Solving the Time-Dependent Schrödinger Equation Using the QUANTICS Package

1. Introduction to QD and Quantics

Graham Worth

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

$^{\triangle}$UCL

The Quantics Code

Solve TDSE for distinguishable particles

- Grid-based systems
- Direct dynamics
- Obtain eigenvalues
- Include a light field
- Time-dependent spectra
- Flux analysis for reaction probabilities

- Text driven input for most operations
- Various DVR / FBR representations
- A range of operators available
- A suite of analysis programs
- Standard F90 + linux packages

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

Methods Available

Table 1
Main methods available in the QUANTICS Program.

Method	Equation solved	Basis sets
Standard WP	TDSE	DVRs or FFT
MCTDH	TDSE	DVRs or FFT
ML-MCTDH	TDSE	DVRs or FFT
GMCTDH	TDSE	DVRs or FFT or GWPs
ML-GMCTDH	TDSE	DVRs or FFT or GWPs
ρMCTDH(I)	LvN	DVRs or FFT
ρMCTDH(II)	LvN	DVRs or FFT
ML-ρMCTDH(I)	LvN	DVRs or FFT
ML-ρMCTDH(II)	LvN	DVRs or FFT
ρGMCTDH(II)	LvN	DVRs or FFT or GWPs
ML-ρGMCTDH(II)	LvN	DVRs or FFT or GWPs
Standard WP	TISE	DVRs or FFT
vMCG	TDSE	GWPs
clMCG	TDSE	GWPs
iMCG	TDSE	GWPs
DD-vMCG	TDSE	GWPs
TSH	TDSE	trajectories
DD-TSH	TDSE	trajectories

Integration schemes	Method
Chebyshev	Standard WP
Second Order Differencing	Standard WP
Split Operator	Standard WP
Constant Mean Field (CMF)	MCTDH (not ML-)
Adams–Bashforth–Moulton	all MCTDH and MCG
Burlisch–Stoer	all MCTDH and MCG
Runge–Kutta	all MCTDH and MCG

DVRs:
Harmonic Oscillator, Sine, Cosine, Exponential, Legendre, Laguerre

2D spherical harmonic basis sets:
Spherical Harmonic FBR, Extended Legendre, 2D Legendre

Methods Available

Table 1
Main methods available in the QUANTICS Program.

Method	Equation solved	Basis sets
Standard WP	TDSE	DVRs or FFT
MCTDH	TDSE	DVRs or FFT
ML-MCTDH	TDSE	DVRs or FFT
GMCTDH	TDSE	DVRs or FFT or GWPs
ML-GMCTDH	TDSE	DVRs or FFT or GWPs
ρMCTDH(I)	LvN	DVRs or FFT
ρMCTDH(II)	LvN	DVRs or FFT
ML-ρMCTDH(I)	LvN	DVRs or FFT
ML-ρMCTDH(II)	LvN	DVRs or FFT
ρGMCTDH(II)	LvN	DVRs or FFT or GWPs
ML-ρGMCTDH(II)	LvN	DVRs or FFT or GWPs
Standard WP	TISE	DVRs or FFT
vMCG	TDSE	GWPs
clMCG	TDSE	GWPs
iMCG	TDSE	GWPs
DD-vMCG	TDSE	GWPs
TSH	TDSE	trajectories
DD-TSH	TDSE	trajectories

Integration schemes	Method
Chebyshev	Standard WP
Second Order Differencing	Standard WP
Split Operator	Standard WP
Constant Mean Field (CMF)	MCTDH (not ML-)
Adams–Bashforth–Moulton	all MCTDH and MCG
Burlisch–Stoer	all MCTDH and MCG
Runge–Kutta	all MCTDH and MCG

DVRs:
Harmonic Oscillator, Sine, Cosine, Exponential, Legendre, Laguerre

2D spherical harmonic basis sets:
Spherical Harmonic FBR, Extended Legendre, 2D Legendre

To Be Covered:
- MCTDH
- vMCG
- DD-vMCG

Dynamical phenomena are described by the
Time-Dependent Schrödinger Equation

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

A **wavepacket** evolves in time driven by the Hamiltonian

$$\Psi(\mathbf{q},t) = \sum_i c_i \psi_i e^{-\frac{i}{\hbar}E_i t} \tag{2}$$

where ψ_i are the eigenfunctions of the Hamiltonian

- D.J. Tannor "Introduction to Quantum Mechanics: A Time-Dependent
  Perspective" (2007) University Science Books
  http://www.weizmann.ac.il/chemphys/tannor/Book/
- G. C. Schatz and M.A. Ratner "Quantum mechanics in chemistry" (2002) Dover
- P.W. Atkins and R.S. Friedman "Molecular Quantum Mechanics" (2004) Oxford
- K.C. Kulander "Time-dependent methods for quantum dynamics" (1991) Elsevier

The Nuclear Schrödinger Equation

The Adiabatic (Or Born-Oppenheimer) TDSE is

$$\left[\hat{T}_n + V\right]\chi = i\hbar\frac{\partial\chi}{\partial t} \tag{3}$$

and the nuclear wavefunction moves over an *adiabatic* potential energy surface, V, which can be obtained from quantum chemistry calculations.

If more than one potential surface involved

$$\left[\hat{T}_n\mathbf{1} + \mathbf{W}\right]\chi = i\hbar\frac{\partial}{\partial t}\chi \tag{4}$$

where $\mathbf{W}$ is a matrix of *diabatic* potential surfaces and couplings and χ a vector of wavepackets.

Steps for quantum dynamics simulations

1. Get the Hamiltonian
    - Specify the system coordinates
    - Work out the Kinetic energy operator
    - Work out the potential energy operator

Steps for quantum dynamics simulations

1. Get the Hamiltonian
   - Specify the system coordinates
   - Work out the Kinetic energy operator
   - Work out the potential energy operator
2. Define a *primitive basis set* to represent the Hamiltonian and wavepacket

Steps for quantum dynamics simulations

1. Get the Hamiltonian
    - Specify the system coordinates
    - Work out the Kinetic energy operator
    - Work out the potential energy operator
2. Define a *primitive basis set* to represent the Hamiltonian and wavepacket
3. Define an initial wavepacket

Steps for quantum dynamics simulations

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

Steps for quantum dynamics simulations

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

The Standard Method

We need to solve

$$i\frac{\partial}{\partial t}\Psi(\mathbf{q}, t) = H\Psi(\mathbf{q}, t) \tag{5}$$

Nuclear wavefunction expanded in *primitive basis* set:

$$\Psi(q_1, \ldots q_f, t) = \sum_{j_1=1}^{N_1} \cdots \sum_{j_p=1}^{N_f} A_{j_1 \ldots j_f}(t)\, \chi_{j_1}^{(1)}(q_1) \cdots \chi_{j_f}^{(f)}(q_f) \tag{6}$$

Variational equations of motion for *A*.

$$i\,\dot{A}_{j_1, \ldots j_f} = \sum_{l_1, \ldots l_f} \langle \chi_{j_1}^{(1)} \cdots \chi_{j_f}^{(f)} | H | \chi_{l_1}^{(1)} \cdots \chi_{l_f}^{(f)} \rangle \, A_{l_1, \ldots l_f} \quad . \tag{7}$$

The Standard Method

We need to solve

$$i\frac{\partial}{\partial t}\Psi(\mathbf{q}, t) = H\Psi(\mathbf{q}, t) \tag{5}$$

Nuclear wavefunction expanded in *primitive basis* set:

$$\Psi(q_1, \ldots q_f, t) = \sum_{j_1=1}^{N_1} \cdots \sum_{j_p=1}^{N_f} A_{j_1 \ldots j_f}(t) \, \chi_{j_1}^{(1)}(q_1) \cdots \chi_{j_f}^{(f)}(q_f) \tag{6}$$

Variational equations of motion for *A*.

$$i\dot{A}_J = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L \tag{7}$$

or simply

$$i\dot{\mathbf{A}} = \mathbf{HA} \tag{8}$$

Exponential increase in computer resources $\sim N^f$

Finding Eigenstates

Can diagonalise the Hamiltonian matrix, but these are large!!

A way of finding the ground-state is to use *energy relaxation*. In this a wavepacket is propagated in imaginary time. As

$$\Psi(\mathbf{q}, t) = \sum_i c_i \psi_i e^{-\frac{i}{\hbar} E_i t} \tag{9}$$

if $it \to \tau$ then

$$\Psi(\mathbf{q}, \tau) = \sum_i c_i \psi_i e^{-\frac{1}{\hbar} E_i \tau} \tag{10}$$

Finding Eigenstates

Can diagonalise the Hamiltonian matrix, but these are large!!

A way of finding the ground-state is to use *energy relaxation*. In this a
wavepacket is propagated in imaginary time. As

$$\Psi(\mathbf{q}, t) = \sum_i c_i \psi_i e^{-\frac{i}{\hbar} E_i t} \tag{9}$$

if $it \to \tau$ then

$$\Psi(\mathbf{q}, \tau) = \sum_i c_i \psi_i e^{-\frac{1}{\hbar} E_i \tau} \tag{10}$$

and all $c_i \to 0$ except c_0.

Finding Eigenstates

Can diagonalise the Hamiltonian matrix, but these are large!!

A way of finding the ground-state is to use *energy relaxation*. In this a wavepacket is propagated in imaginary time. As

$$\Psi(\mathbf{q}, t) = \sum_i c_i \psi_i e^{-\frac{i}{\hbar} E_i t} \tag{9}$$

if $it \rightarrow \tau$ then

$$\Psi(\mathbf{q}, \tau) = \sum_i c_i \psi_i e^{-\frac{1}{\hbar} E_i \tau} \tag{10}$$

and all $c_i \rightarrow 0$ except c_0.

Can also use this to obtain excited states.

The Hamiltonian matrix elements

Need to evaluate matrix elements (integrals)

$$
\begin{aligned}
H_{JL} &= \sum_{l_1,\ldots l_f} \langle \chi_{j_1}^{(1)} \cdots \chi_{j_f}^{(f)} | H | \chi_{l_1}^{(1)} \cdots \chi_{l_f}^{(f)} \rangle \\
&= \sum_{l_1,\ldots l_f} \langle \chi_{j_1}^{(1)} \cdots \chi_{j_f}^{(f)} | T + V | \chi_{l_1}^{(1)} \cdots \chi_{l_f}^{(f)} \rangle
\end{aligned}
\tag{11}
$$

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

The Hamiltonian matrix elements

Need to evaluate matrix elements (integrals)

$$
\begin{aligned}
H_{JL} &= \sum_{l_1,\ldots l_f} \langle \chi_{j_1}^{(1)} \cdots \chi_{j_f}^{(f)} | H | \chi_{l_1}^{(1)} \cdots \chi_{l_f}^{(f)} \rangle \\
&= \sum_{l_1,\ldots l_f} \langle \chi_{j_1}^{(1)} \cdots \chi_{j_f}^{(f)} | T + V | \chi_{l_1}^{(1)} \cdots \chi_{l_f}^{(f)} \rangle \quad (11)
\end{aligned}
$$

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

I. Usually

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

$$
T_{JL} = \sum_{\kappa} \langle \chi_{j_\kappa}^{(\kappa)} | T_{\kappa} | \chi_{l_\kappa}^{(\kappa)} \rangle \delta_{J^\kappa L^\kappa} \quad (12)
$$

$N \times N$ 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

$$
\begin{aligned}
V_{JL} &= \langle \chi_{j_1}^{(1)} \cdots \chi_{j_f}^{(f)} | V | \chi_{l_1}^{(1)} \cdots \chi_{l_f}^{(f)} \rangle \\
&= V(q_{j_1} \ldots q_{j_f}) \delta_{JL}
\end{aligned}
\tag{13}
$$

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

$$
\begin{aligned}
V_{JL} &= \langle \chi_{j_1}^{(1)} \cdots \chi_{j_f}^{(f)} | V | \chi_{l_1}^{(1)} \cdots \chi_{l_f}^{(f)} \rangle \\
&= V(q_{j_1} \ldots q_{j_f}) \delta_{JL}
\end{aligned}
\tag{13}
$$

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

$$
\begin{aligned}
X_{ij} &= \langle \phi_i | \hat{x} | \phi_j \rangle \\
\mathbf{U}\mathbf{X}\mathbf{U}^T &= \mathbf{x}
\end{aligned}
\tag{14}
$$

where ϕ_i are an analytically known FBR. And so

$$
\chi_\alpha = \sum_i U_{\alpha i} \phi_i
\tag{15}
$$

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

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

The MCTDH Method: Larger systems

The Multiconfiguration Time-Dependent Hartree Method

$$\Psi(Q_1, \ldots, Q_f, t) = \sum_{j_1=1}^{n_1} \ldots \sum_{j_f=1}^{n_f} A_{j_1 \ldots j_f}(t) \prod_{\kappa=1}^{f} \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) \qquad (16)$$

The MCTDH Method: Larger systems

The Multiconfiguration Time-Dependent Hartree Method

$$\Psi(Q_1, \ldots, Q_f, t) = \sum_{j_1=1}^{n_1} \ldots \sum_{j_f=1}^{n_f} A_{j_1 \ldots j_f}(t) \prod_{\kappa=1}^{f} \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) \qquad (16)$$

Variational equations of motion for A and φ.

$$i\dot{A}_J = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L \qquad (17)$$

$$i\dot{\varphi}^{(\kappa)} = \left(1 - P^{(\kappa)}\right) \left(\rho^{(\kappa)}\right)^{-1} \langle \mathbf{H} \rangle^{(\kappa)} \varphi^{(\kappa)} \qquad (18)$$

where *single-particle functions* are expanded in primitive basis

$$\varphi_j^{(\kappa)}(q_\kappa) = \sum_{k=1}^{N_\kappa} a_{kj}^{(\kappa)} \chi_k^{(\kappa)}(q_\kappa) \qquad (19)$$

Reduced computer resources $\sim n^f$

$N \sim 50$. $n \sim 10$

f	N^f	standard (MB)	n^f	MCTDH (MB)
2	2,500	0.03	100	0.0015
3	125,000	1.9	1000	0.015
4	6,250,000	95.3	10000	0.15
5	312,500,000	4768.4	100000	1.5

$N \sim 50$. $n \sim 10$

f	N^f	standard (MB)	n^f	MCTDH (MB)
2	2,500	0.03	100	0.0015
3	125,000	1.9	1000	0.015
4	6,250,000	95.3	10000	0.15
5	312,500,000	4768.4	100000	1.5

Can also "combine modes" to reduce effective dimensionality and thus treat ~ 20 DOFs

MCTDH also starting point for further approximations

Reviews:

- Beck *et al* Phys. Rep. (00) 324:1
- Meyer and Worth TCA (03) 109:251
- Meyer, Gatti, andWorth "Multi-Dimensional Quantum Dynamics: MCTDH Theory and Applications (2009) Wiley-VCH

Combined Mode Particles

For a 3D system with 1D SPFs,

$$\Psi(q_1, q_2, q_3, t) = \sum_{j_1} \sum_{j_2} \sum_{j_3} A_{j_1 j_2 j_3}(t) \, \varphi_{j_1}^{(1)}(q_1, t) \varphi_{j_2}^{(2)}(q_2, t) \varphi_{j_3}^{(3)}(q_3, t) \tag{20}$$

and memory required is:

$$Mem = n_1 n_2 n_3 + n_1 N_1 + n_2 N_2 + n_3 N_3$$

A "particle" may contain many coordinates, $Q_i = (q_a, q_b, \ldots, q_w)$

$$\begin{aligned}
\Psi(q_1, q_2, q_3, t) &= \sum_{j_1} \sum_{j_2} A_{j_1 j_2}(t) \, \varphi_{j_1}^{(1)}(q_1, t) \, \varphi_{j_2}^{(2)}(q_2, q_3, t) \quad &(21) \\
&= \sum_{j_1} \sum_{j_2} A_{j_1 j_2}(t) \, \varphi_{j_1}^{(1)}(Q_1, t) \, \varphi_{j_2}^{(2)}(Q_2, t) \quad &(22)
\end{aligned}$$

with

$$Mem = n_1 n_2 + n_1 N_1 + n_2 N_2 N_3$$

Saving in memory

All 1D functions, assuming same no. SPFs and primitive functions per DOF,

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

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 $\tilde{n} = 1$

$$Mem \sim N^f$$

For greatest saving, combine strongly correlated 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

Saving in memory

All 1D functions, assuming same no. SPFs and primitive functions per DOF,

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

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 $\tilde{n} = 1$

$$Mem \sim N^f$$

For greatest saving, combine strongly correlated modes.

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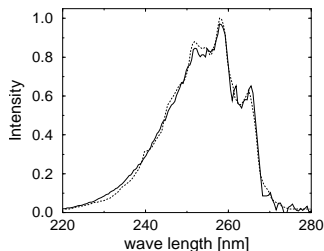
- full 24D QD
- 650 MB (205 MB good result)
- ca 2×10^{22} MB for "standard"

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

Multi-Layer MCTDH (ML-MCTDH)

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

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

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

Wang and Thoss JCP (2003) **119**; 1289
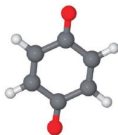
Leads to a recursive sets of variational equations of motion:

$$i\dot{A}_J = \sum_L \langle\Phi_J|H|\Phi_L\rangle A_L \tag{23}$$

$$i\dot{\varphi}^{(\kappa)} = \left(1 - P^{(\kappa)}\right)\left(\rho^{(\kappa)}\right)^{-1}\langle\mathbf{H}\rangle^{(\kappa)}\varphi^{(\kappa)} \tag{24}$$

$$i\dot{\nu}^{(\nu)} = \left(1 - P^{(\nu)}\right)\left(\rho^{(\nu)}\right)^{-1}\langle\mathbf{H}\rangle^{(\nu)}\nu^{(\nu)} \tag{25}$$
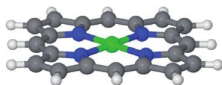
$$\dots = \dots \tag{26}$$

Leads to a recursive sets of variational equations of motion:

$$i\dot{A}_J = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L \tag{23}$$

$$i\dot{\varphi}^{(\kappa)} = \left(1 - P^{(\kappa)}\right) \left(\rho^{(\kappa)}\right)^{-1} \langle \mathbf{H} \rangle^{(\kappa)} \varphi^{(\kappa)} \tag{24}$$

$$i\dot{\nu}^{(\nu)} = \left(1 - P^{(\nu)}\right) \left(\rho^{(\nu)}\right)^{-1} \langle \mathbf{H} \rangle^{(\nu)} \nu^{(\nu)} \tag{25}$$

$$\ldots = \ldots \tag{26}$$

PROBLEM: Multi-dimensional PES (+couplings) required!

135 Mode Quantum Dynamics
Photo-induced ET. Spin-Boson Model.

Borelli *et al* Mol. Phys. (2012) 110: 751
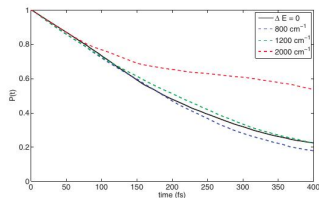
The Quantics Program Structure
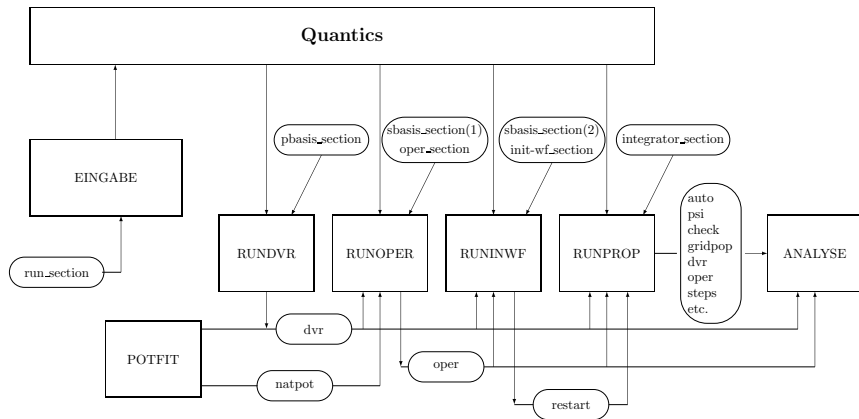
Two input files.

- .inp (inputs) and .op (operator)

Steps for quantum dynamics simulations

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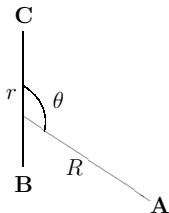
Step I: Coordinates. The Kinetic Energy Operator

In Cartesian coordinates,

$$T = \sum_{i=\hbar^2}^{N} -\frac{1}{2m_i} \sum_{\alpha=1}^{3} \frac{\partial^2}{\partial x_{i\alpha}^2} \tag{27}$$

Step I: Coordinates. The Kinetic Energy Operator

In Cartesian coordinates,

$$T = \sum_{i=\hbar^2}^{N} -\frac{1}{2m_i} \sum_{\alpha=1}^{3} \frac{\partial^2}{\partial x_{i\alpha}^2} \tag{27}$$

This includes COM and ROT - continua. To remove these contributions use, e.g. Jacobi coordinates

$$\begin{aligned}
T &= -\frac{1}{2\mu_R R^2} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r r^2} \frac{\partial^2}{\partial r^2} \\
&\quad + \left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_r r^2} \right) j^2 \\
&\quad - \frac{1}{2\mu_R R^2} (J(J+1) - 2K^2) \\
&\quad - \frac{1}{2\mu_R R^2} \sqrt{(J(J+1) - K(K \pm 1))} j_\pm
\end{aligned} \tag{28}$$

Sukiasyan and Meyer
JCP (02) : 116

Normal modes

Or, rectilinear coordinates can be chosen so that

$$V = \sum_{i=1}^{3N-6} \frac{\omega_i}{2} Q_i^2 + O(3) \tag{29}$$

COM and ROT removed and

$$T = \sum_{i=1}^{3N-6} -\frac{\omega_i}{2} \frac{\partial^2}{\partial Q_i^2} \tag{30}$$

Very simple, but PES only suitable for small displacements.

Wilson, Cross and Decius "Molecular Vibrations" (1980) Dover

Or, ...

Normal modes

Or, rectilinear coordinates can be chosen so that

$$V = \sum_{i=1}^{3N-6} \frac{\omega_i}{2} Q_i^2 + O(3) \tag{29}$$

COM and ROT removed and

$$T = \sum_{i=1}^{3N-6} -\frac{\omega_i}{2} \frac{\partial^2}{\partial Q_i^2} \tag{30}$$
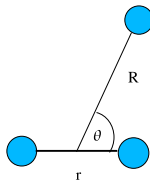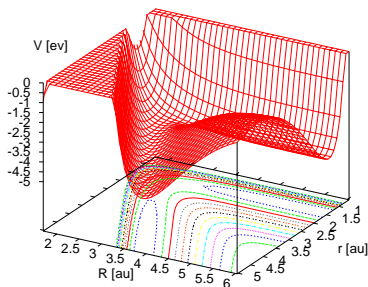
Very simple, but PES only suitable for small displacements.

Wilson, Cross and Decius "Molecular Vibrations" (1980) Dover

Or, ...

Choose the coordinates that are as simple as possible but describe the dynamics correctly

Potential Function

This is required as an analytic function in the coordinates of the KEO, e.g. $V(r, R, \theta)$. In general, simple KEO coordinates are not optimal for PES representation and vice versa.

Vibronic Coupling Model

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

$$\mathbf{H}(\mathbf{Q}) = \mathbf{T}(\mathbf{Q}) + \mathbf{W}(\mathbf{Q}) \tag{31}$$

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

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

$$\hat{T}_\alpha + V_\alpha^0 = \frac{\omega_i}{2}\left(\frac{\partial^2}{\partial Q^2} + Q^2\right) \tag{32}$$

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

Step II: Choose a Primitive Basis

Depends on coordinate type and potential.

DVR	FBR	Coordinate type
HO	$H_j \exp\left(-\frac{1}{2}m\omega(x - x_{eq})^2\right)$	vibrational
Legendre	$P_j^m(\cos\theta)$	angle
Sine	$\sin\left(j\pi(x - x_0)/L\right)$	simple grid
Exp	$\exp\left(2i\pi j(x - x_0)/L\right)$	periodic grid
FFT(x)	FFT(p)	periodic grid
KLeg	$f(j, K)P_j^K(\cos\theta)$	$\sim$Spherical harmonic
etc....		

Each basis set has different input needed. See documentation.

Step III: Initial Wavepacket

The time-dependent Schrödinger Equation is an initial value problem.

Start in a single eigenstate then initiate process.

- Multiply by (transition) dipole operator to model absorption of a photon

$$\Psi(t=0) = \hat{\mu}\psi_i$$

- For a reaction $AB + C$

$$\Psi(t=0) = \psi_{i,AB}\chi_C(R)$$

where

$$\chi_C(R) = Ne^{-\alpha_0(R-R_0)^2}e^{\frac{i}{\hbar}p(R-R_0)}$$

localises incoming atom with an incoming momentum p

- Read in the wavefunction from a previous calculation. E.g. after energy relaxationi, and operate on it, or use a light pulse.
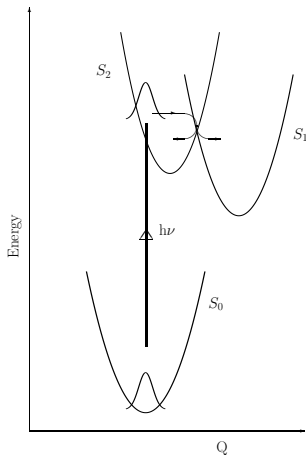
Photo-excitation

For Photo-excited problems use the transition dipole from S_0:

$$\Psi(t=0) = |s\rangle \mu_{s0} \langle 0 | \Psi_0$$

which if $\mu_{s0} = \text{const}$ results in the Condon Approximation. i.e.
Vertical Excitation.
Best in diabatic basis.

Step IV: Integrating the TDSE

For exact dynamics, full solution is

$$\Psi(t) = e^{-\frac{i}{\hbar}\hat{H}t}\Psi(0) \tag{33}$$

Split-operator method.

$$e^{-\frac{i}{\hbar}\hat{H}t} \neq e^{-\frac{i}{\hbar}Tt}e^{-\frac{i}{\hbar}Vt} \tag{34}$$

so divide propagation into short steps and approximate

$$\Psi(t + \delta t) = e^{-\frac{i}{2\hbar}V\delta t}e^{-\frac{i}{\hbar}T\delta t}e^{-\frac{i}{2\hbar}\hat{V}\delta t}\Psi(t) \tag{35}$$

Chebyshev Propagation Represent propagator by polynomial expansion:

$$e^{-\frac{i}{\hbar}\hat{H}t}\Psi = \sum_n a_n P_n(H)\Psi \tag{36}$$

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

MCTDH Integration Scheme

MCTDH cannot use Chebyshev etc. due to time-dependence of SPFs, I..e. the equations of motion for A_J and $\varphi_j^{(\kappa)}$ are coupled.

Standard integration schemes, e.g. ABM predictor-corrector or Runge-Kutte, work, but require short time steps. Referred to as *variable mean-field* integrators (VMF).

The *Constant mean-field* (CMF) scheme provides a short time separation of the two sets of parameters and improves efficiency.

Idea is that as mean-fields / density matrices change slower than SPFs, these can be kept "fixed" over a time-step

$\boxed{1}$ $\mathbf{A}(0)$ $\longmapsto\!\!\xrightarrow{\quad\mathcal{K}(0)\quad}\!\!\longmapsto$ $\mathbf{A}(\tau/2)$ **The CMF**
Scheme

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

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

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

$\boxed{5}$ $\mathbf{A}(0)$ $\longmapsto\!\!\xleftarrow{\quad\mathcal{K}(\tau)\quad}\!\!\longmapsto$ $\mathbf{A}(\tau/2)$

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

$\longmapsto\!\!\!\longrightarrow t$

$t = 0$ $t = \tau/2$ $t = \tau$
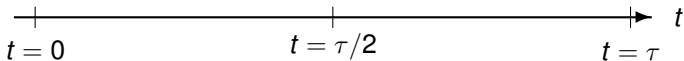
Quantics Input File

Text based input with (mostly) free format keywords. Input divided into sections that reflect the choices to be made:

RUN-SECTION:	type of calculation to be made
PRIMITIVE-BASIS-SECTION:	the coordinates, no. grid points etc.
SPF-BASIS-SECTION:	the no. of MCTDH basis functions
OPERATOR-SECTION:	file containing the operator
INIT_WF-BASIS-SECTION:	the initial wavefuncion
INTEGRATOR-SECTION:	details of the integration scheme
⋮	⋮

```
RUN-SECTION
name = hh2
propagation   tfinal = 120.d0   tout = 1.d0   tpsi = 1.d0
psi gridpop steps
title = Tutorial, H+H2 reactive scattering.
end-run-section

OPERATOR-SECTION
opname = h3j0
alter-labels
CAP_rd = CAP [ 6.04  0.002  3 ]   # starting point, strength, order
end-alter-labels
end-operator-section

SPF-BASIS-SECTION
    rd    = 14
    rv    = 10
    theta = 10
end-spf-basis-section
```

$H + H_2$ in Jacobi Coordinates: MCTDH

```
PRIMITIVE-BASIS-SECTION
#Label   DVR   N      Parameter
    rd    sin   68   1.00d0   9.040d0   # xi, xf
    rv    sin   48   0.60d0   6.240d0   # xi, xf
    theta leg   31   0        even      # l_z, sym (all/even/odd)
end-primitive-basis-section

INTEGRATOR-SECTION
CMF/var =   0.1 , 1.d-5
BS/spf  =     7 , 1.d-6
SIL/A   =    30 , 1.d-5
end-integrator-section

INIT_WF-SECTION
build
    rd    gauss   4.50d0   -8.00d0   0.25d0   # r0,p0, sigma_r
    rv    eigenf  H2       pop=1              # pop=1 -> ground state
    theta leg     0        0         sym      # l_z, l, sym/no-sym
end-build
end-init_wf-section
end-input
```

```
RUN-SECTION
name = hh2      exact
propagation    tfinal = 120.d0    tout = 1.d0    tpsi = 1.d0
psi gridpop steps
title = Tutorial, H+H2 reactive scattering.
end-run-section

OPERATOR-SECTION
opname = h3j0
alter-labels
CAP_rd = CAP [ 6.04  0.002  3 ]    # starting point, strength, order
end-alter-labels
end-operator-section

#SPF-BASIS-SECTION
#    rd   = 14
#    rv   = 10
#    theta = 10
#end-spf-basis-section

PRIMITIVE-BASIS-SECTION
#Label    DVR    N      Parameter
   rd     sin   68   1.00d0    9.040d0    # xi, xf
   rv     sin   48   0.60d0    6.240d0    # xi, xf
   theta  leg   31     0       even       # l_z, sym (all/even/odd)
end-primitive-basis-section

INTEGRATOR-SECTION
#CMF/var =   0.1 , 1.d-5
#BS/spf  =     7 , 1.d-6
SIL/all  =    30 , 1.d-5
end-integrator-section

INIT_WF-SECTION
build
   rd     gauss   4.50d0   -8.00d0   0.25d0   # r0,p0, sigma_r
   rv     eigenf  H2       pop=1             # pop=1 -> ground state
   theta  leg     0        0        sym      # l_z, l, sym/no-sym
end-build
end-init_wf-section
end-input
```

$H + H_2$ in Jacobi Coordinates: Exact

```
RUN-SECTION
name = hh2      diagonalise = 500
#propagation   tfinal = 120.d0   tout = 1.d0   tpsi = 1.d0
#psi gridpop steps
title = Tutorial, H+H2 reactive scattering.
end-run-section

OPERATOR-SECTION
opname = h3j0
#alter-labels
#CAP_rd = CAP [ 6.04  0.002  3 ]   # starting point, strength, order
#end-alter-labels
end-operator-section

#SPF-BASIS-SECTION
#    rd   = 14
#    rv   = 10
#    theta = 10
#end-spf-basis-section

PRIMITIVE-BASIS-SECTION
#Label    DVR    N      Parameter
    rd     sin   68   1.00d0    9.040d0    # xi, xf
    rv     sin   48   0.60d0    6.240d0    # xi, xf
    theta  leg   31    0        even       # l_z, sym (all/even/odd)
end-primitive-basis-section

#INTEGRATOR-SECTION
#CMF/var =   0.1 , 1.d-5
#BS/spf  =     7 , 1.d-6
#SIL/A   =    30 , 1.d-5
#end-integrator-section

INIT_WF-SECTION
build
    rd     gauss   4.50d0   -8.00d0   0.25d0   # r0,p0, sigma_r
    rv     eigenf  H2       pop=1            # pop=1 -> ground state
    theta  leg     0         0        sym     # l_z, l, sym/no-sym
end-build
end-init_wf-section
end-input
```
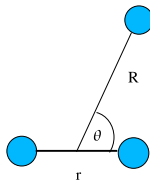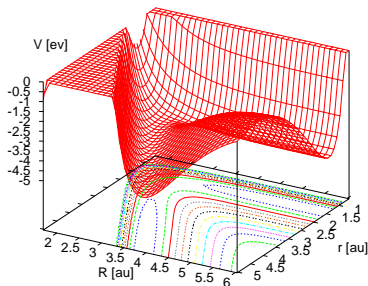
$H + H_2$ in Jacobi Coordinates: Diagonalisation

Operator

For $J = 0$, KEO in Jacobis:

$$
\begin{aligned}
T &= -\frac{1}{2\mu_R R^2}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r r^2}\frac{\partial^2}{\partial r^2} \\
&\quad + \left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_r r^2}\right)j^2
\end{aligned}
$$

$$(37)$$

And potential $V(R, r, \theta)$:

Potential in Product Form

Need to re-evaluate integrals every time-step as SPFs are time-dependent. For efficiency, potential must be in a *product* form

$$V(q_1, q_2, \ldots) = \sum_n c_n h_n^{(1)}(q_1) h_n^{(2)}(q_2) \ldots \tag{38}$$

as then

$$\langle \Phi_I | H | \Phi_J \rangle = \sum_n c_n \langle \varphi_{i_1}^{(1)} | h_n^{(1)} | \varphi_{j_1}^{(1)} \rangle \langle \varphi_{i_2}^{(2)} | h_n^{(2)} | \varphi_{j_2}^{(2)} \rangle \ldots \tag{39}$$

The program POTFIT can provide this form optimally using a tensor deconstruction approach

Jäckle and Meyer JCP (96) **104**: 7974

```
OP_DEFINE-SECTION
title
H+H2 Reactive Scattering in Jacobian Coordinates. J=0.
Minimum of H_2 curve: 4.74746 eV. Zero point energy of vib.: 0.270 eV
end-title
end-op_define-section

PARAMETER-SECTION
mass_rd = 0.6666666666667, H-mass       # Reduced mass of H--H2 system
mass_rv = 0.50, H-mass                   # Reduced mass of H2 molecule
jtot    = 0                              # Total angular momentum
jbf     = 0                              # Projection on BF axis (K, or Omega).
end-parameter-section

HAMILTONIAN-SECTION
---------------------------------------------
  modes     | rd   | rv   | theta
---------------------------------------------
0.5/mass_rd | q^-2 | 1    | j^2
0.5/mass_rv | 1    | q^-2 | j^2
1.0         | KE   | 1    | 1
1.0         | 1    | KE   | 1
1.0         | V
---------------------------------------------
end-hamiltonian-section

LABELS-SECTION
V = lsth {jacobian}
end-labels-section

# The following one-dimensional hamiltonian is used to determine the
# eigenstates of H_2. These are then used as initial rv-spf's.

HAMILTONIAN-SECTION_H2
---------------------------------------------
  modes     | rd   | rv    | theta
---------------------------------------------
1.0         | 1    | KE    | 1
1.0         | 1    | v:H2  | 1
---------------------------------------------
end-hamiltonian-section

end-operator
```

Operator File

```
HAMILTONIAN-SECTION
mode | rd | rv | theta
```

Defines the operators for the coordinates rd, rv etc. The coordinate labels are free to be chosen. The Hamiltonian has the form

$$H = \sum_s H_s = \sum_s c_s h_s^{(1)}(x1) h_s^{(2)}(x2) \ldots \qquad (40)$$

operators $h_s^{(\kappa)}$ are defined in table. E.g.

```
0.5/mass_rv   |  1    | q^-2 |   j^2
```

is

$$H_2 = \frac{1}{m_{rv}} \frac{1}{(r_v)^2} \hat{j}^2 \qquad (41)$$

$\hat{j}^2$ is the angular momentum squared operator for $theta$. Note that the potential in this example is a special case, V. This is defined separately in the LABELS-SECTION.

Any parameters can be given in the PARAMETERS-SECTION

Checking for Accuracy

We have a Hamiltionian and can propagate a wavepacket. How can we check whether the propagation is correct? How does it translate into an observable?

Checking for Accuracy

We have a Hamiltionian and can propagate a wavepacket. How can we check whether the propagation is correct? How does it translate into an observable?

- Convergence

Checking for Accuracy

We have a Hamiltionian and can propagate a wavepacket. How can we check whether the propagation is correct? How does it translate into an observable?

- Convergence
    - Primitive basis
    - Single-particle function basis

Checking for Accuracy

We have a Hamiltionian and can propagate a wavepacket. How can we check whether the propagation is correct? How does it translate into an observable?

- Convergence
  - Primitive basis
  - Single-particle function basis
- Expectation values

Checking for Accuracy

We have a Hamiltionian and can propagate a wavepacket. How can we check whether the propagation is correct? How does it translate into an observable?

- Convergence
  - Primitive basis
  - Single-particle function basis
- Expectation values
- Spectra
  - Golden Rule
  - Time-resolved

Checking for Accuracy

We have a Hamiltionian and can propagate a wavepacket. How can we check whether the propagation is correct? How does it translate into an observable?

- Convergence
  - Primitive basis
  - Single-particle function basis
- Expectation values
- Spectra
  - Golden Rule
  - Time-resolved
- Branching ratio

Convergence Checks

The primitive basis set forms a grid. Need to check

1. Enough grid points (close enough together)?

A simple grid is given by an *exponential DVR*. Basis set:

$$\phi_j(x) = L^{-1/2} \exp\left(2i\pi j(x - x_0)/L\right), \qquad -n \le j \le n. \qquad (42)$$

Defined on interval $x = [0, L]$. N basis functions provide N equidistant DVR functions from eigenvalues of matrix $\langle\phi_i|x|\phi_j\rangle$.

Maximum momentum supported by basis set $\pm\frac{nh}{L}$

Gap between points $\frac{L}{2n}$

Look in `log file` for DVR information:

```
****** Primitive Basis *********

 mode     kappa    DVR    N      xi      xf       dx        p-max

 rd        1      FFT    21    3.800   5.600   0.090000    33.244
 rv        2      HO     24    1.620   2.652   0.044849    70.171
 theta     3      Leg    60    3.102   0.040   0.051900    m= 0, sym= 0
```

And then in `output`: At start

```
 Mode expectation values and variances :
rd         : <q>=   4.3143  <dq>=   0.0794  <p>=   0.0000  <dp>=   6.3079
rv         : <q>=   2.1548  <dq>=   0.0670  <n>=   0.0348  <dn>=   0.2247
theta      : <q>=   2.2285  <dq>=   0.0768  <j>=   4.6280  <dj>=   3.9975
```

And then in `output`: At start

```
 Mode expectation values and variances :
rd         : <q>=   4.3143  <dq>=   0.0794  <p>=    0.0000  <dp>=   6.3079
rv         : <q>=   2.1548  <dq>=   0.0670  <n>=    0.0348  <dn>=   0.2247
theta      : <q>=   2.2285  <dq>=   0.0768  <j>=    4.6280  <dj>=   3.9975
```

And at 50 fs:

```
Mode expectation values and variances :
rd         : <q>=   4.4579  <dq>=   0.1352  <p>=   -7.4775  <dp>=  13.4814
rv         : <q>=   2.1212  <dq>=   0.0737  <n>=    0.3199  <dn>=   0.7575
theta      : <q>=   1.5054  <dq>=   0.1856  <j>=   29.9413  <dj>=   8.7205
```

Where

$$dp = \sqrt{<p^2> - <p>^2} \qquad (43)$$

is the 1-dimensional density standard deviation. Remember that a normal distribution covers 3σ.

2. Are grids long enough?

Increase the no. of grid points for rd to 51.

2. Are grids long enough?

Increase the no. of grid points for rd to 51.

Need to prevent reflection off Edge of coordinate grid.
Add a **C**omplex **A**bsorbing **P**otential

$$H = H_{\mathrm{mol}} + iW(R - R_0)\Theta(R - R_0) \tag{44}$$

where

$$\Theta(R - R_0) \left\{ \begin{array}{l} 0 \text{ if } R < R_0 \\ 1 \text{ if } R > R_0 \end{array} \right. \tag{45}$$

is the Heavyside function and W is a monomial function

$$W = \gamma(R - R_0)^n \tag{46}$$

Addition of CAP makes Hamiltonian non-hermitian past R_0.

2. Are grids long enough?

Increase the no. of grid points for rd to 51.

Need to prevent reflection off Edge of coordinate grid.
Add a **C**omplex **A**bsorbing **P**otential

$$H = H_{\text{mol}} + iW(R - R_0)\Theta(R - R_0) \tag{44}$$

where

$$\Theta(R - R_0) \left\{ \begin{array}{l} 0 \text{ if } R < R_0 \\ 1 \text{ if } R > R_0 \end{array} \right. \tag{45}$$

is the Heavyside function and W is a monomial function

$$W = \gamma(R - R_0)^n \tag{46}$$

Addition of CAP makes Hamiltonian non-hermitian past R_0.

```
OPERATOR-SECTION
opname = nocl1
alter-labels
CAP_rd = CAP [ 5.0 0.3 3 ]    # starting point, strength, order
end-alter-labels
end-operator-section
```

Converging SPFs

$$\Psi(q_1, \ldots, q_f, t) = \sum_{j_1=1}^{n_1} \ldots \sum_{j_f=1}^{n_f} A_{j_1 \ldots j_f}(t) \varphi_{j_1}^{(1)}(q_1, t) \varphi_{j_2}^{(2)}(q_2, t) \ldots \varphi_{j_f}^{(f)}(q_f, t) \tag{47}$$

Can form *reduced density matrices*

$$\rho_{jl}^{(\kappa)} = \sum_{j_1} \ldots \sum_{j_{\kappa-1}} \sum_{j_{\kappa+1}} \ldots \sum_{j_f} A_{j_1 \ldots j_{\kappa-1} j j_{\kappa+1} \ldots j_f}^* A_{j_1 \ldots j_{\kappa-1} l j_{\kappa+1} \ldots j_f} \tag{48}$$

And diagonalise this to get *natural orbitals*

$$\tilde{\varphi} = \mathbf{D}\varphi \tag{49}$$

These span same space as original SPFs and can be associated with a population ρ_j, the eigenvalues of the reduced density matrix.

Want the highest natural orbitals to have small populations, with
same order of magnitude for all modes.

Want the highest natural orbitals to have small populations, with same order of magnitude for all modes.

At start of 4-mode 2-state calculation on pyrazine

```
Time  =        0.00 fs,      CPU =       0.02 s,    Norm   = 1.00000000
E-tot =    0.687485 eV,    E-corr =   0.000000eV,    Delta-E =   -0.0000 meV

 Natural weights *1000 :
v10a       :1000.0000 000.0000 000.0000 000.0000 000.0000 000.0000
v6a        :1000.0000 000.0000 000.0000 000.0000 000.0000 000.0000 000.0000
v1         :1000.0000 000.0000 000.0000 000.0000
v9a        :1000.0000 000.0000 000.0000 000.0000
el         :1000.0000 000.0000
```

Want the highest natural orbitals to have small populations, with same order of magnitude for all modes.

At start of 4-mode 2-state calculation on pyrazine

```
 Time  =       0.00 fs,      CPU =       0.02 s,     Norm   = 1.00000000
 E-tot =  0.687485 eV,    E-corr =  0.000000eV,    Delta-E =   -0.0000 meV

 Natural weights *1000 :
v10a      :1000.0000 000.0000 000.0000 000.0000 000.0000 000.0000
v6a       :1000.0000 000.0000 000.0000 000.0000 000.0000 000.0000 000.0000
v1        :1000.0000 000.0000 000.0000 000.0000
v9a       :1000.0000 000.0000 000.0000 000.0000
el        :1000.0000 000.0000
```

At 120 fs
```
 Time  =     120.00 fs,      CPU =       6.10 s,     Norm   = 1.00000000
 E-tot =  0.687483 eV,    E-corr = -0.720516eV,    Delta-E =   -0.0020 meV

 Natural weights *1000 :
 v10a      : 423.0730 220.7056 158.8816 101.9055  72.8217  22.6125
 v6a       : 421.7683 223.8043 125.2888  90.3534  64.6473  45.2166  28.9214
 v1        : 536.9188 241.5997 122.9245  65.1834  33.3736
 v9a       : 733.5285 202.0629  51.8535  12.5551
 el        : 802.6602 197.3398
```

Want the highest natural orbitals to have small populations, with same order of magnitude for all modes.

At start of 4-mode 2-state calculation on pyrazine

```
 Time  =         0.00 fs,     CPU =        0.02 s,    Norm   = 1.00000000
 E-tot =   0.687485 eV,    E-corr =   0.000000eV,    Delta-E =    -0.0000 meV

 Natural weights *1000 :
v10a      :1000.0000 000.0000 000.0000 000.0000 000.0000 000.0000
v6a       :1000.0000 000.0000 000.0000 000.0000 000.0000 000.0000 000.0000
v1        :1000.0000 000.0000 000.0000 000.0000
v9a       :1000.0000 000.0000 000.0000 000.0000
el        :1000.0000 000.0000
```

At 120 fs
```
 Time  =       120.00 fs,      CPU =        6.10 s,    Norm   = 1.00000000
 E-tot =   0.687483 eV,    E-corr =  -0.720516eV,    Delta-E =    -0.0020 meV

 Natural weights *1000 :
 v10a     : 423.0730 220.7056 158.8816 101.9055  72.8217  22.6125
 v6a      : 421.7683 223.8043 125.2888  90.3534  64.6473  45.2166  28.9214
 v1       : 536.9188 241.5997 122.9245  65.1834  33.3736
 v9a      : 733.5285 202.0629  51.8535  12.5551
 el       : 802.6602 197.3398
```

Need more SPFs.

Of course convergence only makes sense in relation to a property.
E.g. an autocorrelation function:

Of course convergence only makes sense in relation to a property.
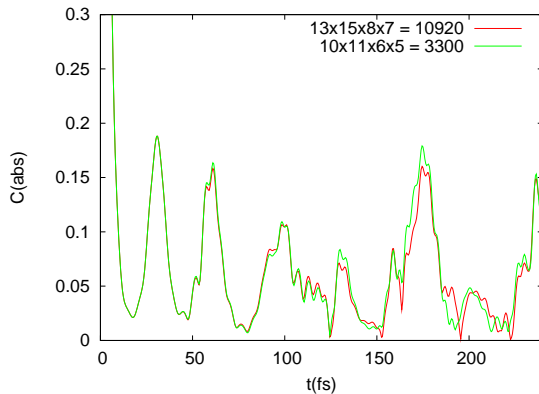E.g. an autocorrelation function:
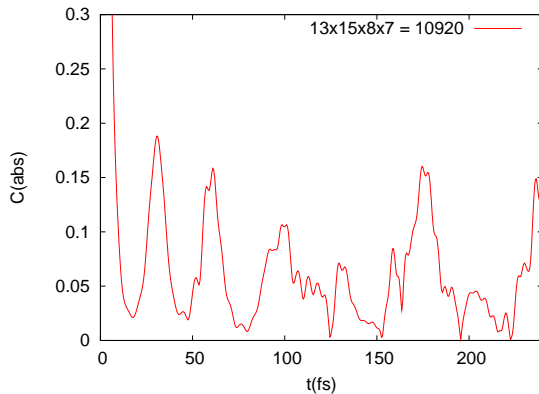
CPU   Nat Pop

22s   0.0001

Of course convergence only makes sense in relation to a property.
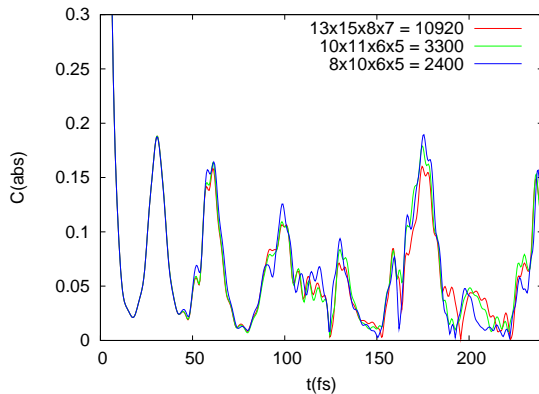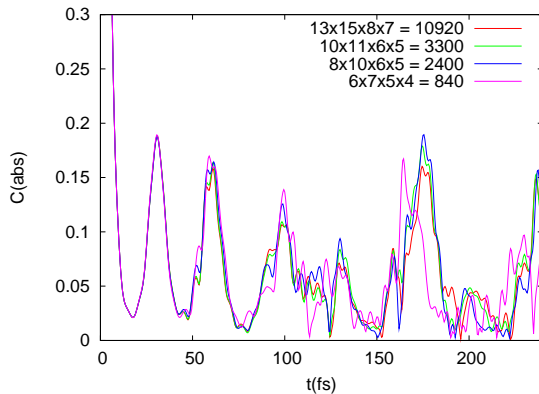E.g. an autocorrelation function:

CPU	Nat Pop
22s	0.0001
7s	0.005

Of course convergence only makes sense in relation to a property.
E.g. an autocorrelation function:

CPU	Nat Pop
22s	0.0001
7s	0.005
6s	0.010

Of course convergence only makes sense in relation to a property.
E.g. an autocorrelation function:

CPU	Nat Pop
22s	0.0001
7s	0.005
6s	0.010
2.8s	0.025

Or the spectrum:

Or the spectrum:
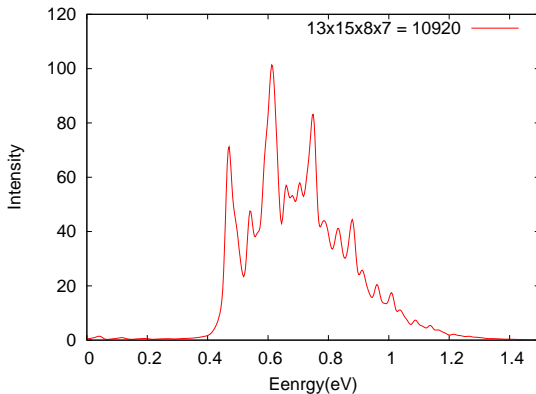
CPU   Nat Pop

22s   0.0001

Or the spectrum:
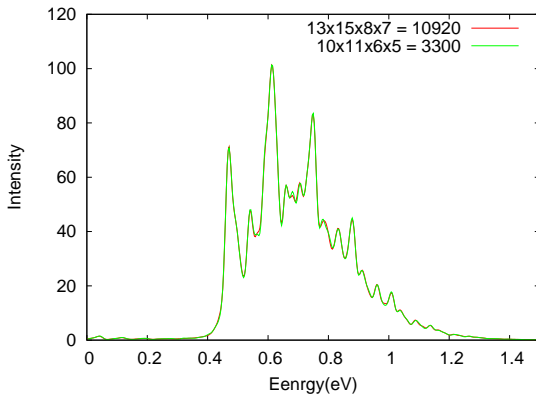
CPU	Nat Pop
22s	0.0001
7s	0.005

Or the spectrum:
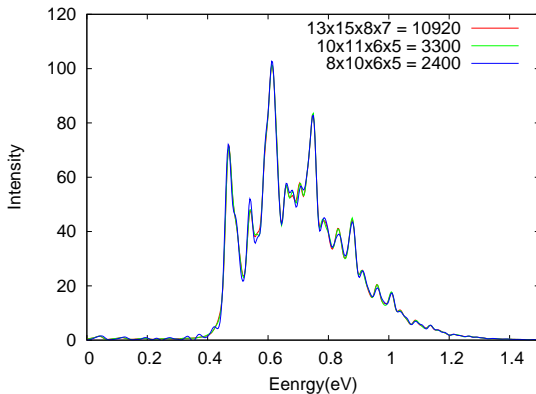
CPU	Nat Pop
22s	0.0001
7s	0.005
6s	0.010

Or the spectrum:
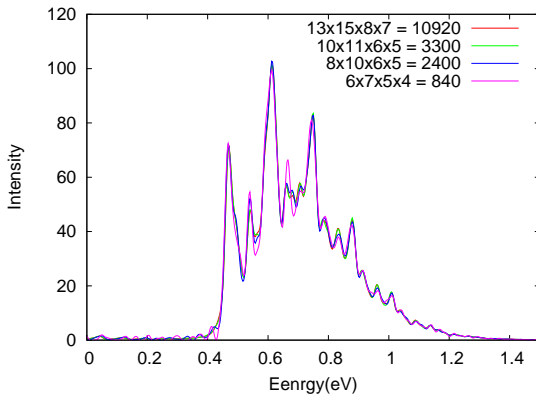
CPU	Nat Pop
22s	0.0001
7s	0.005
6s	0.010
2.8s	0.025

Expectation Values

Typical "observables" of interest to the system dynamics are coordinates, momentum and their spread

$$< q_\kappa >, < q_\kappa^2 > \text{ and } < p_\kappa >, < p_\kappa^2 > .$$

Expectation Values

Typical "observables" of interest to the system dynamics are coordinates, momentum and their spread

$$< q_\kappa >, < q_\kappa^2 > \text{ and } < p_\kappa >, < p_\kappa^2 > .$$

Energy flow into modes can be obtained using a "zero-order" Hamiltonian, e.g. if

$$H = \sum_{i=1}^{2} \frac{\omega_i}{2} \left(\frac{\partial^2}{\partial q_i^2} + q_i^2 \right) + q_1 q_2 \tag{50}$$

then evaluate

$$< E_i >= \langle \frac{\omega_i}{2} \frac{\partial^2}{\partial q_i^2} + q_i^2 \rangle \tag{51}$$

Branching ratios and reactivity

Want to know how much goes into different channels. Divide wavefunction

$$\Psi(t) = \Psi_0(t) + \sum_\gamma \Psi_\gamma(t) \tag{52}$$

where

$$\Psi_\gamma(t) = \Theta_\gamma(R - R_c)\Psi(t) \tag{53}$$

Branching ratios and reactivity

Want to know how much goes into different channels. Divide wavefunction

$$\Psi(t) = \Psi_0(t) + \sum_\gamma \Psi_\gamma(t) \tag{52}$$

where

$$\Psi_\gamma(t) = \Theta_\gamma(R - R_c)\Psi(t) \tag{53}$$

Amount in a particular channel γ is $\langle \Psi_\gamma(t)|\Psi_\gamma(t)\rangle$

Change is the *flux density*

$$\frac{\partial}{\partial t}\langle \Psi_\gamma(t)|\Psi_\gamma(t)\rangle = i\langle \Psi(t)|[H, \Theta_\gamma]|\Psi(t)\rangle = \langle \Psi(t)|\hat{F}|\Psi(t)\rangle \tag{54}$$

Branching ratios and reactivity

Want to know how much goes into different channels. Divide wavefunction

$$\Psi(t) = \Psi_0(t) + \sum_\gamma \Psi_\gamma(t) \tag{52}$$

where

$$\Psi_\gamma(t) = \Theta_\gamma(R - R_c)\Psi(t) \tag{53}$$

Amount in a particular channel γ is $\langle \Psi_\gamma(t)|\Psi_\gamma(t)\rangle$

Change is the *flux density*

$$\frac{\partial}{\partial t}\langle \Psi_\gamma(t)|\Psi_\gamma(t)\rangle = i\langle \Psi(t)|[H, \Theta_\gamma]|\Psi(t)\rangle = \langle \Psi(t)|\hat{F}|\Psi(t)\rangle \tag{54}$$

And total amount of system that has flowed into γ is

$$\sigma_\gamma = \int_{-\infty}^\infty dt\langle \hat{F}(t)\rangle \tag{55}$$

Flux analysis

When a dissociative channel is present, must add a CAP

$$H = H_{sys} - iW_\gamma \tag{56}$$

where $W_\gamma = ax^b\Theta_\gamma$. Can now write

$$\sigma_\gamma = \int_{-\infty}^{\infty} dt \langle \Psi(t)|W|\Psi(t)\rangle \tag{57}$$

Flux analysis

When a dissociative channel is present, must add a CAP

$$H = H_{sys} - iW_{\gamma} \tag{56}$$

where $W_{\gamma} = ax^b\Theta_{\gamma}$. Can now write

$$\sigma_{\gamma} = \int_{-\infty}^{\infty} dt \langle \Psi(t)|W|\Psi(t)\rangle \tag{57}$$

Can use same formalism to get scattering matrix elements

$$\sum_{\nu'} |S_{\gamma\nu',\alpha\nu}(E)|^2 = \frac{2}{\pi|\Delta(E)|^2}\text{Re} \int_0^T d\tau\, g(\tau)e^{iE\tau} \tag{58}$$

with

$$g_w(\tau) = \int_0^{T-\tau} dt\, \langle \Psi(t)|W_{\gamma}|\Psi(t+\tau)\rangle \tag{59}$$