $1\,^1A_1$ | 0.00 | |
| $\mathbf{S_1}(n_2\pi^*)$ | $1\,^1B_1$ | 3.37 (0.00) | 3.33[b] |
| $\mathbf{S_2}(n_1\pi^*)$ | $1\,^1A_2$ | 3.96 (0.00) | ( – ) |
| $\mathbf{S_3}(\pi_2\pi^*)$ | $1\,^1B_2$ | 4.62 (0.03) | 4.72[a],4.48[b],4.67[c] |
| $\mathbf{S_4}(\pi_1\pi^*)$ | $2\,^1B_2$ | 5.80 (0.46) | 5.95[a], 6.20[b,c] |



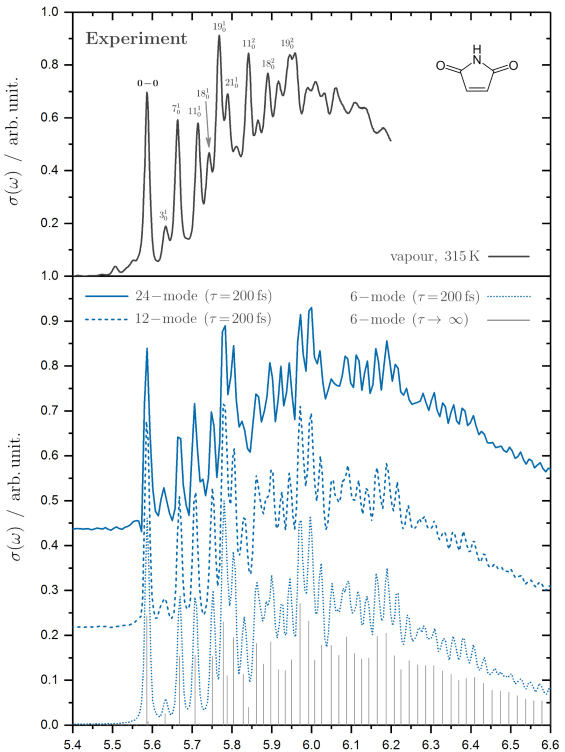

EOM-CCSD/cc-pVDZ shifted to CASPT2(12,9)/cc-pVDZ at FC point.

# Maleimide Absorption Spectra

## Excitation to $S_3$




## Excitation to $S_4$

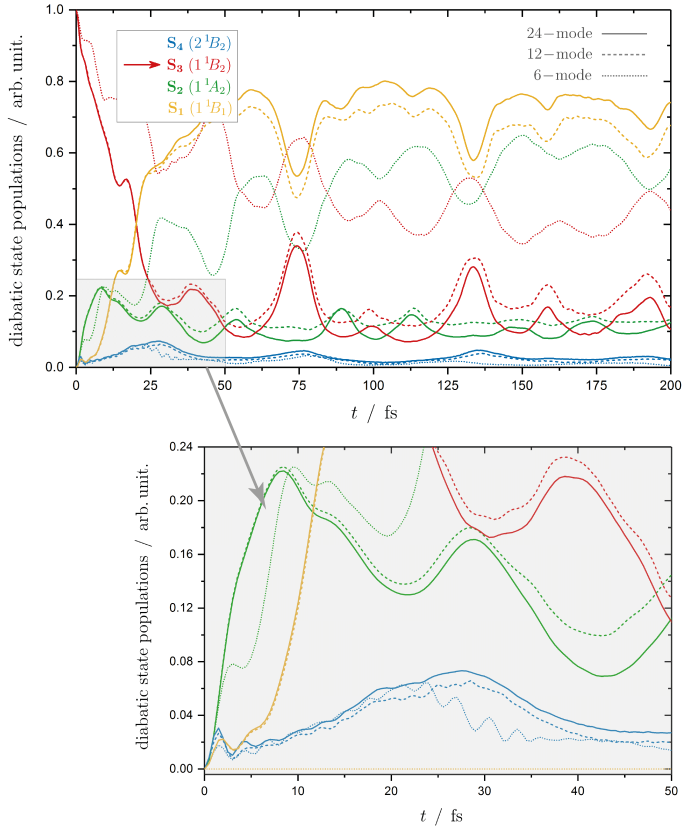



Spectra calculated from dynamics simulation

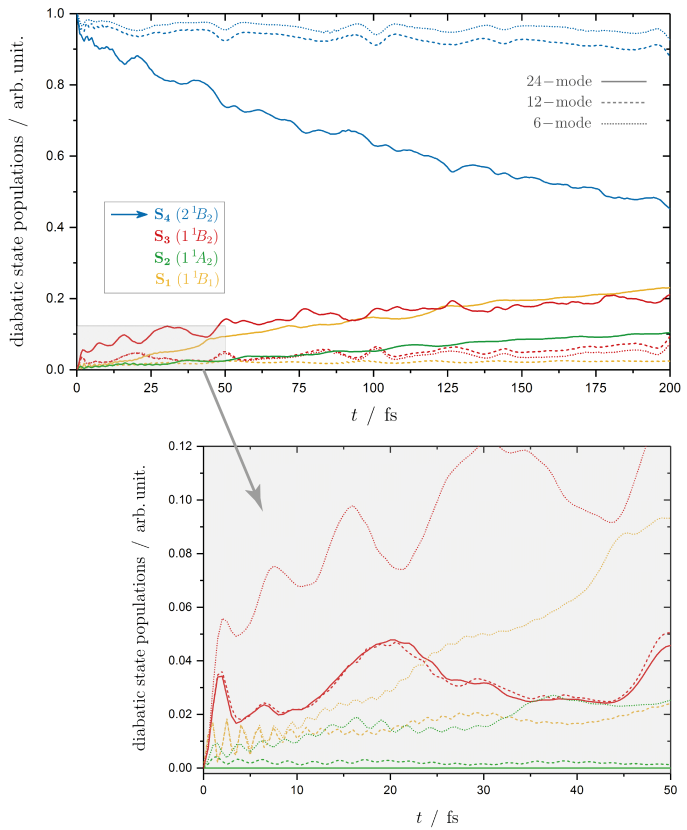
$$I(\omega) \sim \int \langle \Psi(0) | \Psi(t) \rangle e^{i\omega t} dt$$

# Maleimide Relaxation Dynamics

## Excitation to $S_3$




## Excitation to $S_4$




Lehr *et al* PCCP (20) **22**: 25272

# Grid-free Quantum Dynamics: 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 grid-based SPFs with Gaussian Basis Functions (GWPs)

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

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

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

Fewer GWP parameters than grid points.

Burghardt *et al* JCP (99) 99:2927

# Grid-based QD $\longrightarrow$ Gaussian Wavepackets

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

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

Related to other GWP based methods such as Spawning (Martinez) and CCS (Shalashilin).

- Conceptually simple
- Possible to use for *direct dynamics*.

## EoMs for GWPs

$$\begin{aligned} \dot{q}_j &= \frac{p_j}{m} + \frac{1}{2\alpha_j} \mathrm{Im} \sum_m C_{jm}^{-1} \tilde{Y}_m \\ \dot{p}_j &= -V_j' + \mathrm{Re} \sum_m C_{jm}^{-1} \tilde{Y}_m \end{aligned}$$

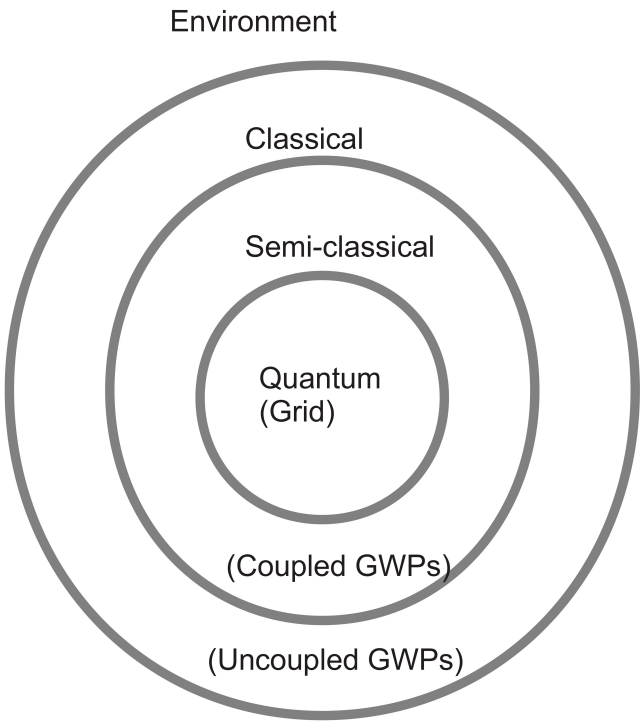
NB they do not follow classical trajectories, but are coupled.

For GWP matrix elements $\langle g_i|H|g_j\rangle$ use Local Harmonic Approximation (LHA), i.e. expand potential around centre $q_j$

$$V_l(\mathbf{x}) = V_{0\alpha} + \sum_{\alpha} V'_{\alpha}(x_\alpha - q_{l\alpha}) + \frac{1}{2}\sum_{\alpha\beta} V''_{\alpha\beta}(x_\alpha - q_{l\alpha})(x_\beta - q_{l\beta})$$

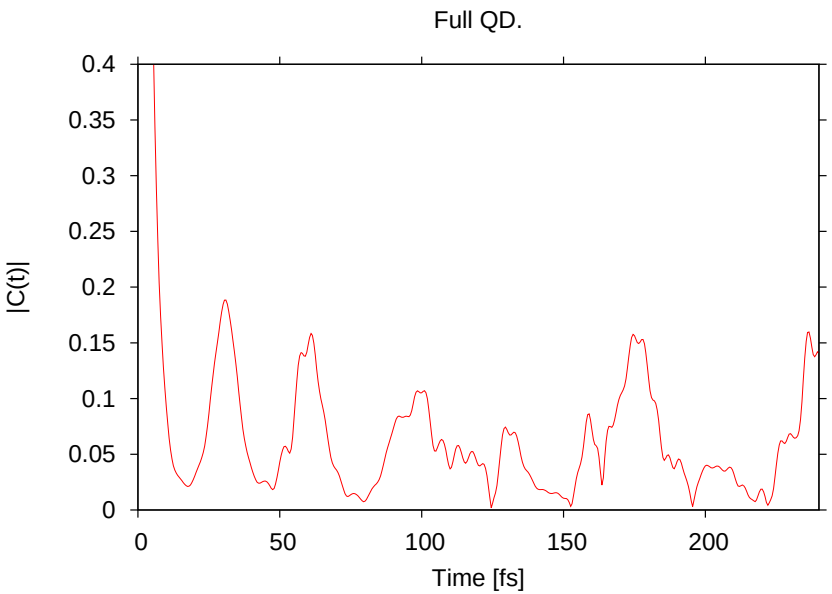
No longer exact result....

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

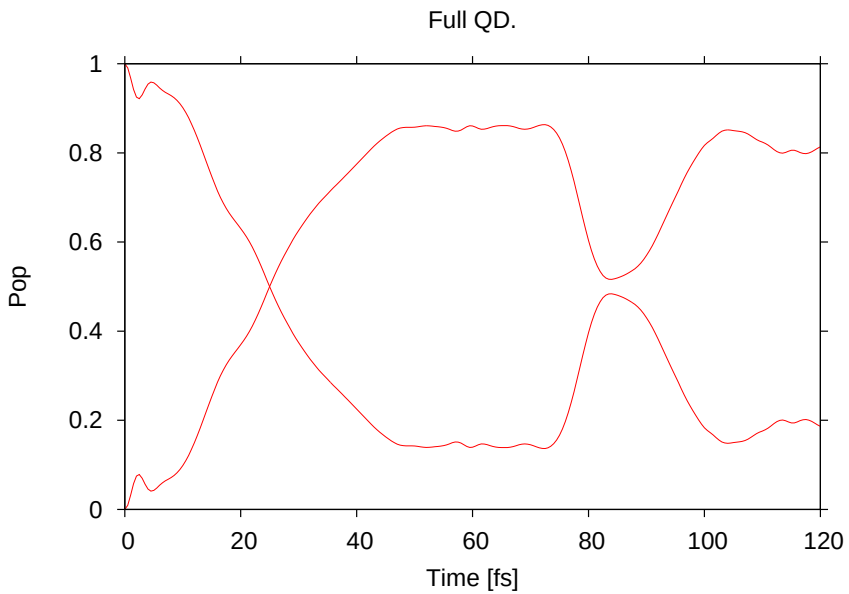


# 4D model: Linear Coupling

Autocorrelation function:




State Populations:




QD basis size: 4060 SPFs, 355,000 primitives

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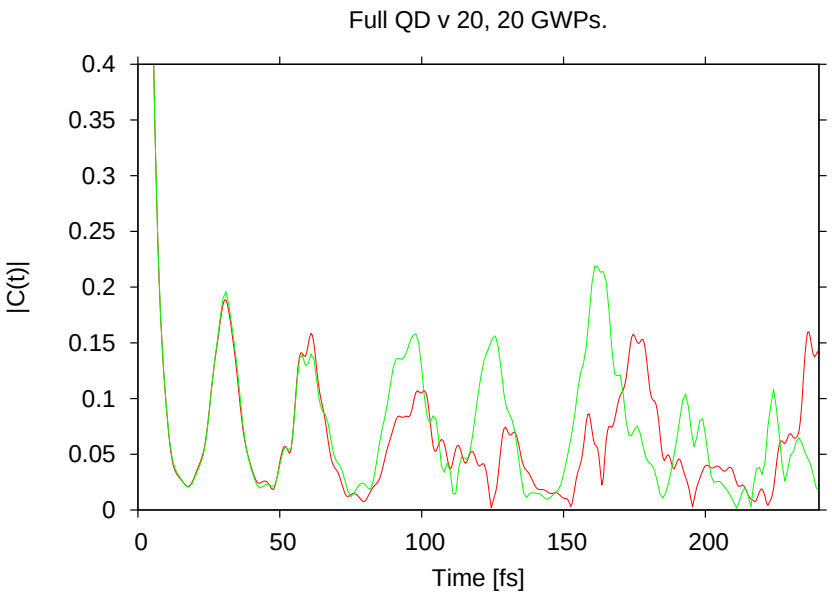


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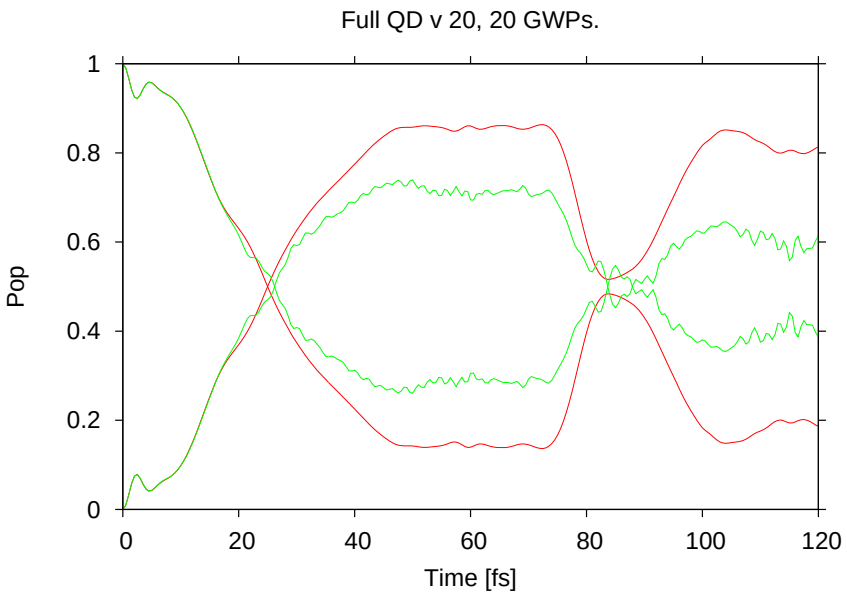


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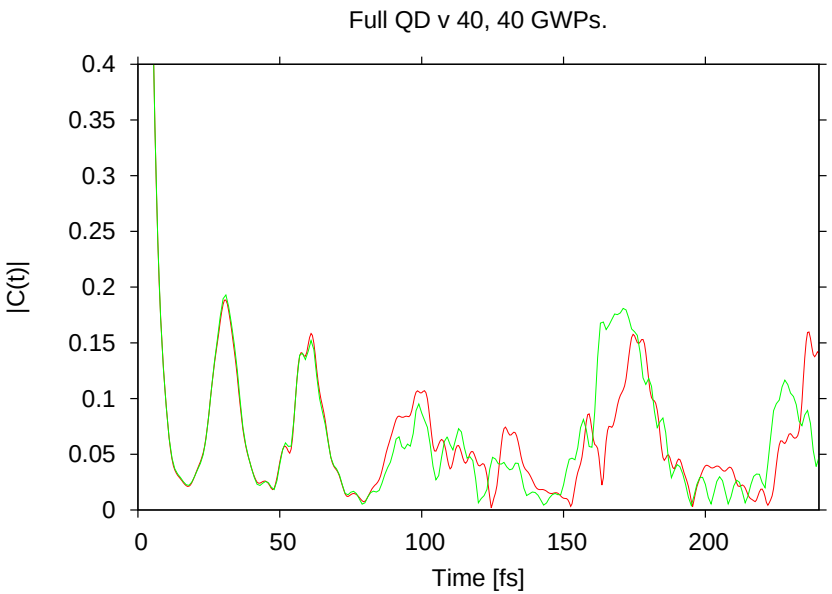
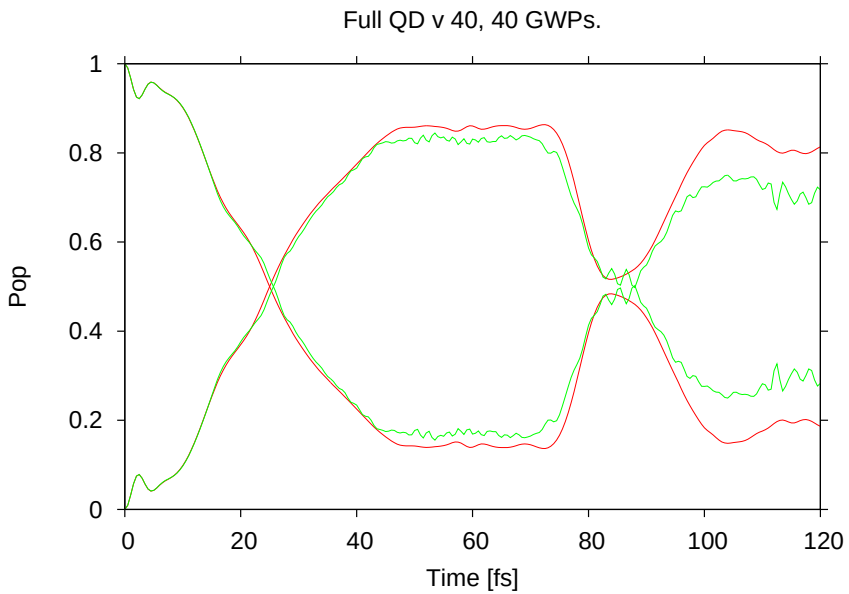



State Populations:

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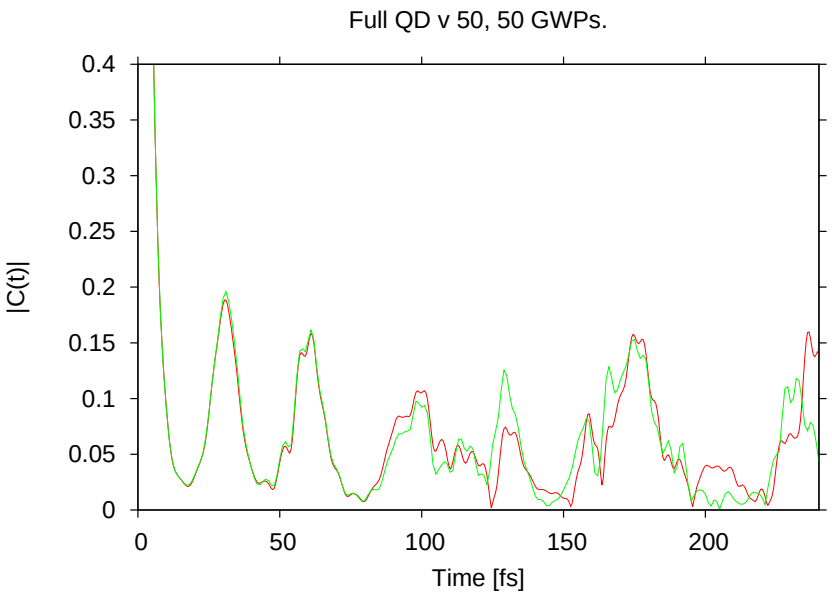


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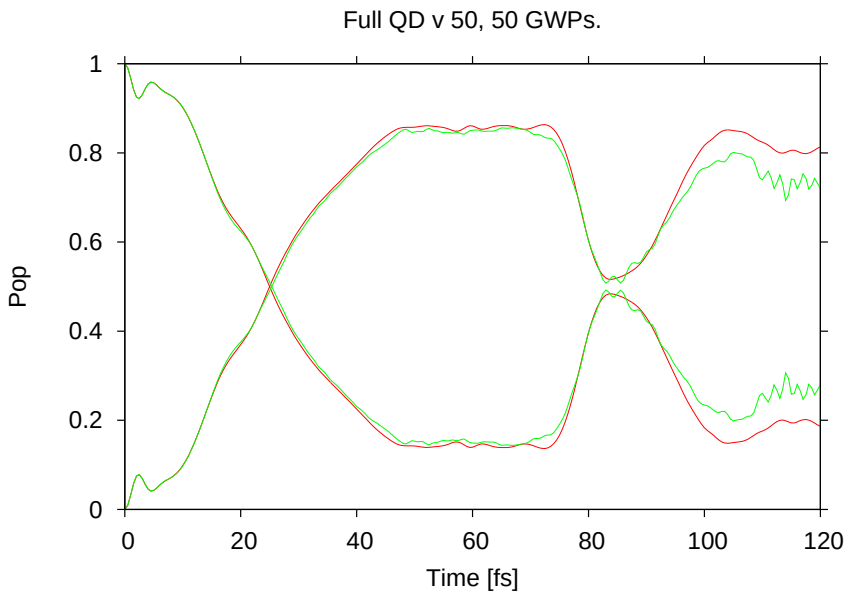


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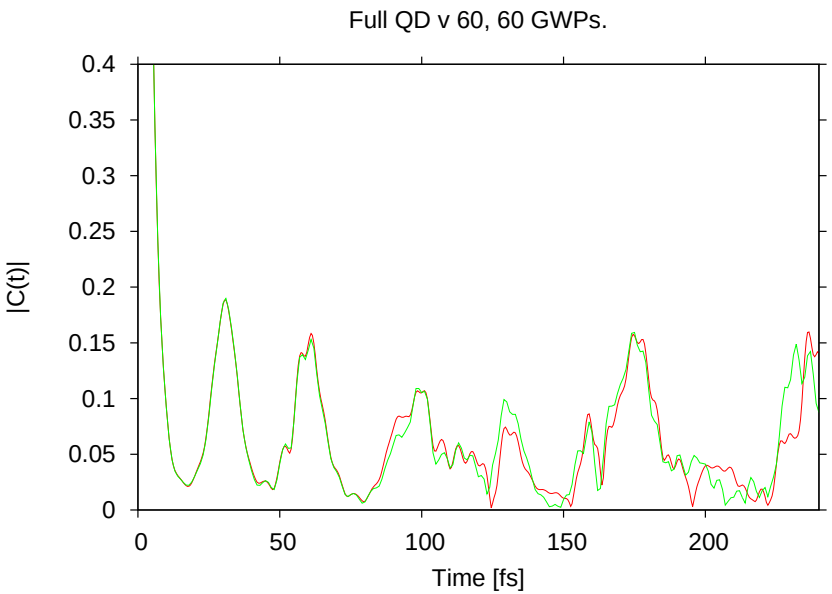


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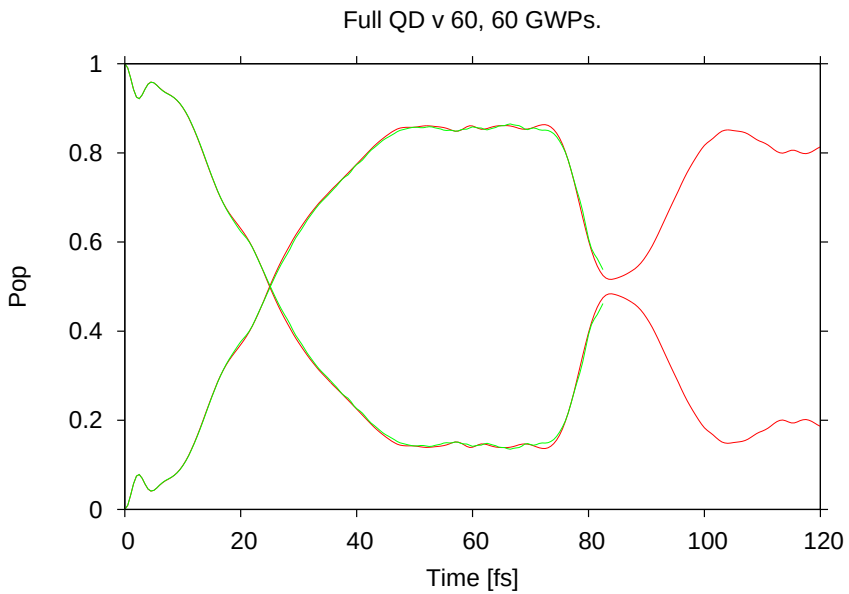
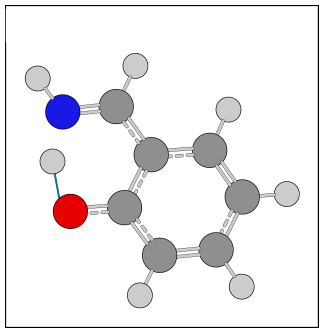
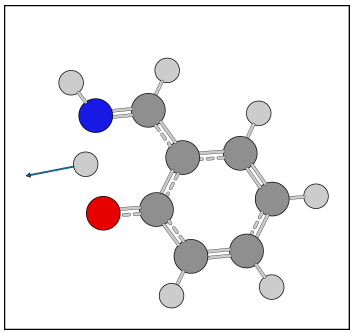



QD basis size: 4060 SPFs, 355,000 primitives

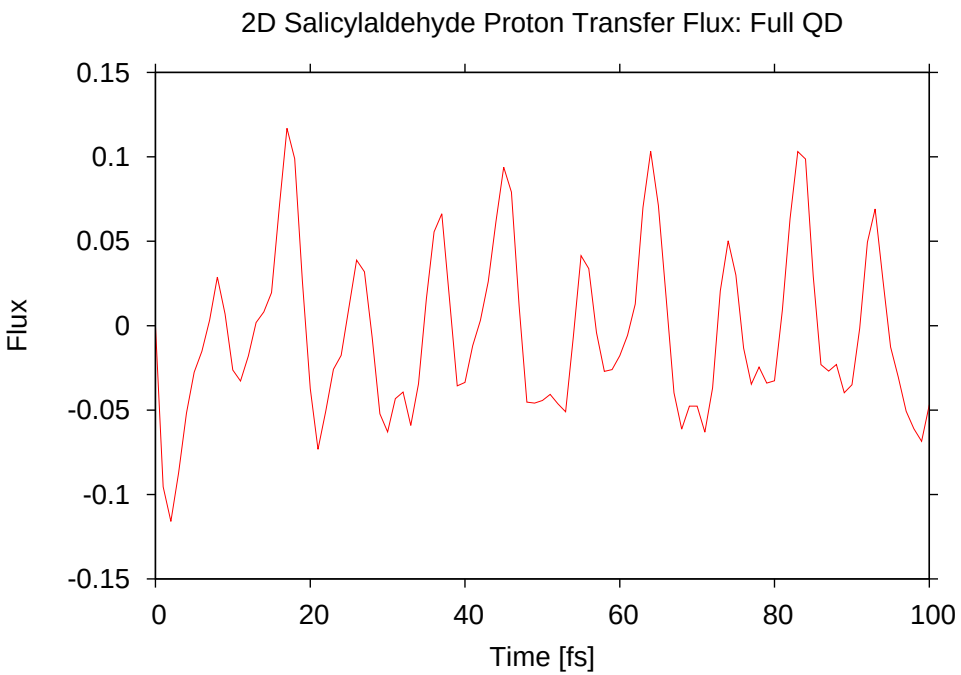
# Salicylaldimine Test Case: 2D Proton transfer

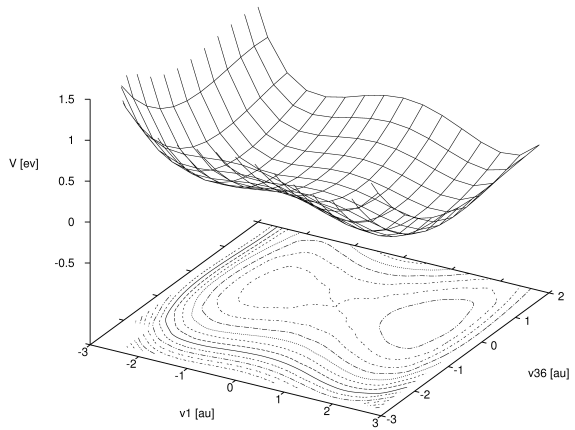
$$H = \sum_{\kappa=1,18} \frac{\omega_\kappa}{2}\left(\frac{\partial^2}{\partial q_\kappa^2} + q_\kappa^2\right) + \sum_{n=1}^{4} A_n q_1^n + B_{11} q_1 q_{18} + B_{22} q_1^2 q_{18}^2 + B_{31} q_1^3 q_{18} + B_{13} q_1 q_{18}^3$$





$\nu_1$ $\nu_{18}$




Exact flux

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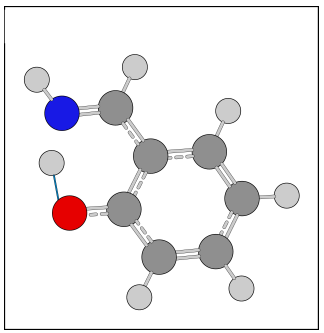
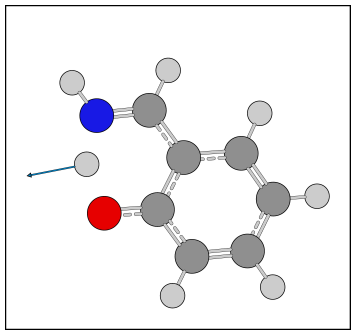
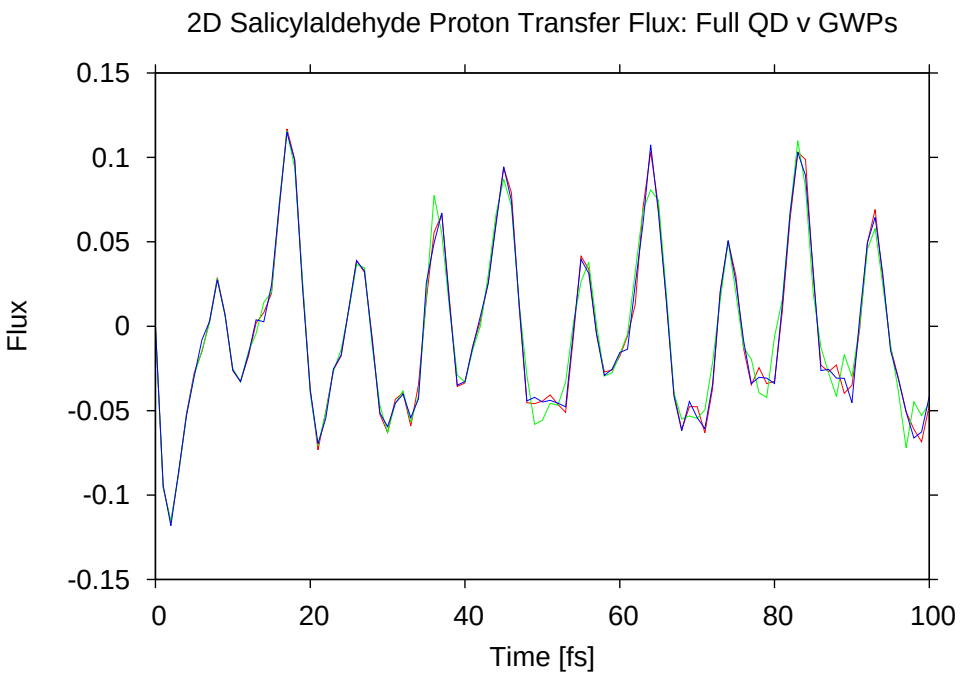
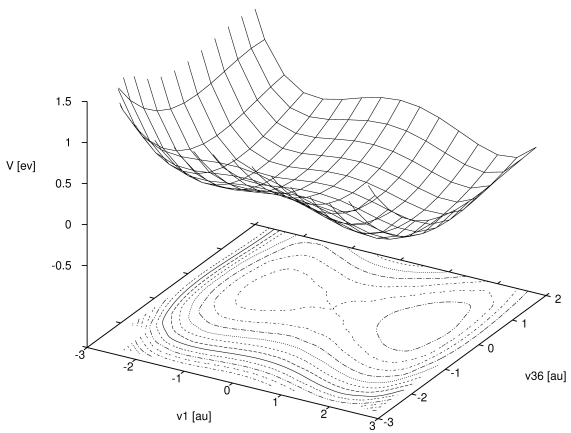
$$H = \sum_{\kappa=1,18} \frac{\omega_\kappa}{2}\left(\frac{\partial^2}{\partial q_\kappa^2} + q_\kappa^2\right) + \sum_{n=1}^{4} A_n q_1^n + B_{11} q_1 q_{18} + B_{22} q_1^2 q_{18}^2 + B_{31} q_1^3 q_{18} + B_{13} q_1 q_{18}^3$$





$\nu_1$ $\nu_{18}$

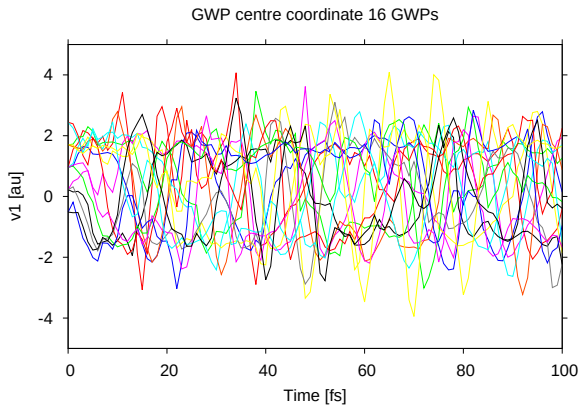


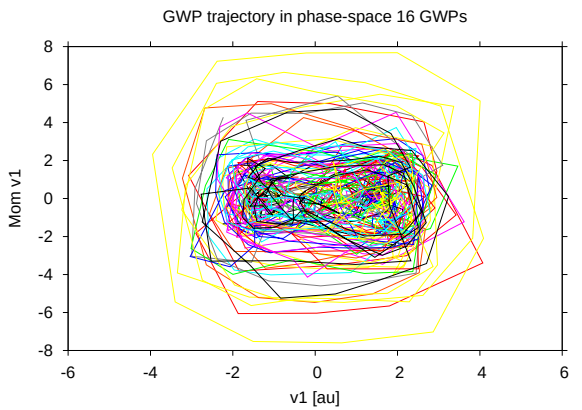




16 / 32 GWPs

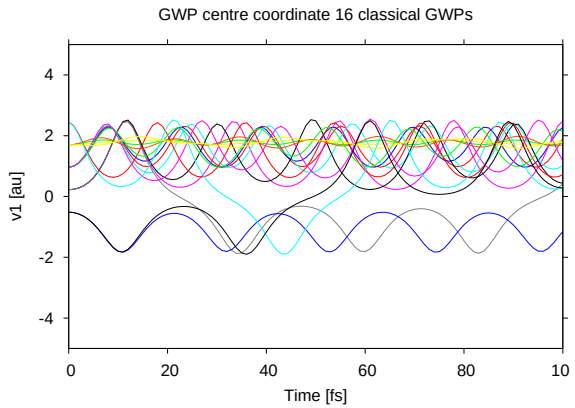
# Trajectories with 16 GWPs

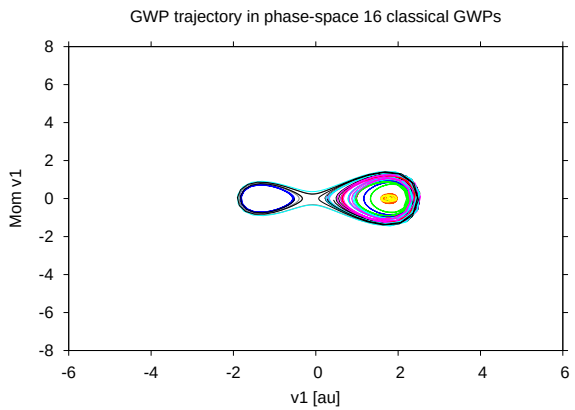
## vMCG

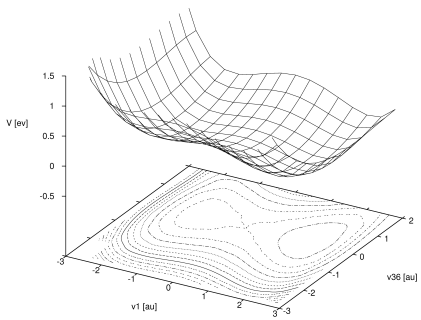



## Classical




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

# Grid-based QD $\longrightarrow$ Gaussian Wavepackets

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

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

- 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 accuracy of integrals

- Possible to use for *direct dynamics* with LHA for integrals.
- Can also use ML-GMCTDH to improve scaling

# Recipe for Direct Dynamics

- Gradients and Hessians directly from quantum chemistry. (Hessian update).
- Store results in a database (energy, gradient, Hessian)
- Shepard Interpolate between points

$$w_(\mathbf{x}) = \left[ \left( \frac{|\mathbf{x} - \mathbf{x}_i|}{rad_i} \right)^4 + \left( \frac{|\mathbf{x} - \mathbf{x}_i|}{rad_i} \right)^{24} \right]$$

- 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.

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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

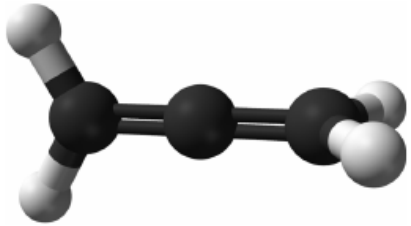
$$\nabla \mathbf{S} = -\mathbf{F}\mathbf{S}$$

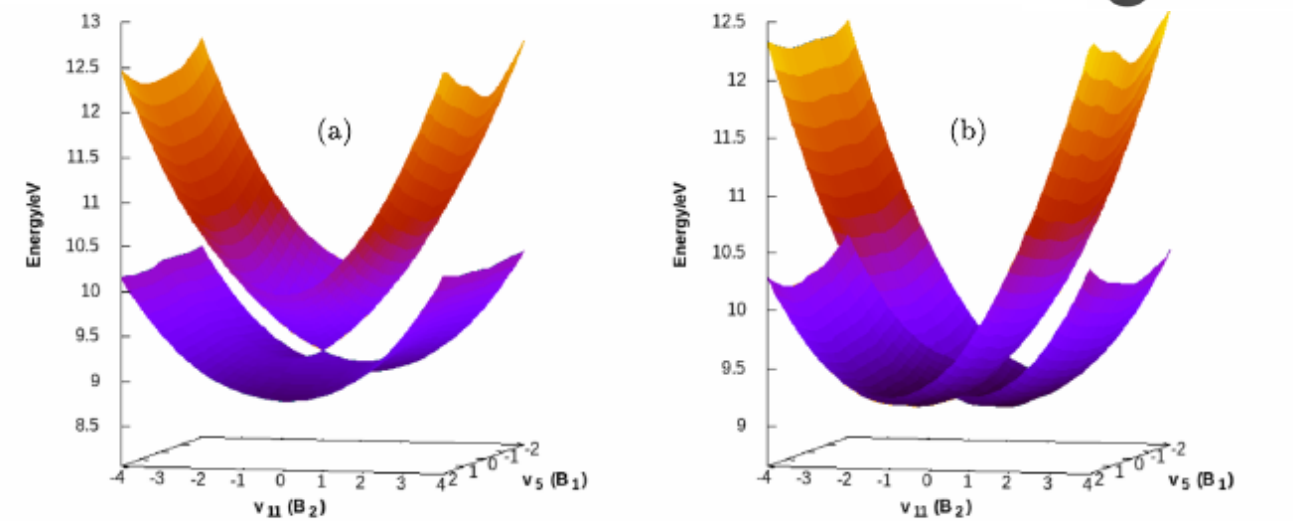
where **F** is derivative coupling. Exact for complete set of states.

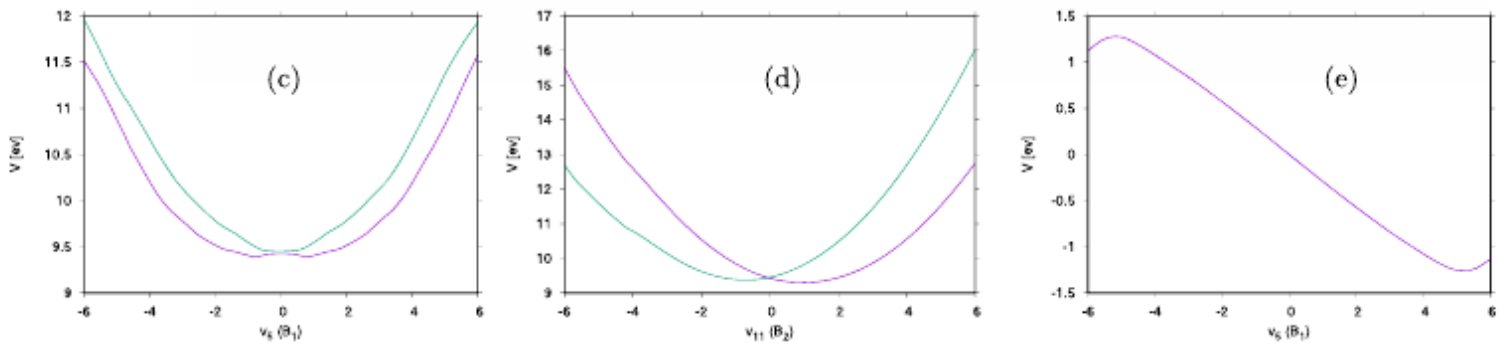
- Choose $\mathbf{S} = \mathbf{1}$ at the initial point of the propagation.
- Solve for **S** by propagating from the nearest point.
- Applicable to any number of states.

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

# Allene Cation DD-vMCG

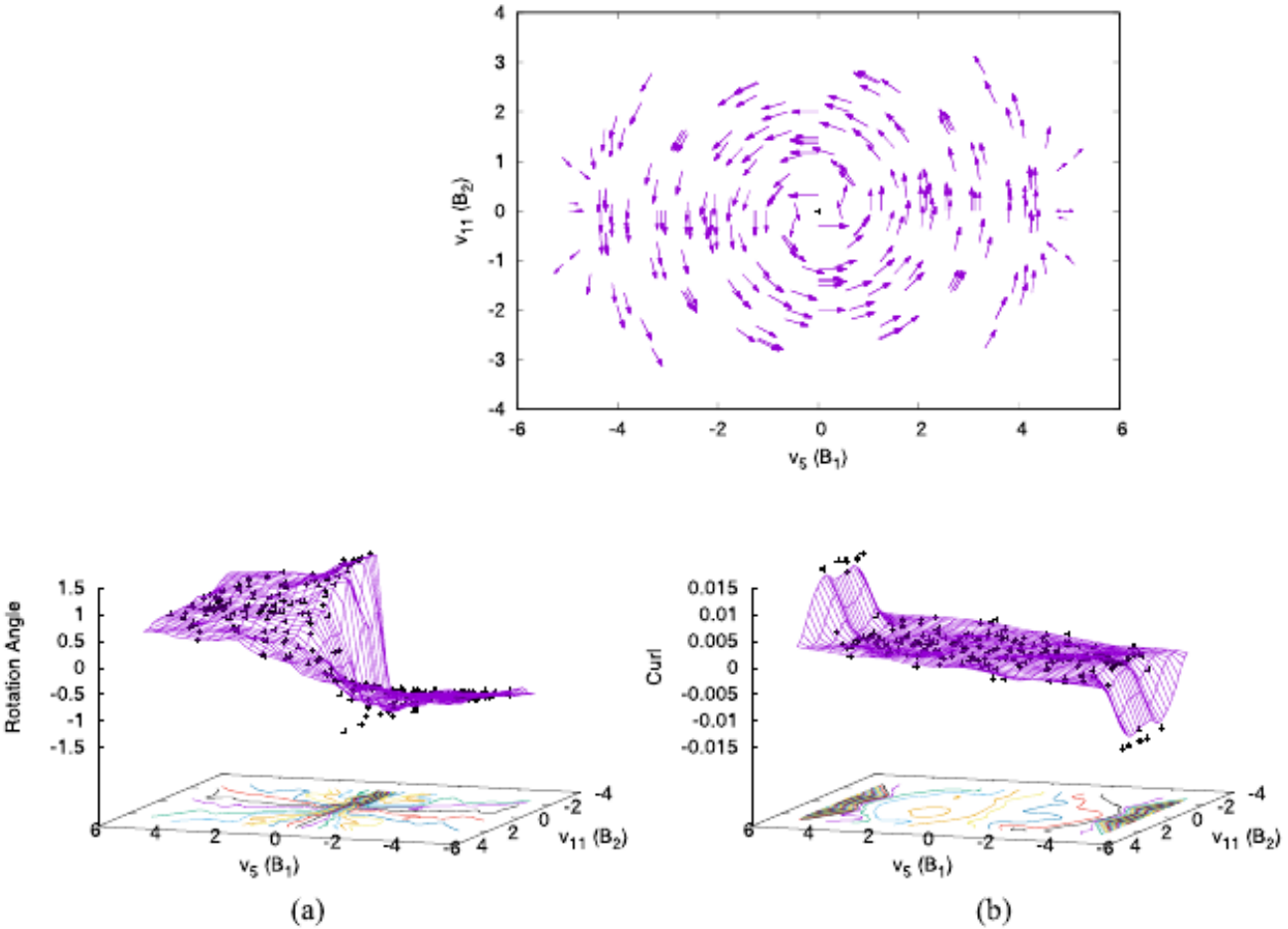




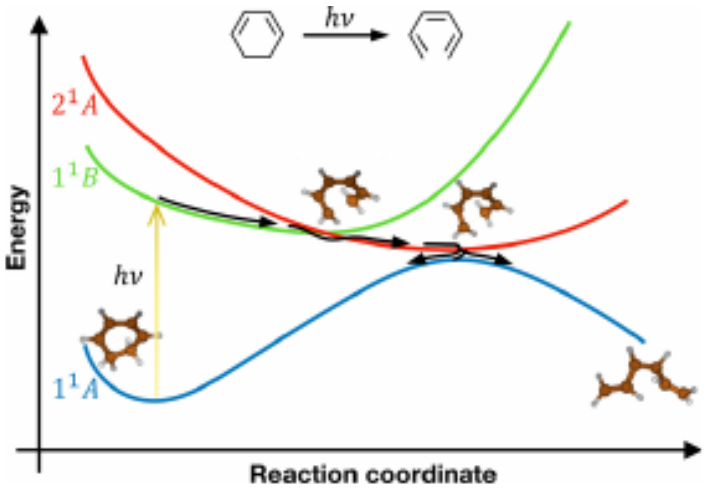
# Allene Cation DD-vMCG

Analysis of diabatisation:

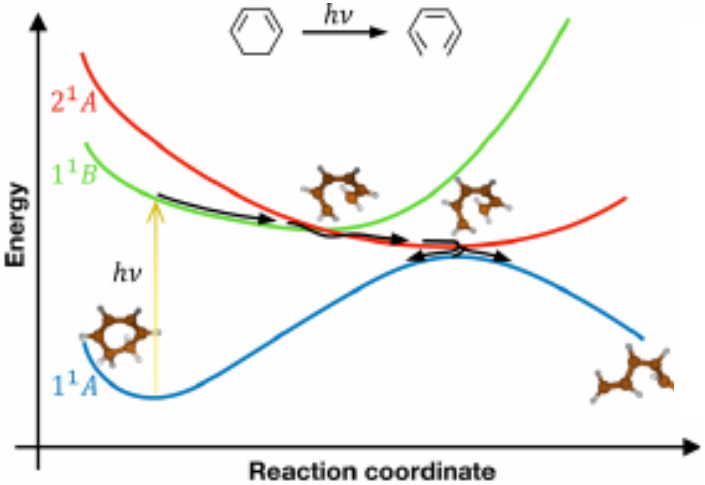


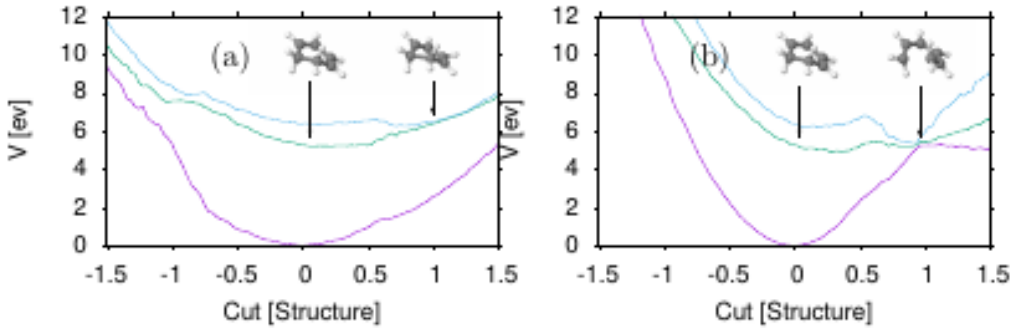

Christopoulou, Freibert and Worth JCP (21) 154: 124127

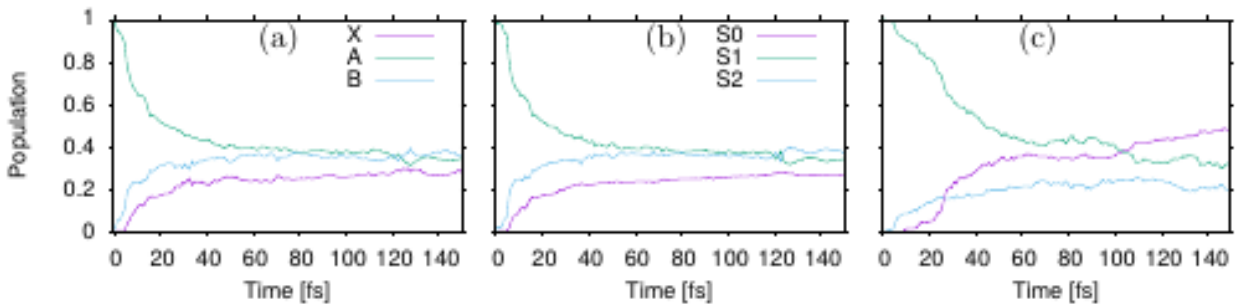
# DDvMCG. CHD $\longrightarrow$ HT



# DDvMCG. CHD $\longrightarrow$ HT



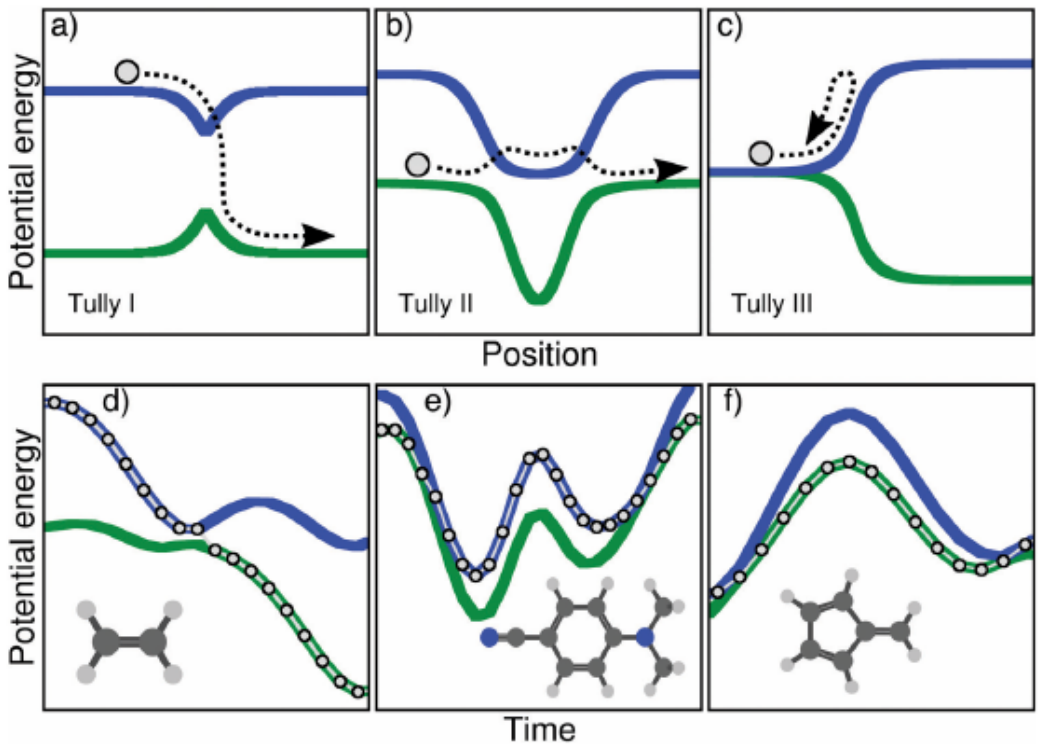




32×32 18D GWPs v 200 trajectories.
XMS-CASPT2(6,6)//6-31G* 3 hours / point. 1900 structures in DB.
For TSH if QC at each step (0.5 fs) then 60,150 calculations.

Coonjobeeharry et al Phil. Trans. Roy. Soc. A (22) **380**: 20200386

# Ethylene

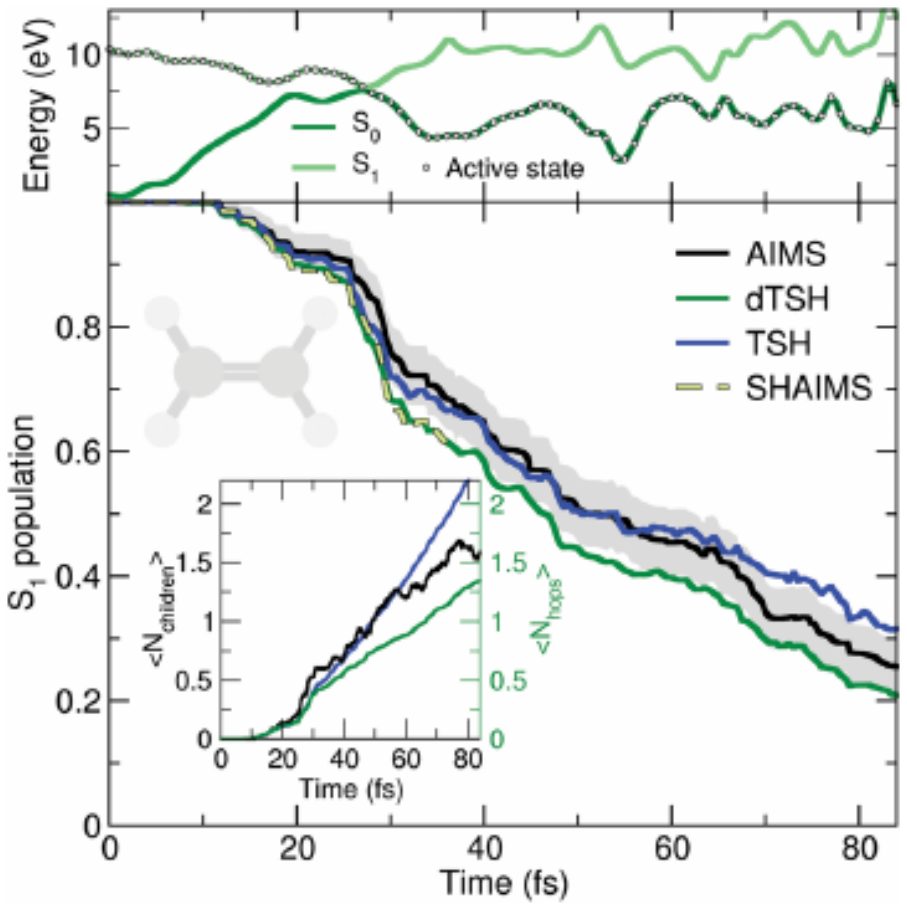
"Molecular Tully Models"




Ibele and Curchod PCCP (20) **22**: 15061

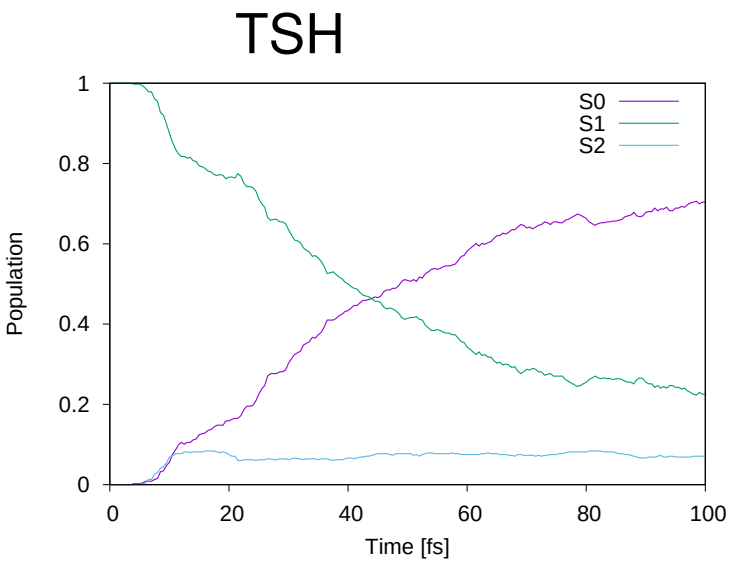
# Ethylene

"Molecular Tully Models"




- Fast torsional motion leads to CoIn
- Fast crossing $S_1 \longrightarrow S_0$

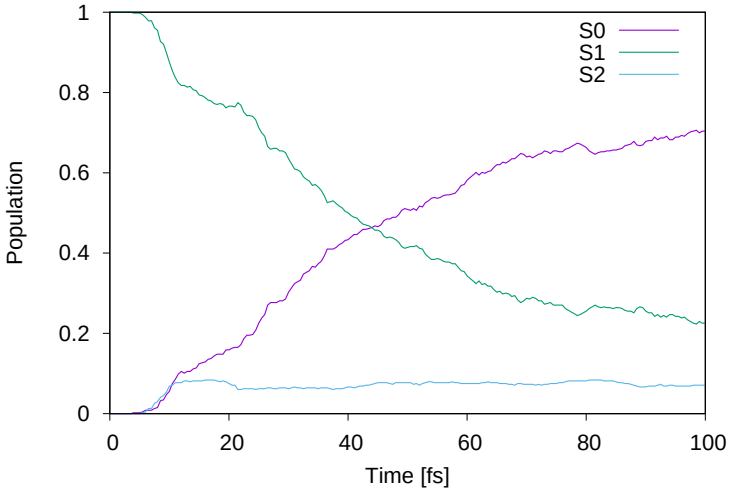
# Quantics



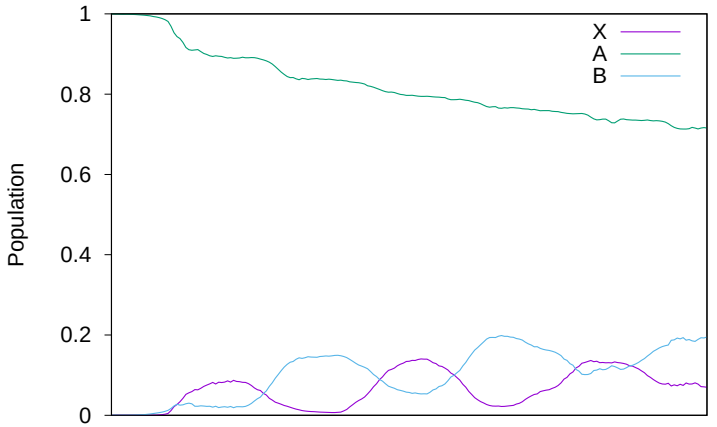

SA(3)-CAS(2,2)/6-31G*. Start in $S_1$. Normal Mode coordinates.
TSH: 500 trajectories. Wigner Sampling. (100,500 QC calculations)

# Quantics

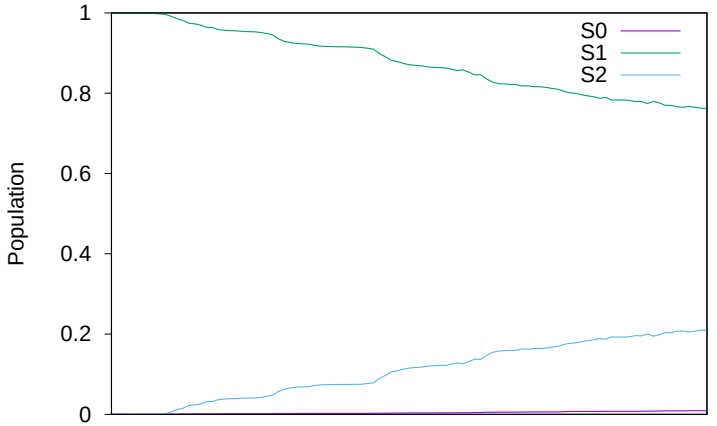
TSH




DDvMCG




diabatic

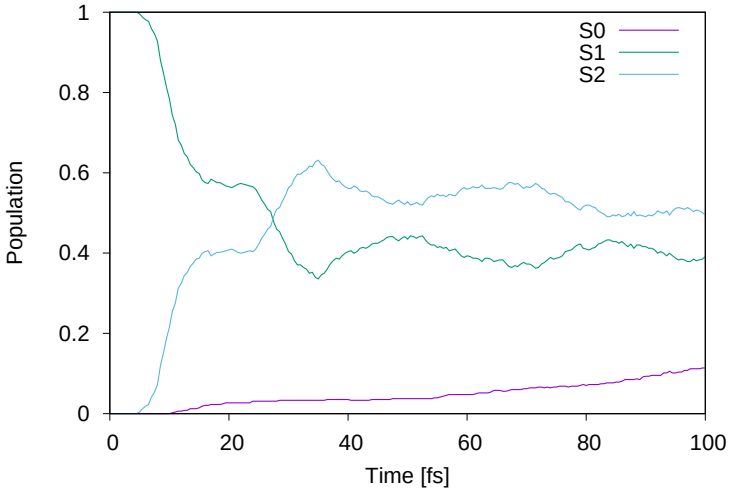



adiabatic

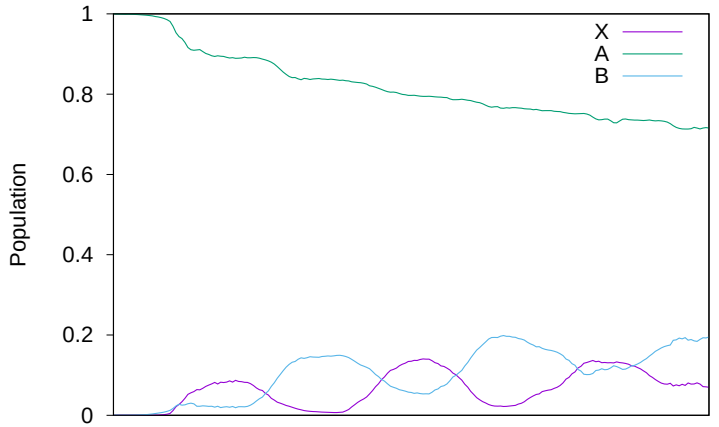
SA(3)-CAS(2,2)/6-31G*. Start in $S_1$. Normal Mode coordinates.
TSH: 500 trajectories. Wigner Sampling. (100,500 QC calculations)
DD-vMCG: $40 \times 40$ 6D GWPs. 45,000 DB points. $D_{2h}$ symmetry.

# Quantics

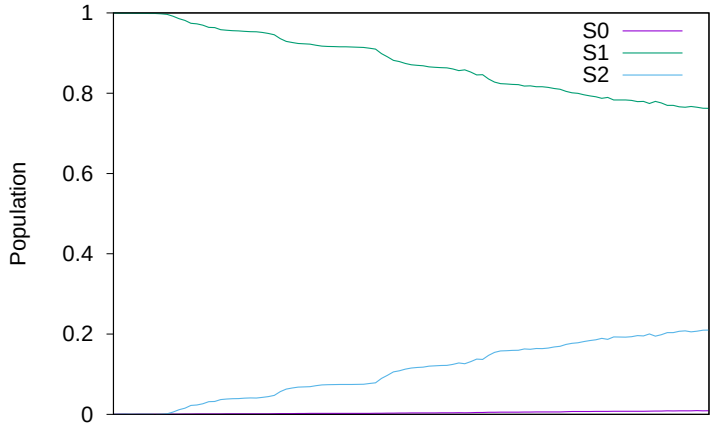
TSH




DDvMCG




diabatic

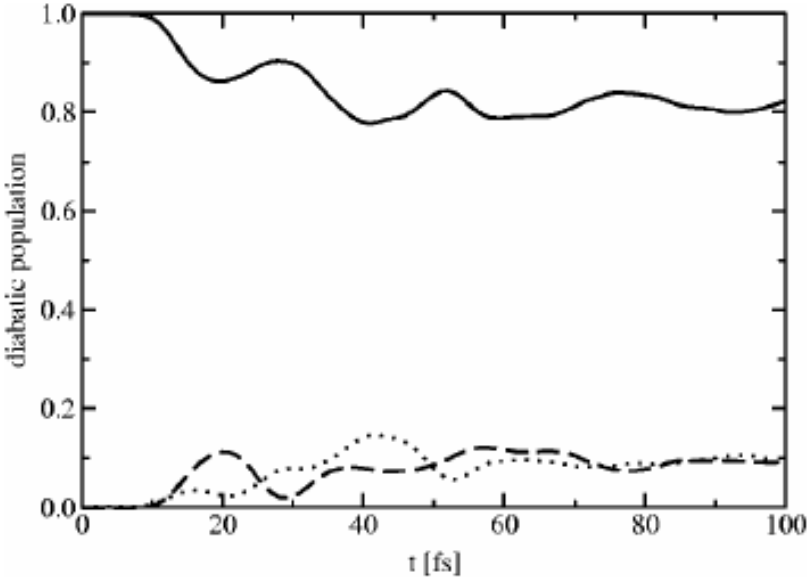



adiabatic

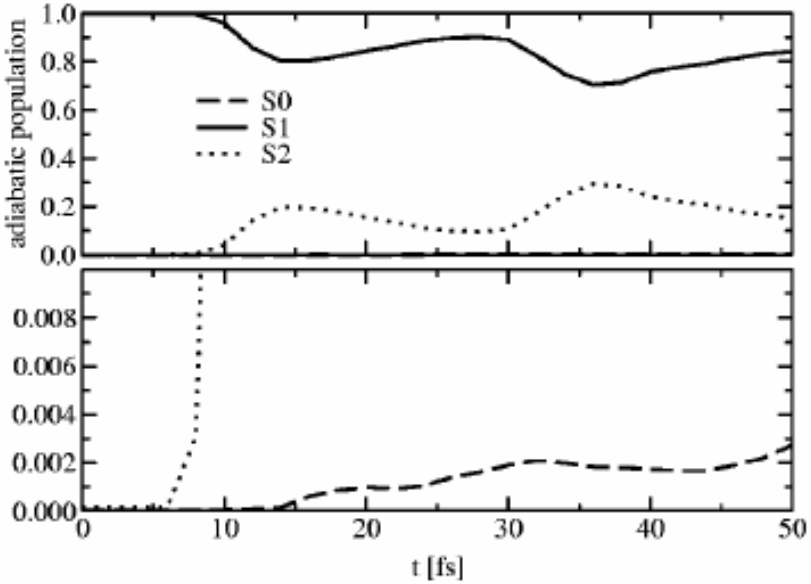
SA(3)-CAS(2,2)/6-31G*. Start in $S_1$. Normal Mode coordinates.
TSH: 500 trajectories. Wigner Sampling. (100,500 QC calculations)
DD-vMCG: 40$\times$40 6D GWPs. 45,000 DB points. $D_{2h}$ symmetry.

# Ethene: Full QD

diabatic



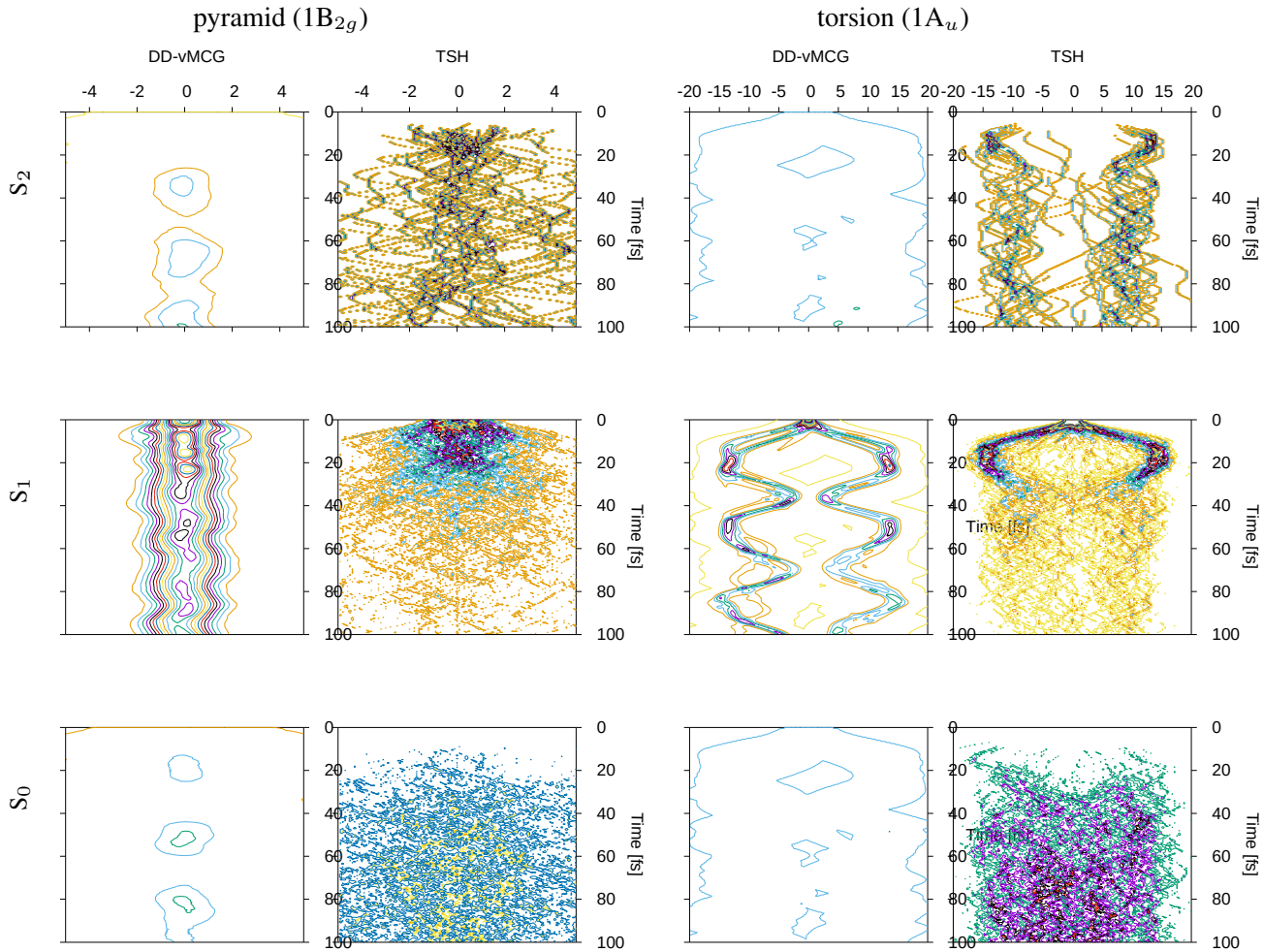

adiabatic




3 coupled PES (CASPT2), 6D, MCTDH.

Viel *et al* JCP (04) **120**: 11000

# Ethene: Densities




$S_1$ / $S_0$ Conical Intersection lies along torsion + pyramidalisation.
Initial wavepacket coherence prevents access.

Gomez, Spinlove and Worth. In preparation

# Summary

Quantum Dynamics needed to completely describe coherent nuclear motion in non-adiabatic systems. Can also include light fields in a straightforward way to extract experimental signal.

- MCTDH provides a complete framework for quantum dynamics
  - ML-MCTDH grid-based for truly large systems - simple PES
  - G-MCTDH flexible route to approximate dynamics - any PES
- G-MCTDH $\longrightarrow$ vMCG $\longrightarrow$ GWP methods
  - still complete solution possible
  - numerically difficult
- Vibronic Coupling Model can be used to study simple non-adiabatic dynamics
- Direct Dynamics (DD-vMCG) allow complete QD in full dimensionality
  - General diabatisation by propagating ADT matrix
  - Present bottleneck: Electronic Structure theory!

# Acknowledgements


Quantics:

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Tom Penfold, Newcastle

Eryn Spinlove, UCL

Sandra Gomez Rodriguez

Alice van Haeften,UCL

Georgia Christopolou, UCL

Thierry Tran, UCL

Calculations:

Maleimide: Sandra Gomez and Andreas Lehr

CHD/HT: Cristina Sanz Sanz and Jaymee Coonjobeeharry

Allene: Georgia Christopoulou and Antonia Freibert

Ethene: Sandra Gomez and Eryn Spinlove