

Solving the Time-Dependent Schrödinger Equation Using the QUANTICS Package

3. Grid Free QD

Graham Worth

Dept. of Chemistry, University College London, U.K.



Summary So Far

- Grid-based QD (DVRs) provide accurate solutions to the TDSE
- MCTDH able to treat ca 10-20 degrees of freedom
- ML-MCTDH able to treat > 100 degrees of freedom
- **Need of global potential energy surfaces**
- Vibronic Coupling Hamiltonian can capture the initial dynamics and calculate absorption spectra.
- **VC Hamiltonian cannot treat long-range motion. I.e. photochemistry**

How do we make QD easy to use and flexible?

- Direct dynamics (on-the-fly potentials)

How do we adapt MCTDH for direct dynamics?

- Use (local) Gaussian basis functions in place of grid.

Grid-free Quantum Dynamics: G-MCTDH

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

Replace single-particle functions with Gaussian functions

$$g_j(\mathbf{Q}, t) = \exp (\mathbf{Q}^T \boldsymbol{\zeta}_j \mathbf{Q} + \mathbf{Q}^T \boldsymbol{\xi}_j + \eta_j) \quad (2)$$

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

$$\begin{aligned} i\dot{A}_j &= \sum_{lk} S_{jk}^{-1} \langle \Phi_k | H | \Phi_l \rangle A_l - \sum_{\kappa=1}^p \sum_{l=1}^{n_\kappa} iS_{jk}^{-1} \langle g_k | \frac{\partial}{\partial t} g_l \rangle A_{J_l^\kappa} \\ &= \sum_{lk} S_{jk}^{-1} H_{kl} A_l - \sum_{\kappa=1}^p \sum_{l=1}^{n_\kappa} iS_{jk}^{-1} \tau_{kl} A_{J_l^\kappa} \end{aligned} \quad (3)$$

$$i\dot{\Lambda} = \mathbf{C}^{-1} \mathbf{Y} \quad (4)$$

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

Burghardt *et al* JCP (08) 129:174104

ADVANTAGES

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

ADVANTAGES

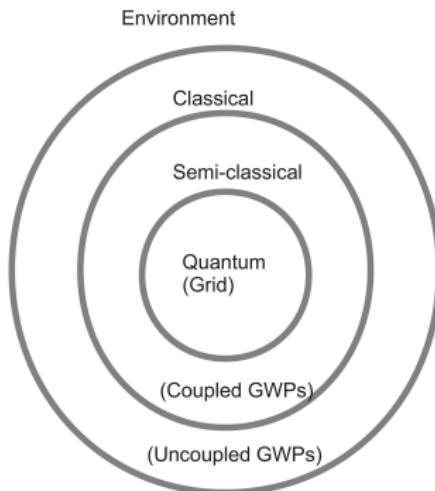
- Need more GFs than SPF_s,
- **BUT** set of parameters smaller than no. of grid points
- spatially unrestricted

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 accuracy of integrals

General Scheme

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



Grid-based QD → Gaussian Wavepackets

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

$$\Psi(\mathbf{x}, t) = \sum_J A_J g_J(\mathbf{x}, t) \quad (5)$$

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 - no “natural population”
- limited to rectilinear coordinates

vMCG Equations of Motion

Following Heller (JCP (75) 62: 1544), basis functions can be wrtten as Gaussian Wavepackets

$$g_j(x, t) = \exp(-\alpha_j(x - q_j)^2 + ip_j(x - q_j) + i\gamma) \quad (6)$$

EoMs for vMCG GWP

$$\dot{q}_j = \frac{p_j}{m} + \frac{1}{2\alpha_j} \text{Im} \sum_m C_{jm}^{-1} \tilde{Y}_m \quad (7)$$

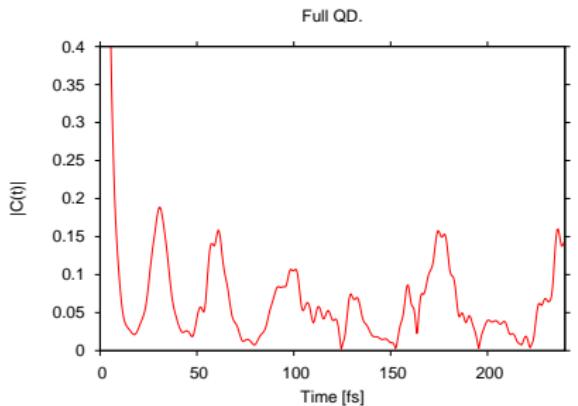
$$\dot{p}_j = -V'_j + \text{Re} \sum_m C_{jm}^{-1} \tilde{Y}_m \quad (8)$$

i.e. they do not follow classical trajectories, but are coupled with

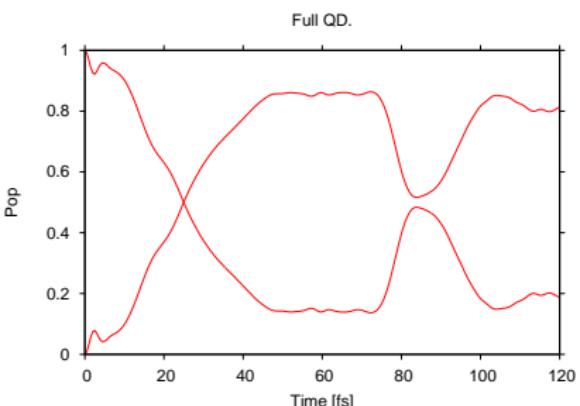
$$\tilde{Y}_{m\alpha} = \frac{4\zeta_{j\alpha}^2}{m_\alpha} q_{j\beta} + \sum_{\beta \neq \alpha} V''_{j\alpha\beta} q_{l\alpha} + \sum_{\alpha, \beta=1}^f S_{jl}^{(\alpha\beta)} X_l^{(\alpha\beta)} + \dots \quad (9)$$

4D model: Linear Coupling

Autocorrelation function:



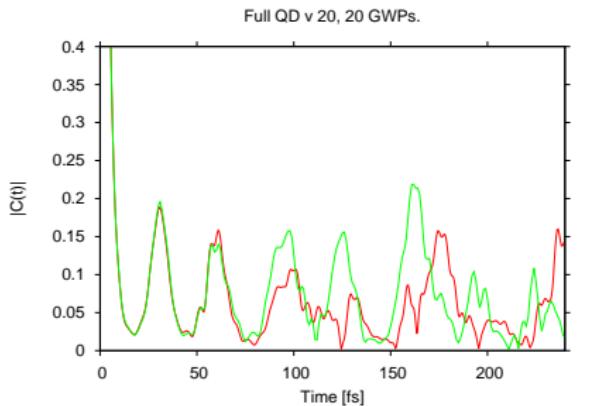
State Populations:



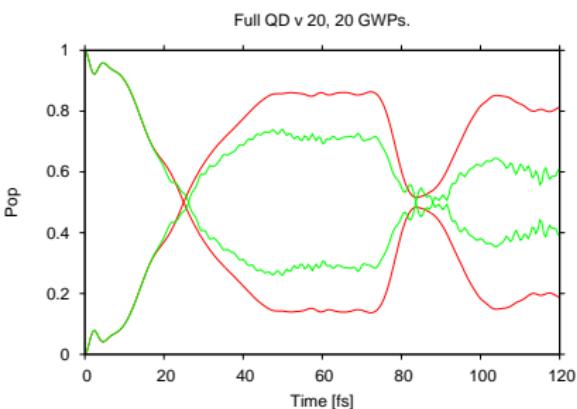
QD basis size: 4060 SPF_s, 355,000 primitives

4D model: Linear Coupling

Autocorrelation function:



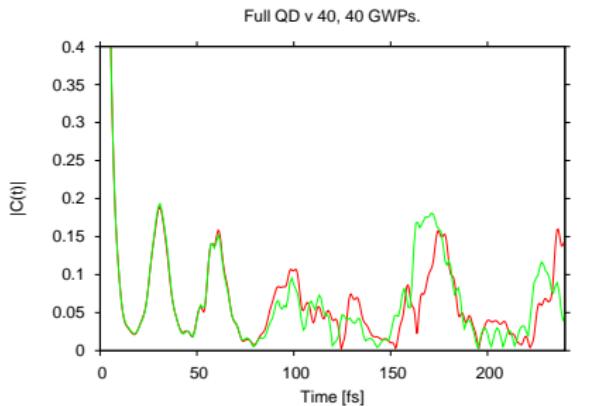
State Populations:



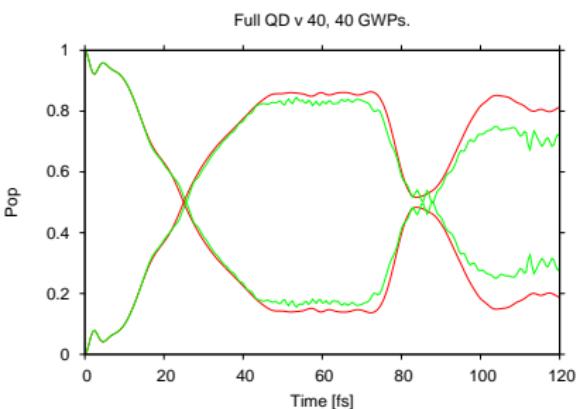
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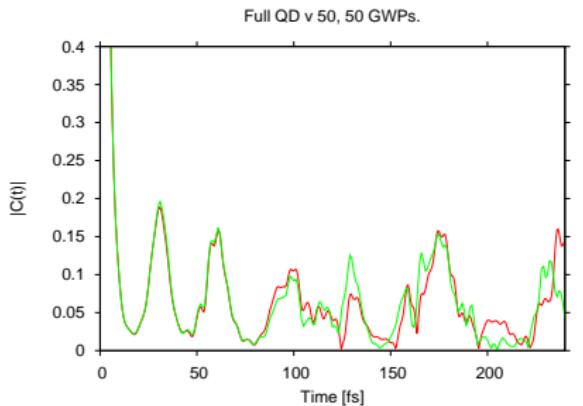
State Populations:



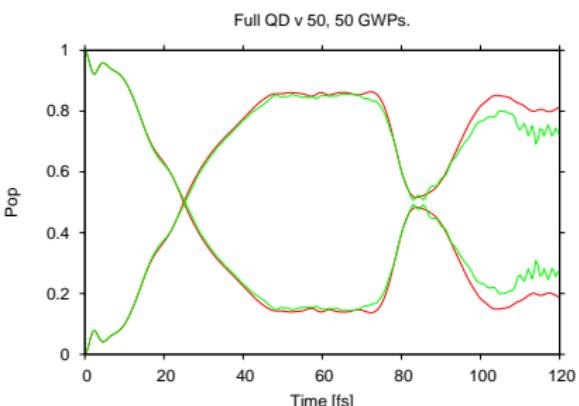
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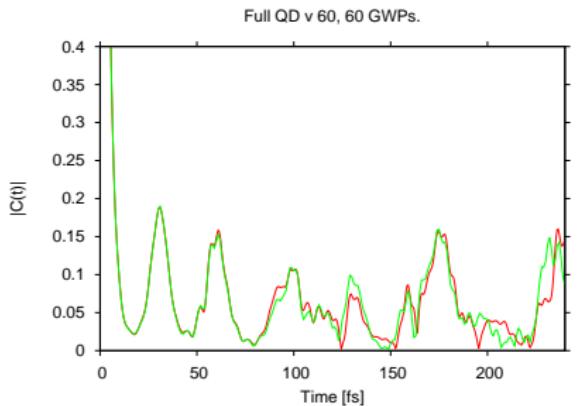
State Populations:



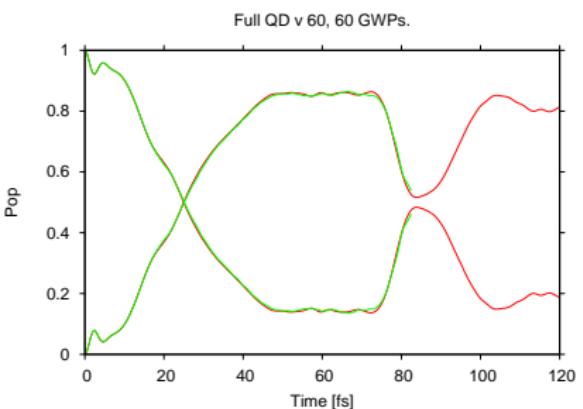
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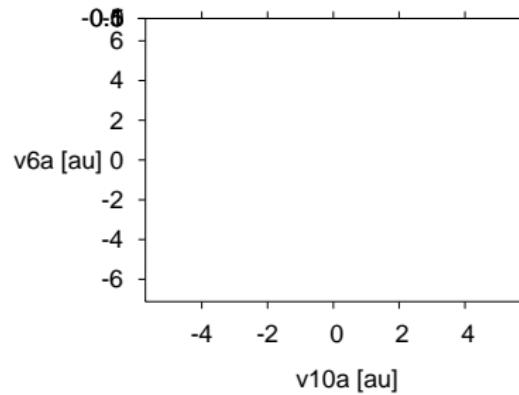
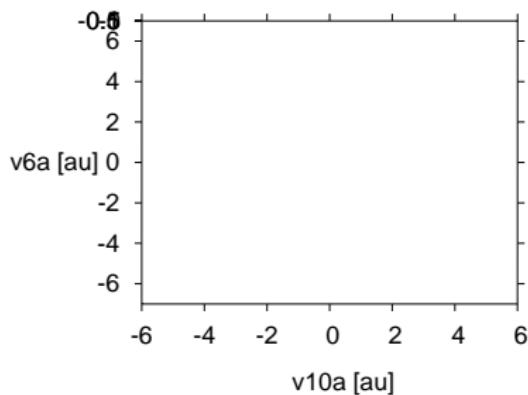
Pyrazine wavepacket on S₁

GWP: 10,10

MCTDH

Time : 0.000

Time : 0.000



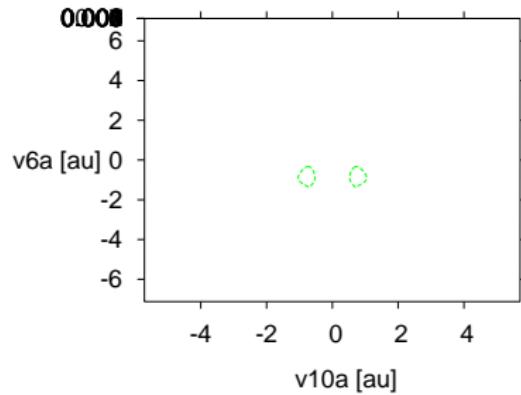
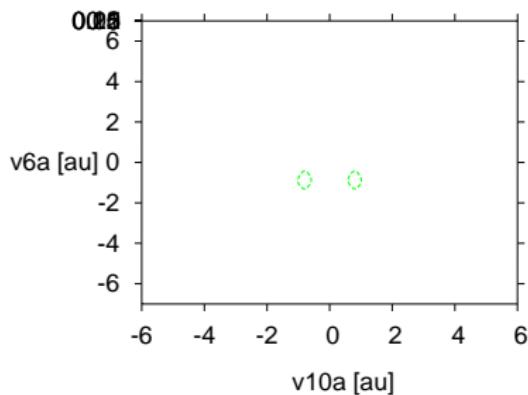
Pyrazine wavepacket on S₁

GWP: 10,10

MCTDH

Time : 5.000

Time : 5.000



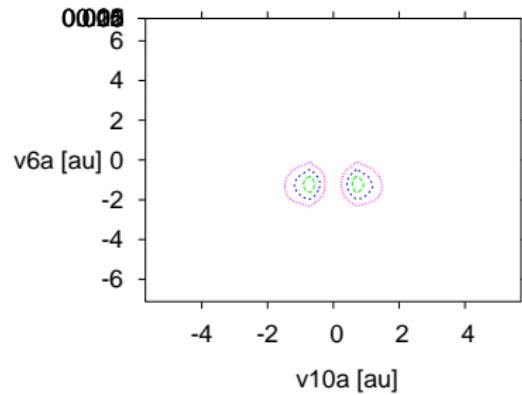
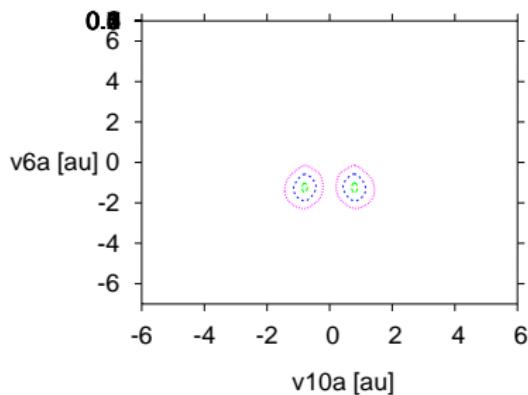
Pyrazine wavepacket on S₁

GWP: 10,10

MCTDH

Time : 10.000

Time : 10.000



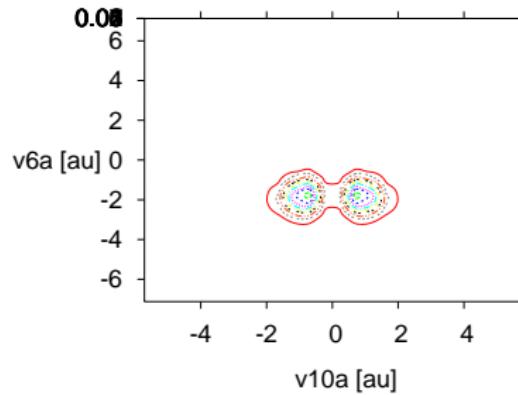
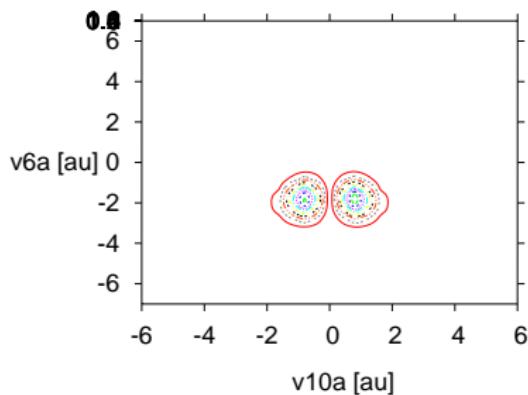
Pyrazine wavepacket on S₁

GWP: 10,10

MCTDH

Time : 15.000

Time : 15.000



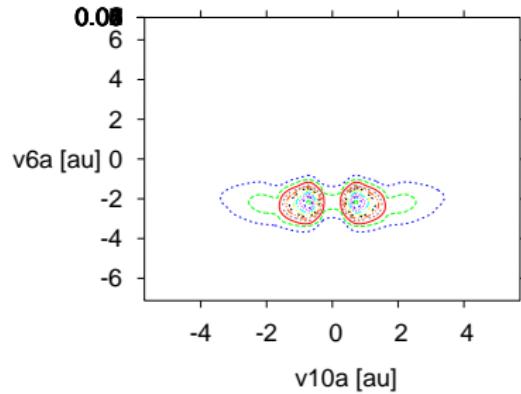
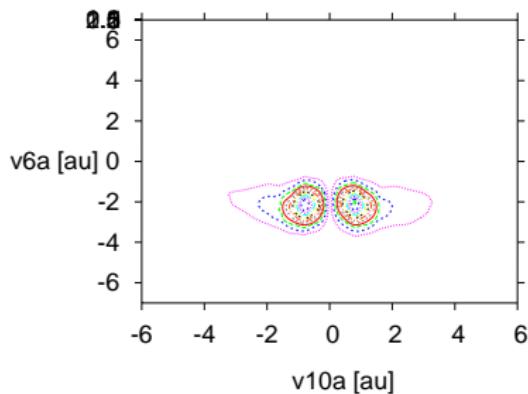
Pyrazine wavepacket on S₁

GWP: 10,10

MCTDH

Time : 20.000

Time : 20.000



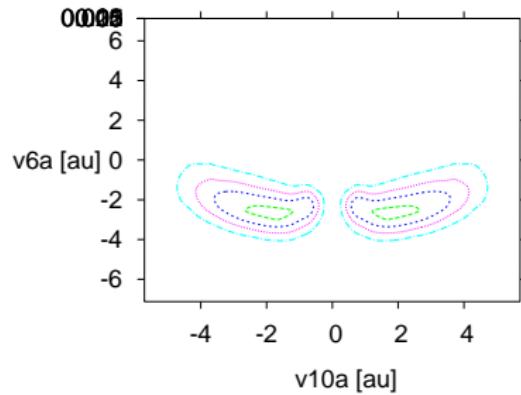
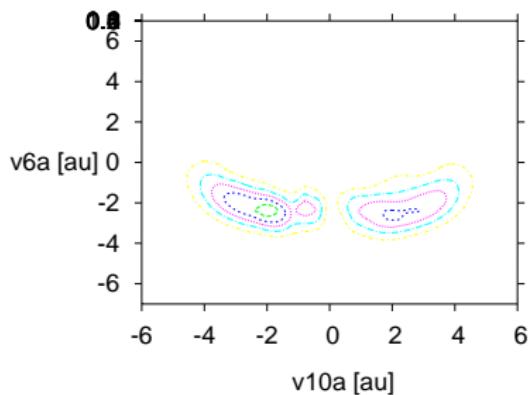
Pyrazine wavepacket on S₁

GWP: 10,10

MCTDH

Time : 25.000

Time : 25.000



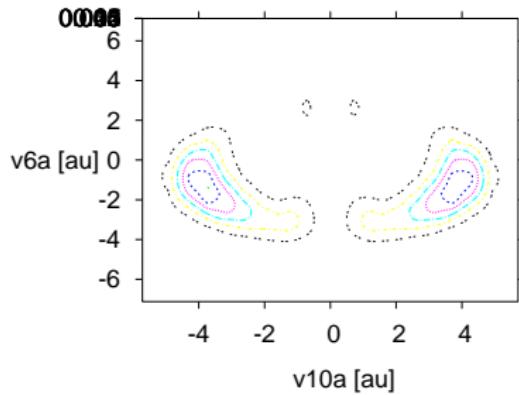
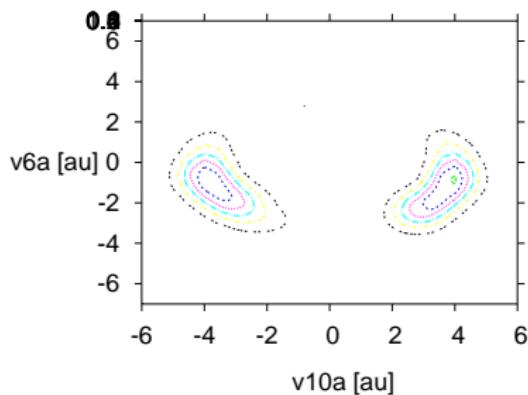
Pyrazine wavepacket on S₁

GWP: 10,10

MCTDH

Time : 30.000

Time : 30.000



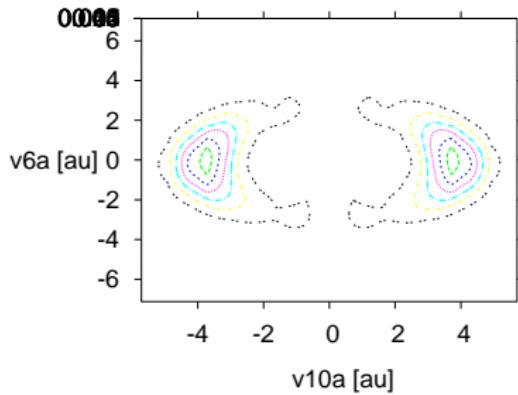
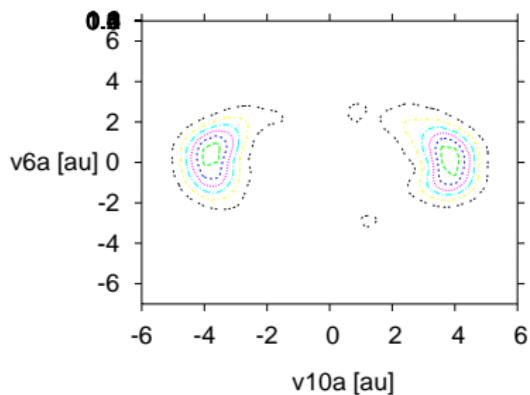
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GWP: 10,10

MCTDH

Time : 35.000

Time : 35.000



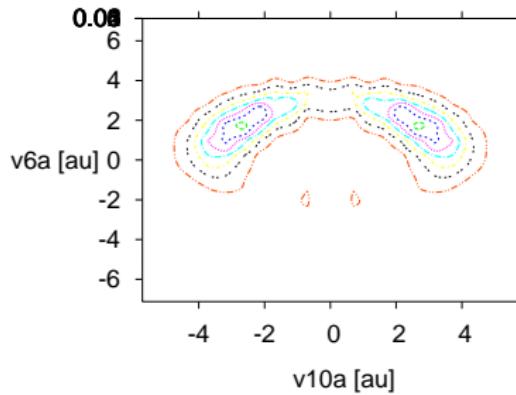
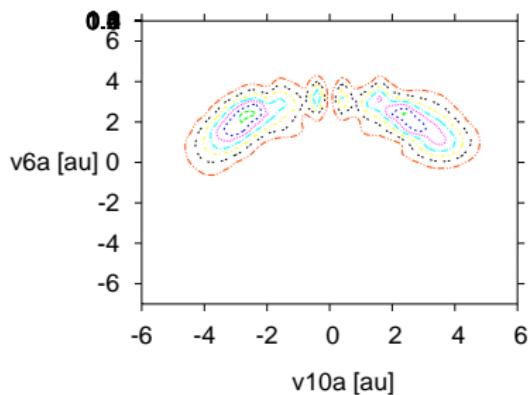
Pyrazine wavepacket on S₁

GWP: 10,10

MCTDH

Time : 40.000

Time : 40.000



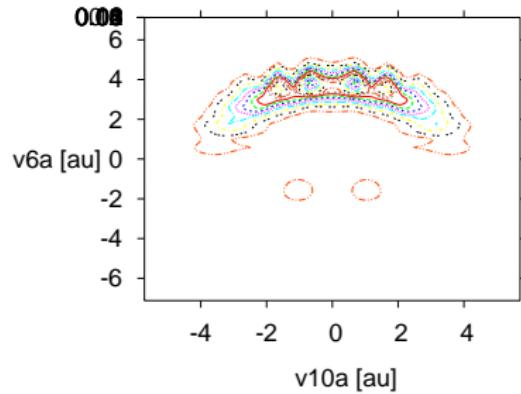
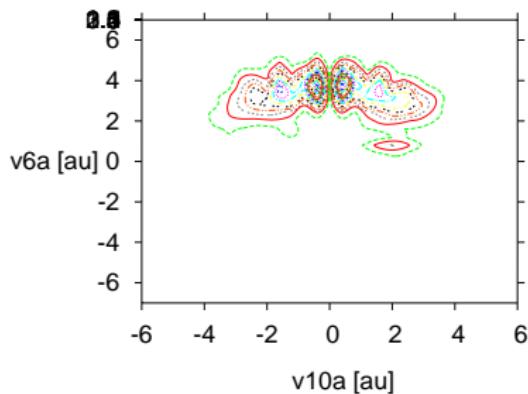
Pyrazine wavepacket on S₁

GWP: 10,10

MCTDH

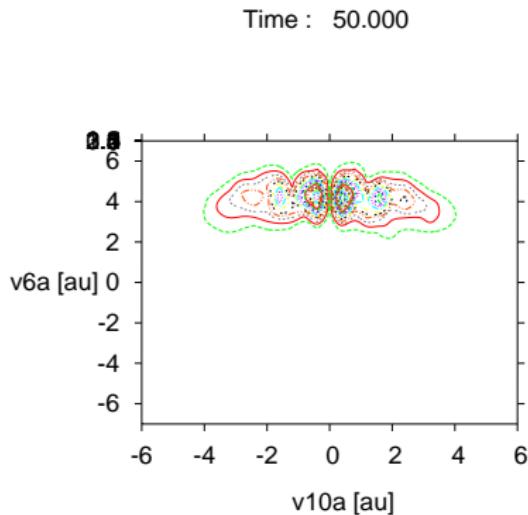
Time : 45.000

Time : 45.000

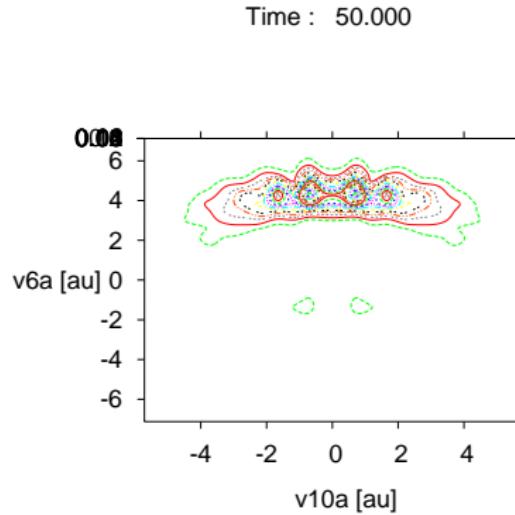


Pyrazine wavepacket on S₁

GWP: 10,10



MCTDH



Direct Dynamics

GWPs are suitable for use with on-the-fly potentials For integrals $\langle g_j | H | g_k \rangle$, Quantum chemistry to second order (LHA).

- 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.

- NACTs

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

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

Avoid these problems by transforming to the diabatic picture.

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

Diabatisation by Propagation

- Adiabatic - Diabatic transformation, \mathbf{S} , defined by the differential equation

$$\nabla \mathbf{S} = -\mathbf{FS} \quad (10)$$

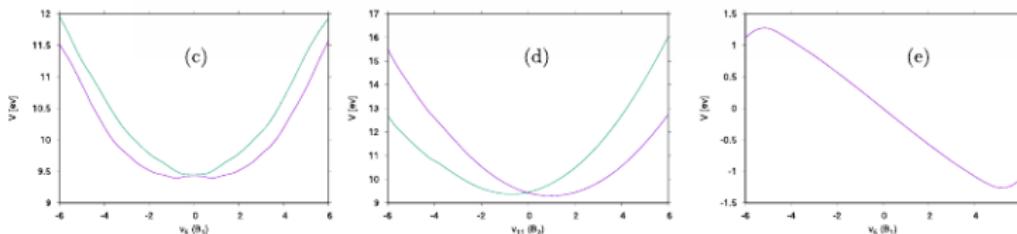
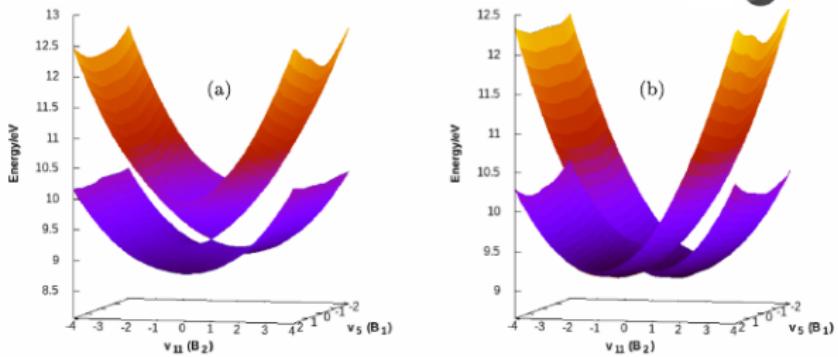
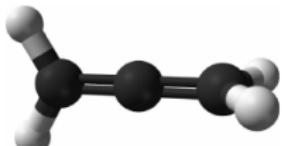
where \mathbf{F} is derivative coupling matrix

- At each GBF position evaluate \mathbf{F} .
- Choose $\mathbf{S} = \mathbf{1}$ at the initial point of the propagation.
- Solve for \mathbf{S} by propagating from the nearest, previously calculated, point.
- PES and gradients transformed by \mathbf{S} .
- Applicable to any number of states.

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

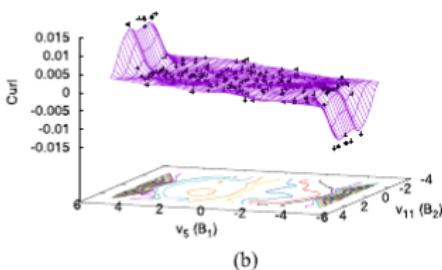
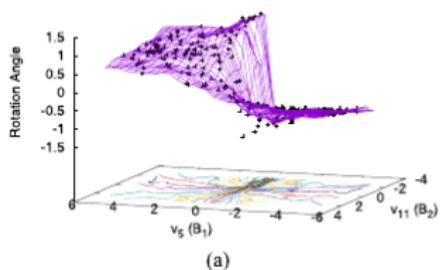
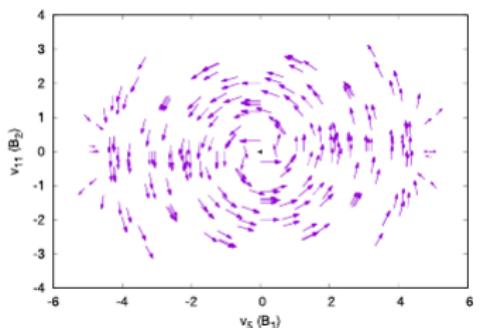
Allene Cation DD-vMCG

CAS(3,4)/6-31G* using Molpro.



Allene Cation DD-vMCG

Analysis of diabatisation:



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

The Database is the Centre...

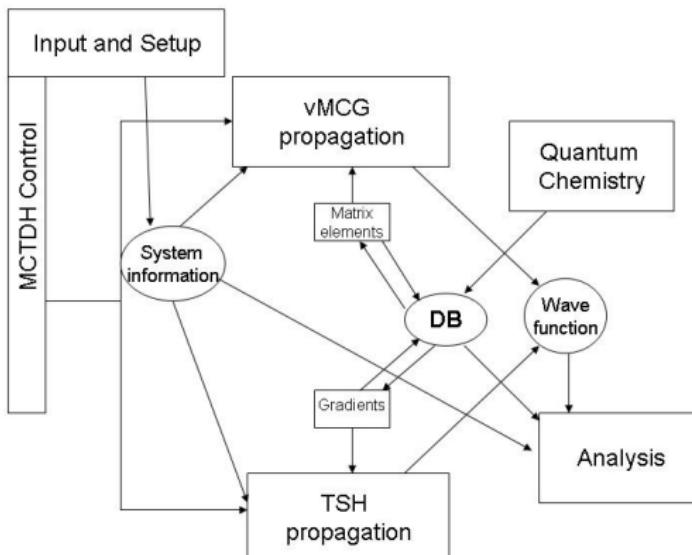


Fig. 1. Information flow of MCTDH propagation showing database (DB) as central element linking alternative propagation schemes (vMCG or TSH) to the Quantum Chemistry programs and the Analysis programs

Shepard Interpolation

QC calculations made when a GWP center (representing a molecular structure) moves far enough from any points previously calculated and stored in the DB.

PES formed from datapoints by Shepard Interpolation

$$V(\mathbf{x}) = \sum_i w_i(\mathbf{x}) T_i(\mathbf{x}) \quad (11)$$

i.e. a weighted sum of PES at all datapoints. Each point is a local “Vibronic Coupling Hamiltonian” to second order.

Weight given by

$$w_i(\mathbf{x}) = \frac{v_i(\mathbf{x})}{\sum_j v_j(\mathbf{x})} \quad ; \quad v_i(\mathbf{x}) = \left[\left(\frac{\|\mathbf{x} - \mathbf{x}_i\|}{\text{rad}_i} \right)^4 + \left(\frac{\|\mathbf{x} - \mathbf{x}_i\|}{\text{rad}_i} \right)^{24} \right]^{-1} \quad (12)$$

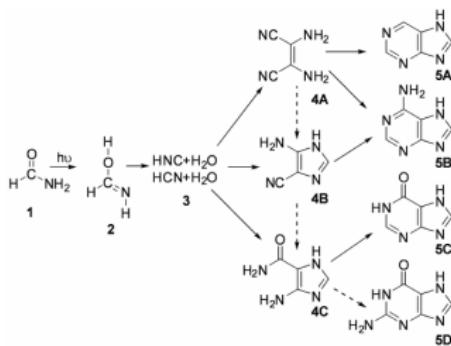
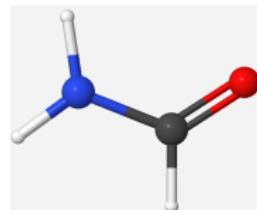
where rad_i is a confidence radius (given by nearest N points)

Christopoulou *et al* JCP 154: 124127 (2021)

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

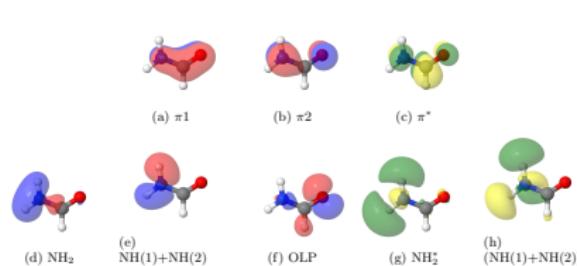


[1] D. Bockelée-Morvan, et al, Astron. Astrophys. (2000) 353 1101-1114

[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

Formamide: Electronic Structure

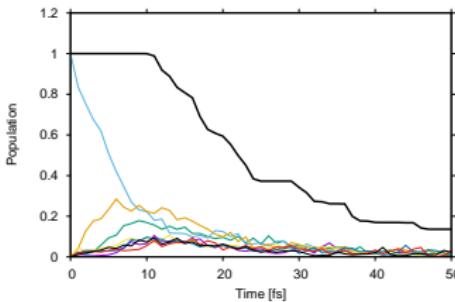
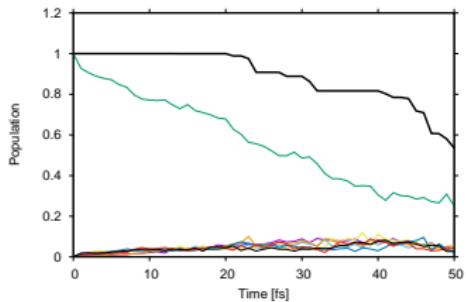


- SA-CAS(10,8)/6-31G*
- 8 states

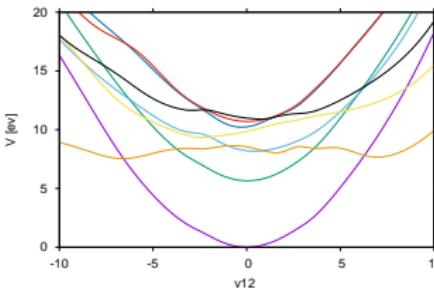
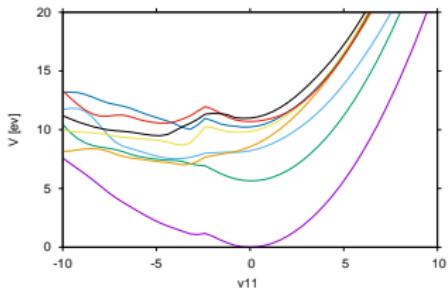
State	VEE/eV	Transition Dipole/au	Character
S ₁	5.607	0.000	Olp π^*
S ₂	8.015	0.000	$\pi\sigma^*$
S ₃	8.159	0.023	Olp π^*
S ₄	9.118	0.000	$\pi\sigma^*$
S ₅	10.033	0.071	Olp σ^*
S ₆	10.574	0.726	$\pi\pi^*$
S ₇	11.450	0.001	$\pi\sigma^*$

Formamide Direct Dynamics

Diabatic Populations: 48 GWPs CAS(10,8)/6-31G* SA 8.
 $S_1(\text{Olp}\pi^*)$ $S_2(\pi\sigma^*)$



Potential Surfaces: 6000 structures in DB
 Along NH₂ sym Along NH₂ anti-sym

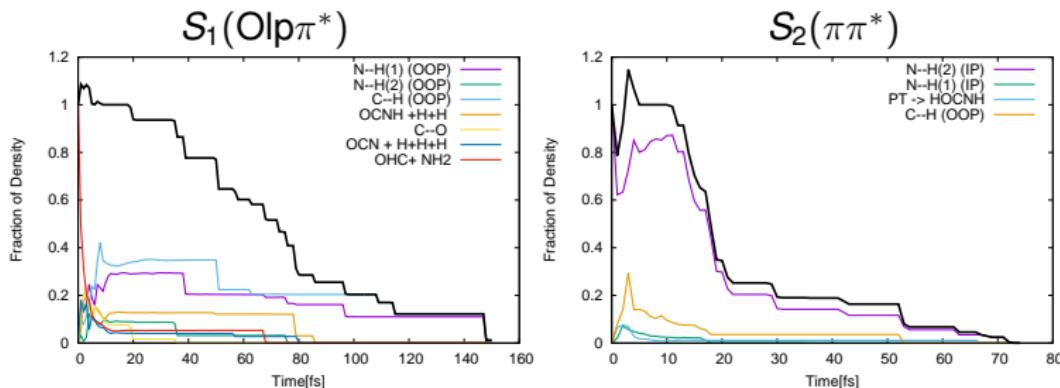
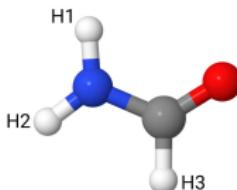


Reaction Channels

To get an estimate of the products, need to know how much density goes into different channels. Can follow trajectory at centre of a GWP and weight by *Gross Gaussian Population*

Allan *et al* JPC A (10) 114:8713

$$\text{GGP}_i = \sum_j \text{Re}(A_i^* S_{ij} A_j)$$



Spinlove, Robb and Worth Farad. Discuss. (2018) 212: 191

```
#####
# DD / Propagation in normal modes #####
#####

RUN-SECTION
name = butatriene
propagation      direct = nmodes          ngwp = 4
title = Butatriene test dynamics
tfinal = 50.0    tout = 1.0   tpsi= 1.0
psi  gridpop  update steps auto
end-run-section

DIRDYN-SECTION
data = but_db
transfile = but_fc_cas_freq.out
update = always
qcprogram = molpro    method = cas
ener0 = -152.9326464722
# substitute db = only for next 2 lines to generate DB
db = rdwr    dbmin = 0.2
subcmd = /user/gworth/bin/run_g09 , 2
dd_diab=global      hess_upd
end-dirdyn-section
```

```
INITIAL-GEOMETRY-SECTION
nstates = 2      init_state = 2
cartesian = angst
6              0.000000  0.000000  1.959948
6              0.000000  0.000000  0.630953
6              0.000000  0.000000 -0.630953
6              0.000000  0.000000 -1.959948
1              0.000000  0.917846 -2.515682
1              0.000000 -0.917846 -2.515682
1              0.000000  0.917846  2.515682
1              0.000000 -0.917846  2.515682
end-cartesian
nmode
1B2U 0.0000 176.6640, cm-1 width = 0.7071 freeze
2B3U 0.0000 213.6528, cm-1 width = 0.7071 freeze
3B3G 0.0000 328.5543, cm-1 width = 0.7071 freeze
4B2G 0.0000 539.8168, cm-1 width = 0.7071 freeze
5AU 0.0000 767.6318, cm-1 width = 0.7071
6B2G 0.0000 866.1461, cm-1 width = 0.7071 freeze
7B3U 0.0000 866.9727, cm-1 width = 0.7071 freeze
8AG' 0.0000 900.9714, cm-1 width = 0.7071
9B3G 0.0000 1139.5870, cm-1 width = 0.7071 freeze
10B2U 0.0000 1152.6015, cm-1 width = 0.7071 freeze
11B1U 0.0000 1534.7996, cm-1 width = 0.7071 freeze
12AG  0.0000 1629.9697, cm-1 width = 0.7071
13B1U 0.0000 1701.6918, cm-1 width = 0.7071 freeze
14AG  0.0000 2196.1724, cm-1 width = 0.7071
15AG  0.0000 3308.4750, cm-1 width = 0.7071
16B1U 0.0000 3310.2740, cm-1 width = 0.7071 freeze
17B3G 0.0000 3393.2925, cm-1 width = 0.7071 freeze
18B2U 0.0000 3393.3208, cm-1 width = 0.7071 freeze
end-nmode
end-initial-geometry-section

end-input
```

DB Files

Set up a directory but_db.

1. Put in any required files: e.g. transfile, orbital file,

...
2. Template file template.dat

```
%mem=800mb
%chk=$chk$
#P CAS(5,6,NRoot=$root$)/3-21G*
Guess=Read NoSymm scf=(maxcycle=128)
$Swap:IOp(5/97=100,10/97=100)$
$Freq:Freq IOp(5/17=41000200,10/10=700007)$
$SA-SP:IOp(5/17=11000000)$
```

butatriene cation

1 2

<geometry>

\$SA-SP:0.5 0.5\$

Molpro Template

```
***Butatriene
nosym
geomtyp=xyz
geometry={
 8
butatriene geometry
<geometry>
}
basis=6-31G*

$Orbread:{matrop;read,oldorbitals,file=<corbfile>;save,oldorbitals,2140.2,orbitals}$

! State 1
{multi,gradient=1.0d-6,energy=1.0d-8;occ,17;
start,2140.2;
closed,11;
$Force:CPMCSCF,grad,1.1,accu=1.0d-8,record=5101.1;$ 
wf,27,1,1;
state,2;
weight,0.5,0.5
orbital,2141.2;
orbprint,100;
}
$Force:{Force;SAMC,5101.1}$
$Freq:{Frequencies,analytical,noproject,new;print,hessian}$

! State 2
$Force:{multi,gradient=1.0d-6,energy=1.0d-8;occ,17;start,2141.2;closed,11;
CPMCSCF,grad,2.1,accu=1.0d-8,record=5102.1;wf,27,1,1;state,2;weight,0.5,0.5;}$
$Force:{Force;SAMC,5102.1}$
$Freq:{Frequencies,analytical,noproject,new;print,hessian}$

! 2-1
$NACT:{multi,gradient=1.0d-6,energy=1.0d-8;occ,17;closed,11;start,2141.2;
cpmcscf,nacm,2.1,1.1,accu=1.0d-10,record=5103.1;wf,27,1,1;state,2;weight,0.5,0.5;}$
$NACT:{Force;SAMC,5103.1}$
```

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- Require a primitive basis
- MCTDH a general algorithm for polyatomic systems

Aim is to simulate a signal that can be related to an experiment

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More flexibility provided by grid-free methods and direct dynamics

- DD-vMCG fast convergence
- **Present bottleneck: Electronic Structure theory!**