Using time-dependent Gaussian basis sets in quantum dynamics simulations.

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- The G-MCTDH algorithm
- Stability of GWP propagation
- Phase space coverage and convergence
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Collaboration: Irene Burghardt, Frankfurt
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Quantum Dynamics of Large Molecules

Aim is to follow nuclear dynamics over potential surfaces:

Ammonia branching ratio:
\[ \Gamma_A^{X}(2D) \approx 2 \]
\[ \Gamma_A^{X}(6D) \approx 100 \]
Quantum Dynamics of Large Molecules

Aim is to follow nuclear dynamics over potential surfaces:

\[ \frac{r^3}{\text{a.u}} \]

\[ \frac{\phi}{V/10^3 \text{cm}^{-1}} \]

Ammonia branching ratio:

\[ \Gamma_A^X(2D) \approx 2 \]

\[ \Gamma_A^X(6D) \approx 100 \]

Bottlenecks:

- Dimensionality of wavefunction
- Obtaining potential

Pyrrole absorption
Quantum Dynamics of Large Molecules

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\[ \Gamma_X^A(2D) \approx 2 \]
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- Dimensionality of wavefunction
- Obtaining potential

Gaussian Wavepackets?
The MCTDH method

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

Variational equations of motion for \( A \) and \( \varphi \).

\[ i \dot{A}_J = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L - \sum_{\kappa=1}^{p} \sum_{l=1}^{n_\kappa} g_{j_{\kappa}l} A_{j_{\kappa}} \]

\[ i \dot{\varphi}_{(\kappa)} = (f_{(\kappa)})^T \varphi_{(\kappa)} + \left(1 - P_{(\kappa)}\right) \left(\rho_{(\kappa)}\right)^{-1} \langle H \rangle_{(\kappa)} \varphi_{(\kappa)} \]

with the constraint operator matrix

\[ f_{ij} = \langle \phi_i | f | \phi_j \rangle = i \langle \phi_i | \dot{\phi}_j \rangle \]

computer resources \( \sim n^p + nNp \)

The G-MCTDH Method

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

Replace single-particle functions with Gaussian functions

\[ g_{j}(Q, t) = \exp \left( Q^T \zeta_j Q + Q^T \xi_j + \eta_j \right) \]
The G-MCTDH Method

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

Replace single-particle functions with Gaussian functions

\[ g_j(Q, t) = \exp \left( Q^T \zeta_j Q + Q^T \xi_j + \eta_j \right) \]

Propagate parameters \( \lambda = \{ \zeta, \xi, \eta \} \)

\[
\begin{align*}
  i \dot{A}_j &= \sum_{lk} S_{jk}^{-1} \langle \Phi_k | H | \Phi_l \rangle A_l - \sum_{\kappa=1}^{p} \sum_{l=1}^{n_\kappa} i S_{jk}^{-1} \langle g_k | \frac{\partial}{\partial t} g_l \rangle A_{j_{\kappa}}^{l} \\
  &= \sum_{lk} S_{jk}^{-1} H_{kl} A_l - \sum_{\kappa=1}^{p} \sum_{l=1}^{n_\kappa} i S_{jk}^{-1} \tau_{kl} A_{j_{\kappa}}^{l} \\
  i \dot{\Lambda} &= C^{-1} Y
\end{align*}
\]

Burghardt et al JCP (99) 99:2927
\[ Y_{i\alpha} = \sum_l \rho_{il} \left( H_{il}^{(\alpha^0)} - \left[ S^{(\alpha^0)} S^{-1} H \right]_{il} \right) \]

\[ C_{i\alpha,j\beta} = \rho_{ij} \left( S_{ij}^{(\alpha\beta)} - \left[ S^{(\alpha^0)} S^{-1} S^{(0\beta)} \right]_{il} \right) \]

where \( \alpha \) is a parameter and \( i \) a function

\[ S_{il}^{(\alpha\beta)} = \left\langle \frac{\partial g_i}{\partial \lambda_{i\alpha}} \bigg| \frac{\partial g_l}{\partial \lambda_{l\beta}} \right\rangle ; \quad H_{il}^{(\alpha\beta)} = \left\langle \frac{\partial g_i}{\partial \lambda_{i\alpha}} \bigg| H \bigg| \frac{\partial g_l}{\partial \lambda_{l\beta}} \right\rangle \]

e.g. if \( \lambda_{i\alpha} = \xi_{i\alpha} \)

\[ S_{il}^{(\alpha^0)} = \left\langle \frac{\partial g_i}{\partial \xi_{i\alpha}} \bigg| g_l \right\rangle = \left\langle g_i \bigg| x_{\alpha} \bigg| g_l \right\rangle \]

If only GWPs known as variational Multi-Configurational Gaussian (vMCG) approach
Alternative Ansatz

Return to original MCTDH equation and variational derivation:

\[ \Psi(Q_1, \ldots, Q_f, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_p=1}^{n_p} A_{j_1 \ldots j_p}(t) \prod_{\kappa=1}^{p} \varphi^{(\kappa)}(Q_1, t) \]
Alternative Ansatz

Return to original MCTDH equation and variational derivation:

\[ \Psi(Q_1, \ldots, Q_f, t) = \sum_{j_1=1}^{n_1} \ldots \sum_{j_f=1}^{n_p} A_{j_1 \ldots j_p}(t) \prod_{\kappa=1}^{p} \varphi^{(\kappa)}_{j_\kappa}(Q_\kappa, t) \]

and now using

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

vary \( \delta A_J, \delta \varphi_j \) (grid-based SPFs), \( \delta D_{ir} \) and \( \delta g_\alpha = \sum_a \delta \lambda_{a\alpha} \frac{\partial g_\alpha}{\partial \lambda_{a\alpha}} \)

obtain the same EOMs for the \( A_J, \varphi_j \) and \( \lambda_{a\alpha} \) as before, but SPFs represented by

\[ i\dot{D}_{\gamma i} = \sum_{lj\alpha} S_{\gamma\alpha}^{-1} \rho_{ij}^{-1} \langle g_\alpha | (1 - P) \langle H |_{jl} | \varphi_l \rangle + \sum_{m} f_{mi} D_{\gamma m} - \sum_{\alpha\beta} S_{\gamma\alpha}^{-1} \tau_{\alpha\beta} D_{\beta i} \]

with \( P = \sum_r |\varphi_r\rangle \langle \varphi_r| \).
Thus GWPs act as a time-dependent primitive basis.
1. This should provide a better G-MCTDH, with a normalised A-vector and so able to use the CMF integrator.
2. A-vector will be shorter than the original G-MCTDH.

This is the first layer of “Multi-layer G-MCTDH”
Römer, Ruckenbauer and Burghardt JCP (13) 138: 064106
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If $m = n$ then equivalent to original G-MCTDH

For vMCG, only 1 “SPF” expanded in basis. Can now write:

\[
\begin{align*}
    i\dot{A} &= EA; \quad E = \langle \varphi | H | \varphi \rangle \\
    i\dot{D}_\alpha &= \sum_{\alpha\beta} S_{\gamma\alpha}^{-1} (H_{\alpha\beta} - i\tau_{\alpha\beta}) D_\beta - ED_\alpha
\end{align*}
\]

and the overall phase is moved into the A-coefficient.
Connection to trajectories

For frozen GWPs, taking

\[ H = \sum_{\kappa} \frac{p_{\kappa}^2}{2m_{\kappa}} + V \]
Connection to trajectories

For frozen GWPs, taking

\[ H = \sum_{\kappa} \frac{p_{\kappa}^2}{2m_{\kappa}} + V + H_R \]
Connection to trajectories

For frozen GWPs, taking

\[ H = \sum_\kappa \frac{p_\kappa^2}{2m_\kappa} + V \]

In terms of the moments,

\[ \langle H \rangle_{jl} = S_{jl} X_1^{(0)} + \sum_{\beta=1}^f S_{jl}^{(0\beta)} X_1^{(\beta)} + \sum_{\alpha,\beta=1}^f S_{jl}^{(\alpha\beta)} X_1^{(\alpha\beta)} + \ldots \]

For example

\[ X_1^{(\beta)} = -2i \frac{A_{\beta\beta j}}{m_r} p_{\beta j} + \frac{4A^2_{\beta\beta j}}{m_r} q_{\beta j} + \frac{\partial V}{\partial x_\beta} \bigg|_{q_l} + \sum_\alpha \frac{\partial^2 V}{\partial x_\beta \partial x_\alpha} q_{\alpha l} \bigg|_{q_l} + \ldots \]
and as

\[ i \dot{\xi}_{l\beta} = 2iA_{l\beta} \dot{q}_{l\beta} - \dot{p}_{l\beta} \]

the EOMs for the linear parameters can be written

\[ \dot{q}_{l\beta} = \frac{p_{l\beta}}{m_{\beta}} + \frac{1}{2A_{l\beta}} \text{Im} \sum_{m_{\alpha}} C_{l\beta m_{\alpha}}^{-1} \tilde{Y}_{m_{\alpha}} \]

\[ \dot{p}_{l\beta} = -V'_{l\beta} + \text{Re} \sum_{m_{\alpha}} C_{l\beta m_{\alpha}}^{-1} \tilde{Y}_{m_{\alpha}} \]

with

\[ \tilde{Y}_{m_{\alpha}} = \frac{4A_{j_{\alpha}}^2}{m_{\alpha}} q_{j_{\beta}} + \sum_{\beta \neq \alpha} V''_{j_{\alpha \beta}} q_{l_{\alpha}} + \sum_{\alpha, \beta = 1}^{f} S_{ji}^{(\alpha \beta)} X_{l}^{(\alpha \beta)} + \ldots \]
Salicylaldehyde Test Case: 2D Proton transfer

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

$$H = \frac{1}{2} \sum_{\kappa=1,18} \frac{\omega_\kappa}{2} \left( \frac{\partial^2}{\partial q^2_\kappa} + q^2_\kappa \right)$$

$$+ \sum_{n=1}^{4} A_n q^n_1$$

$$+ B_{11} q_1 q_{18} + B_{22} q_1^2 q_{18}^2$$

$$+ B_{31} q_1^3 q_{18} + B_{13} q_1 q_{18}^3$$
Inversion C-matrix: Stability and Convergence

At the start, \( \mathbf{C} \) is singular. Values are due to density matrix, \( \rho \) and the projection of the derivative functions out of the GWP space

\[
C_{i\alpha j\beta} = \rho_{ij} \langle \frac{\partial g_i}{\partial \lambda_{i\alpha}} | 1 - \sum_{rs} | g_r \rangle S_{rs}^{-1} \langle g_s | \frac{\partial g_j}{\partial \lambda_{j\beta}} \rangle
\]

Need only to include functions that have a significant population AND significantly contribute to the projected space (i.e. where the basis functions can move to).

Assume functions do not change much over a step, yet populations do. Estimate coefficients at end of step:

\[
A_j(t + \delta t) = A_j(t) + \dot{A}_j(t) \delta t
\]

Look at eigenvalues \( c_i \) of \( \mathbf{C} \) and count \( n_{\text{ignore}} \) with \( c_i < \varepsilon \).
If $n_{\text{ignore}} > 0$, project $\frac{\partial g_i}{\partial \lambda_{i\alpha}}$ onto space spanned by $N - n_{\text{ignore}}$ eigenvectors,

$$C_{i\alpha} = \sum_{a=n_{\text{ignore}}+1}^{N} \left\langle \frac{\partial g_i}{\partial \lambda_{i\alpha}} \right| a \right\rangle \left\langle a \left| \frac{\partial g_i}{\partial \lambda_{j\alpha}} \right. \right\rangle$$

and ignore $n_{\text{ignore}}$ parameters with lowest values of $C_{i\alpha}$

With $\varepsilon = 1 \times 10^{-6}$:
32 GWPs (left) and 64 GWPs (right)
Linear Dependence

With large basis sets linear dependencies occur. Seen as step sizes drop as lowest eigenvaule of $S$ matrix drop below $1 \times 10^{-6}$.

Test 2D salicylaldehyde with 32 functions w/o dynamic selection requires 63784 steps and with 64 does not finish.

use similar procedure as dynamic selection

Look at eigenvalues $s_i$ of $S$ and count $n_{\text{linear}}$ with $s_i < \varepsilon$.

If $n_{\text{linear}} > 0$, project $g_i$ onto space spanned by $n - n_{\text{linear}}$ eigenvectors,

$$S_i = \sum_{a} = n_{\text{linear}} + 1^n \langle g_i | a \rangle \langle a | g_j \rangle$$

and ignore $n_{\text{ignore}}$ functions with lowest values of $S_i$

with $\varepsilon = 1 \times 10^{-6}$

32 GWP finds 2 dependencies at 4 fs and 42 fs.
64 GWP test finds 7 dependencies at 4 fs and 42 fs.
Flux through barrier

Starting with \((q_1, q_{18}) = (0.96, -0.07)\). Corresponds to O–H bond stretched as lower minimum is at \((q_1, q_{18}) = (1.26, -0.04)\). Energy below barrier height.

4th order integrals.

![Graph of 2D Salicylaldehyde Proton Transfer Flux: Full QD](image)

Exact solution.
Flux through barrier

Starting with \((q_1, q_{18}) = (0.96, -0.07)\). Corresponds to O–H bond stretched as lower minimum is at \((q_1, q_{18}) = (1.26, -0.04)\). Energy below barrier height.

4th order integrals.

![Graph of 2D Salicylaldehyde Proton Transfer Flux: Full QD v 128 time independent GWPs](image)

Exact (red).
Size: 2542 Time 16 s
vMCG 128 t-ind (green).
Size: 512 Time: 2294 s
Flux through barrier

Starting with \((q_1, q_{18}) = (0.96, -0.07)\). Corresponds to O–H bond stretched as lower minimum is at \((q_1, q_{18}) = (1.26, -0.04)\). Energy below barrier height.

4th order integrals.

![Graph of flux through barrier](image)

Exact (red).
Size: 2542. Time: 16 s
vMCG 16 (green).
Size: 64. Time: 68 s
vMCG 32 (blue).
Size: 128. Time: 205 s
Flux through barrier

Starting with \((q_1, q_{18}) = (0.96, -0.07)\). Corresponds to O–H bond stretched as lower minimum is at \((q_1, q_{18}) = (1.26, -0.04)\). Energy below barrier height.

4th order integrals.

2D Salicylaldehyde Proton Transfer Flux: Full QD v 16 classical GWPs

Exact (red). Time: 16 s
16 class GWPs (green).
Size: 64 Time: 8 s
Flux through barrier

Starting with \((q_1, q_{18}) = (0.96, -0.07)\). Corresponds to O–H bond stretched as lower minimum is at \((q_1, q_{18}) = (1.26, -0.04)\). Energy below barrier height.

4th order integrals.
Flux through barrier

Starting with \((q_1, q_{18}) = (0.96, -0.07)\). Corresponds to O–H bond stretched as lower minimum is at \((q_1, q_{18}) = (1.26, -0.04)\). Energy below barrier height.

4th order integrals.
Trajectories with 16 GWPs

**vMCG**

GWP centre coordinate 16 GWPs

GWP trajectory in phase-space 16 GWPs

**Classical**

GWP centre coordinate 16 classical GWPs

GWP trajectory in phase-space 16 classical GWPs
Local Harmonic Approximation

For GWP calculations, common to use LHA, i.e. expand potential around centre $q_l$

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

For GWP calculations, common to use LHA, i.e. expand potential around centre $q_i$

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

2D Salicylaldehyde Proton Transfer Flux: Full QD v 32 GWPs LHA. Full width = 0.
Local Harmonic Approximation

For GWP calculations, common to use LHA, i.e. expand potential around centre $q_l$

\[ V_I(x) = V_{0\alpha} + \sum_{\alpha} V'_\alpha(x_{\alpha} - q_{l\alpha}) + \frac{1}{2} \sum_{\alpha\beta} V''_{\alpha\beta}(x_{\alpha} - q_{l\alpha})(x_{\beta} - q_{l\beta}) \]
Local Harmonic Approximation

For GWP calculations, common to use LHA, i.e. expand potential around centre \( q_l \)

\[
V_I(x) = V_0 + \sum \alpha V'_\alpha (x_\alpha - q_{l\alpha}) + \frac{1}{2} \sum_{\alpha \beta} V''_{\alpha\beta} (x_\alpha - q_{l\alpha})(x_\beta - q_{l\beta})
\]

2D Salicylaldehyde Proton Transfer Flux: Full QD v 32 GWPs LHA. Width = 0.3
Local Harmonic Approximation

For GWP calculations, common to use LHA, i.e. expand potential around centre $q_l$

$$V_l(x) = V_0 + \sum_{\alpha} V_\alpha' (x_\alpha - q_l) + \frac{1}{2} \sum_{\alpha\beta} V_{\alpha\beta}'' (x_\alpha - q_l)(x_\beta - q_l)$$
Local Harmonic Approximation

For GWP calculations, common to use LHA, i.e. expand potential around centre $q_l$

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

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

The pyrazine molecule has 24 vibrational modes. NB. LHA is exact

\[
H = \sum_i \frac{\omega_i}{2} \left( -\partial^2 \over \partial Q_i^2 + Q_i^2 \right) 1 + \left( \begin{array}{cc} -\Delta & 0 \\ 0 & \Delta \end{array} \right) + \sum_{i \in G_1} \left( \begin{array}{cc} \kappa_i^{(1)} & 0 \\ 0 & \kappa_i^{(2)} \end{array} \right) Q_i + \\
\sum_{(i,j) \in G_2} \left( \begin{array}{cc} \gamma_{i,j}^{(1)} & 0 \\ 0 & \gamma_{i,j}^{(2)} \end{array} \right) Q_i Q_j + \sum_{i \in G_3} \left( \begin{array}{cc} 0 & \lambda_i \\ \lambda_i & 0 \end{array} \right) Q_i + \sum_{(i,j) \in G_4} \left( \begin{array}{cc} 0 & \mu_{i,j} \\ \mu_{i,j} & 0 \end{array} \right) Q_i Q_j .
\]
4D model: Linear Coupling

Autocorrelation function: 

State Populations:
4D model: Linear Coupling

Autocorrelation function:

State Populations:
4D model: Linear Coupling

Autocorrelation function:

State Populations:

Full QD v 40, 40 GWPs.
4D model: Linear Coupling

Autocorrelation function:

State Populations:

Full QD v 50, 50 GWPs.
4D model: Linear Coupling

Autocorrelation function:

State Populations:
Conclusions

- Can use GWP basis in vMCG to provide converged quantum dynamics calculations
- vMCG moves to cover phase space as required
- Numerical problems due to linear dependencies and projector.