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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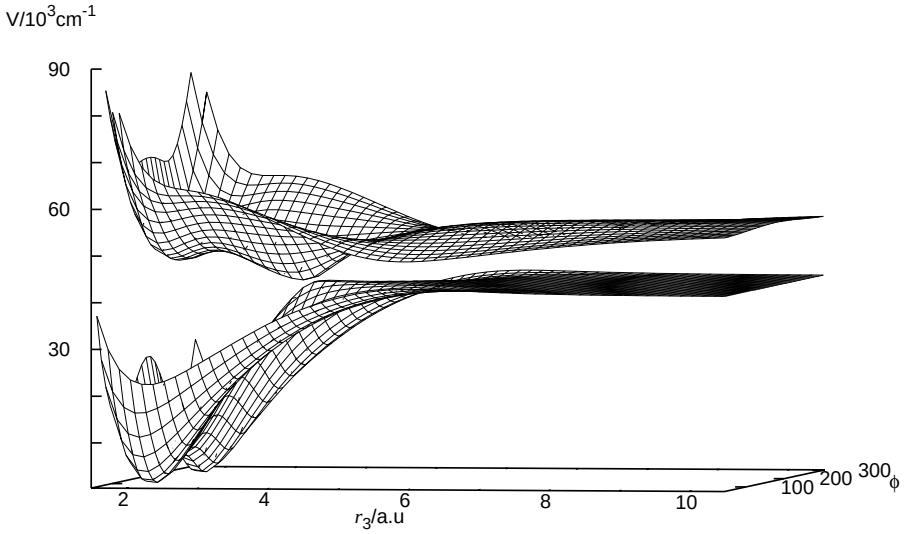
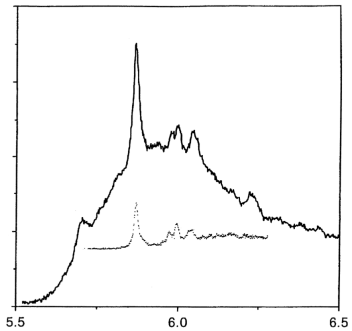
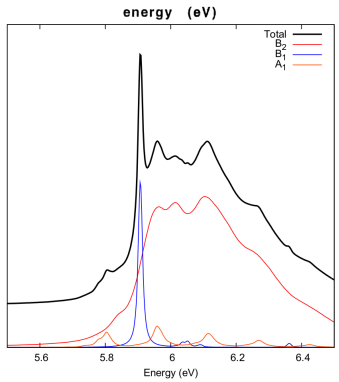
Collaboration: Irene Burghardt, Frankfurt
Benjamin Lasorne, Montpellier

Quantum Dynamics of Large Molecules

Aim is to follow nuclear dynamics over potential surfaces:





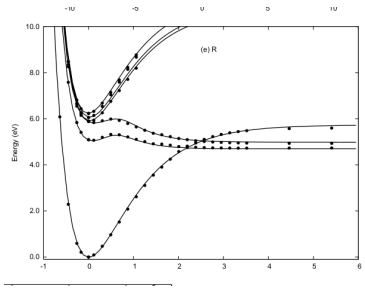


Pyrrole absorption

Ammonia branching ratio:

$\Gamma_A^X(2D) \approx 2$

$\Gamma_A^X(6D) \approx 100$



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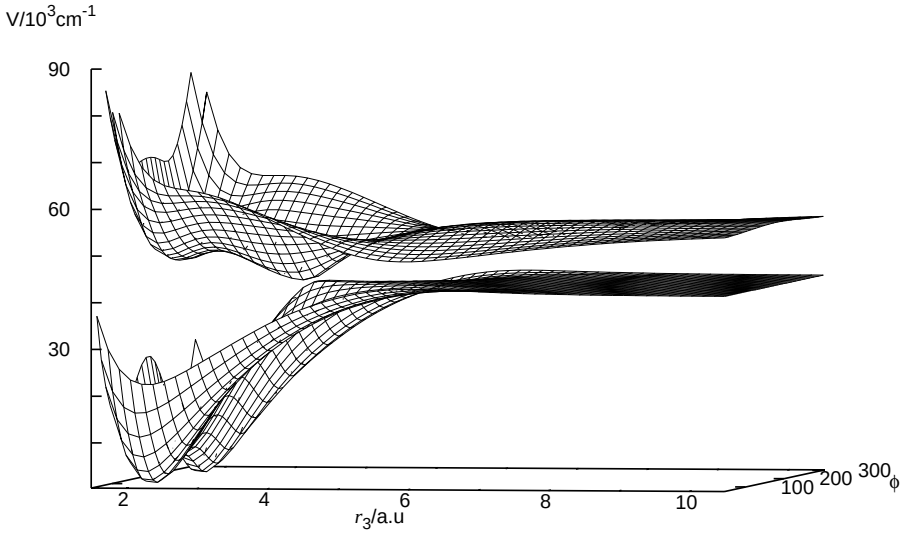

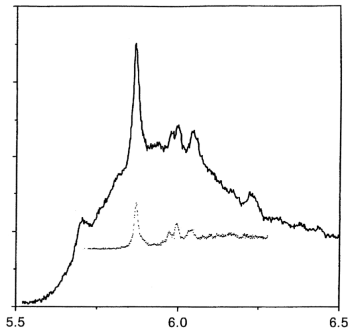

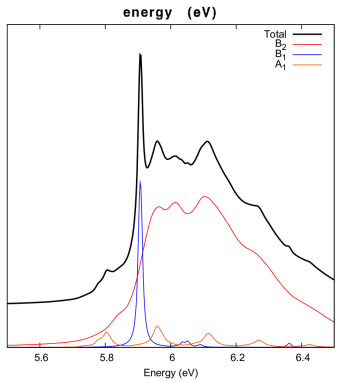

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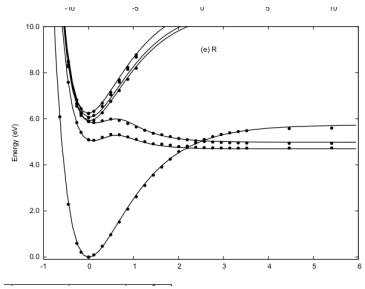
- Dimensionality of wavefunction
- Obtaining potential



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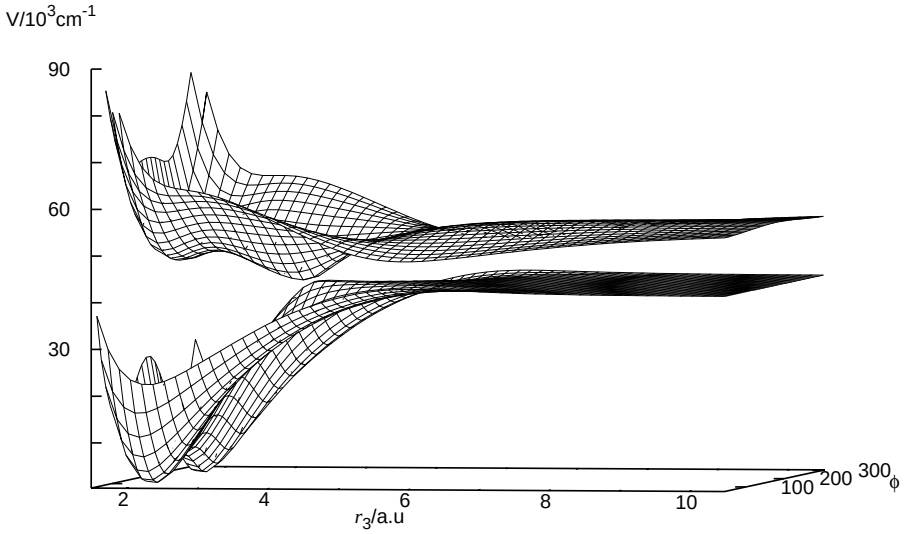

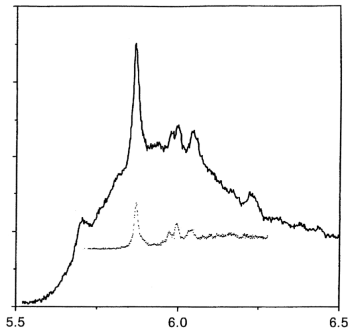

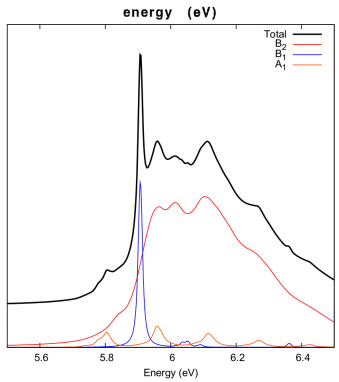

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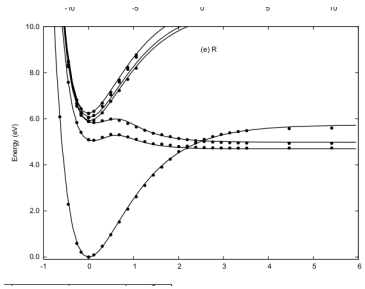

Gaussian Wavepackets?

The **MCTDH** method

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

Variational equations of motion for A and φ.

$$\begin{aligned} i\dot{A}_J &= \sum_L \langle\Phi_J|H|\Phi_L\rangle A_L - \sum_{\kappa=1}^{p}\sum_{l=1}^{n_\kappa} g_{j_\kappa l}^{(\kappa)} A_{J_l^\kappa} \\ i\dot{\varphi}^{(\kappa)} &= (\mathbf{f}^{(\kappa)})^T\varphi^{(\kappa)} + \left(1-P^{(\kappa)}\right)\left(\rho^{(\kappa)}\right)^{-1}\langle\mathbf{H}\rangle^{(\kappa)}\varphi^{(\kappa)} \end{aligned}$$

with the constraint operator matrix

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

computer resources $\sim n^p + nNp$

Reviews: Beck *et al* Phys. Rep. (00) 324:1 Meyer and Worth TCA (03) 109:251

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

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

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Replace single-particle functions with Gaussian functions

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

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

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

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

$$
\begin{aligned}
Y_{i\alpha} &= \sum_l \rho_{il} \left(H_{il}^{(\alpha 0)} - \left[\mathbf{S}^{(\alpha 0)} \mathbf{S}^{-1} \mathbf{H} \right]_{il} \right) \\
C_{i\alpha,j\beta} &= \rho_{ij} \left(S_{ij}^{(\alpha\beta)} - \left[\mathbf{S}^{(\alpha 0)} \mathbf{S}^{-1} \mathbf{S}^{(0\beta)} \right]_{il} \right)
\end{aligned}
$$

where α is a parameter and i a function

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

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

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

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

Alternative Ansatz

Return to original MCTDH equation and variational derivation:

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

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and now using

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

vary δA_J, $\delta\varphi_j$ (grid-based SPFs), δD_{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, φ_j and $\lambda_{a\alpha}$ as before, but SPFs represented by

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

with $P=\sum_r|\varphi_r\rangle\langle\varphi_r|$.

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:

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

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

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In terms of the moments,

$$\langle H \rangle_{jl} = S_{jl} X_l^{(0)} + \sum_{\beta=1}^{f} S_{jl}^{(0\beta)} X_l^{(\beta)} + \sum_{\alpha,\beta=1}^{f} S_{jl}^{(\alpha\beta)} X_l^{(\alpha\beta)} + \dots$$

For example

$$X_l^{(\beta)} = -2i \frac{A_{\beta\beta j}}{m_r} p_{\beta j} + \frac{4A_{\beta\beta j}^2}{m_r} q_{\beta j} + \left. \frac{\partial V}{\partial x_\beta} \right|_{q_l} + \sum_{\alpha} \left. \frac{\partial^2 V}{\partial x_\beta \partial x_\alpha} q_{\alpha l} \right|_{q_l} + \dots$$

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

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

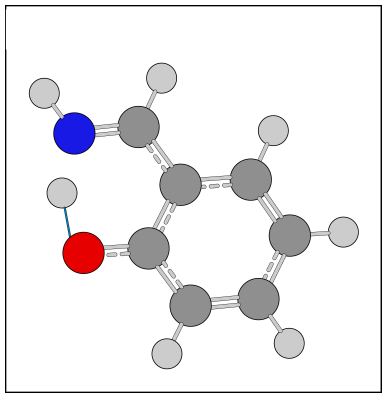
with

$$\tilde{Y}_{m\alpha} = \frac{4A^2_{j\alpha}}{m_\alpha}q_{j\beta} + \sum_{\beta\neq\alpha} V''_{j\alpha\beta}q_{l\alpha} + \sum_{\alpha,\beta=1}^{f} S^{(\alpha\beta)}_{jl}X^{(\alpha\beta)}_{l} + \ldots$$

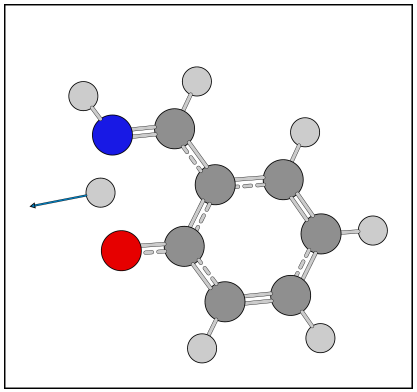
Salicylaldehyde Test Case: 2D Proton transfer

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

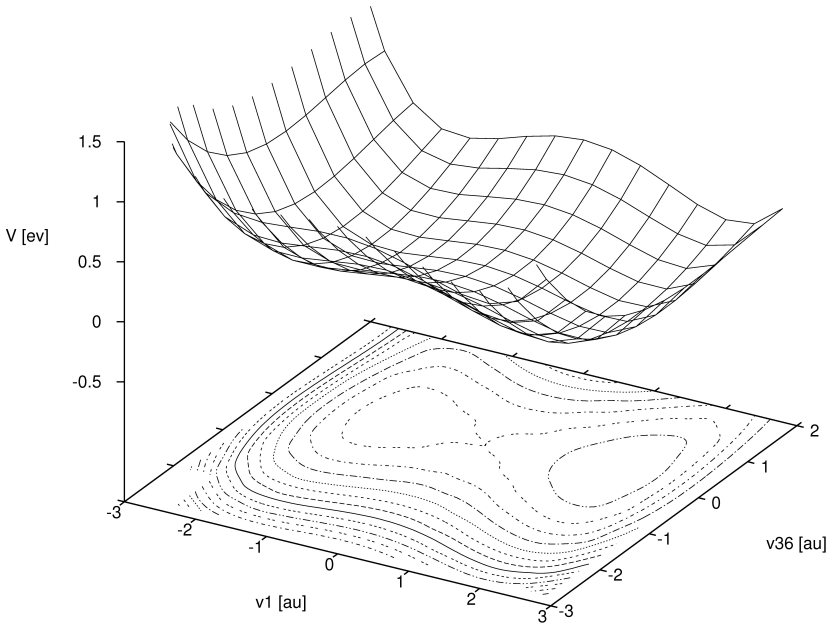
$$
\begin{aligned}
H &= \frac{1}{2}\sum_{\kappa=1,18}\frac{\omega_\kappa}{2}\left(\frac{\partial^2}{\partial q_\kappa^2}+q_\kappa^2\right) \\
&\quad +\sum_{n=1}^{4} A_n q_1^n \\
&\quad + B_{11}\,q_1\,q_{18} + B_{22}\,q_1^2\,q_{18}^2 \\
&\quad + B_{31}\,q_1^3\,q_{18} + B_{13}\,q_1\,q_{18}^3
\end{aligned}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



ν_1



ν_{18}



Invertion C-matrix: Stability and Convergence

At the start, **C** is singular. Values are due to density matrix, ρ and the projection of the derivative functions out of the GWP space

$$C_{i\alpha j\beta} = \rho_{ij}\left\langle \frac{\partial g_i}{\partial \lambda_{i\alpha}} \middle| 1 - \sum_{rs} \mid g_r\rangle S^{-1}_{rs} \langle g_s \mid \middle| \frac{\partial g_j}{\partial \lambda_{j\beta}} \right\rangle$$

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:

$$A_J(t + \delta t) = A_j(t) + \dot{A}_j(t)\delta t$$

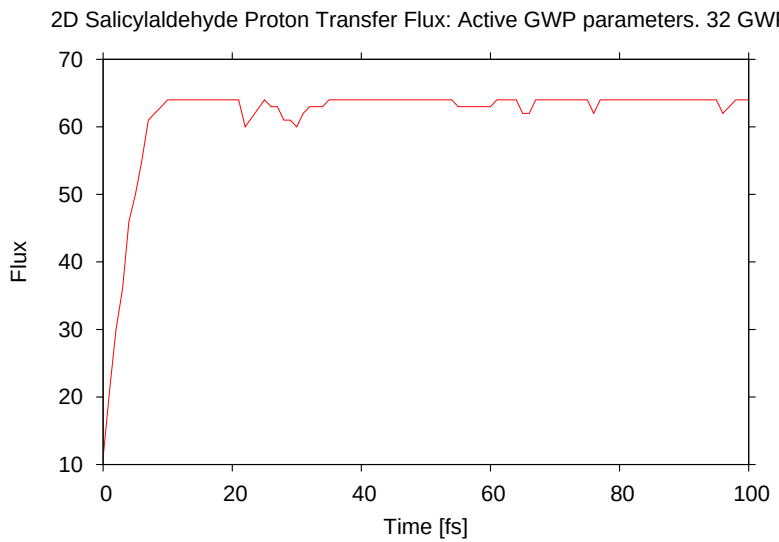
Look at eigenvalues c_i of **C** and count n_{ignore} with $c_i < \varepsilon$.

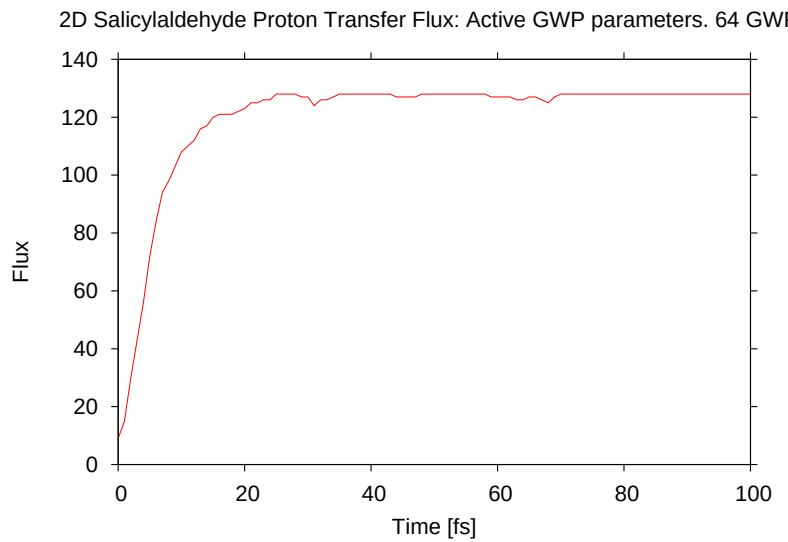
If $n_{\text{ignore}} > 0$, project $\frac{\partial g_i}{\partial \lambda_{i\alpha}}$ onto space spanned by $N - n_{\text{ignore}}$ eigenvectors,

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

and ignore n_{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 1×10^{-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_{linear} with $s_i < \varepsilon$.

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

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

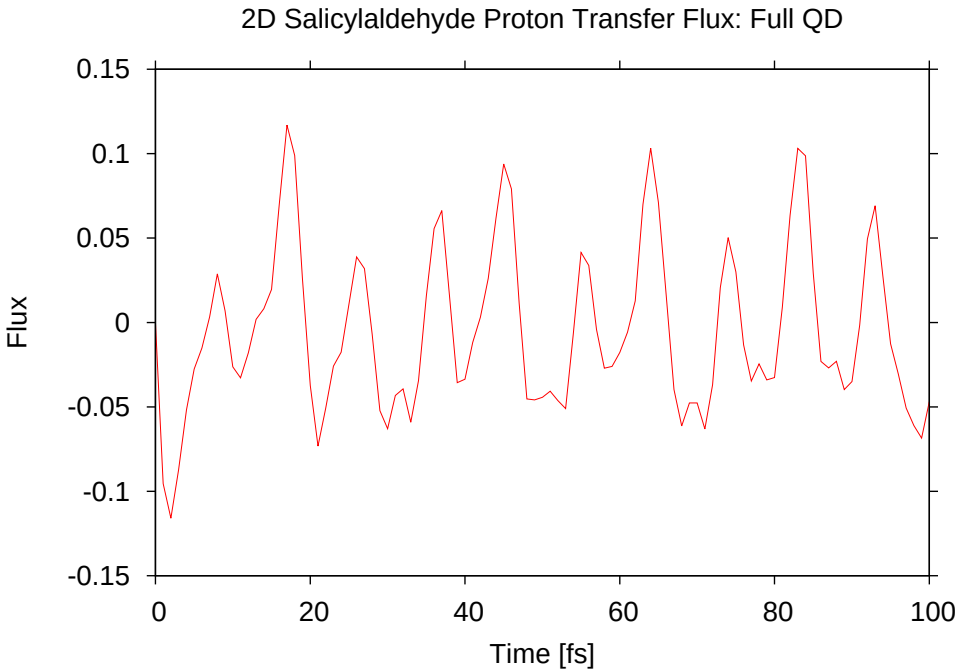
and ignore n_{ignore} functions with lowest values of S_i

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.



Exact solution.

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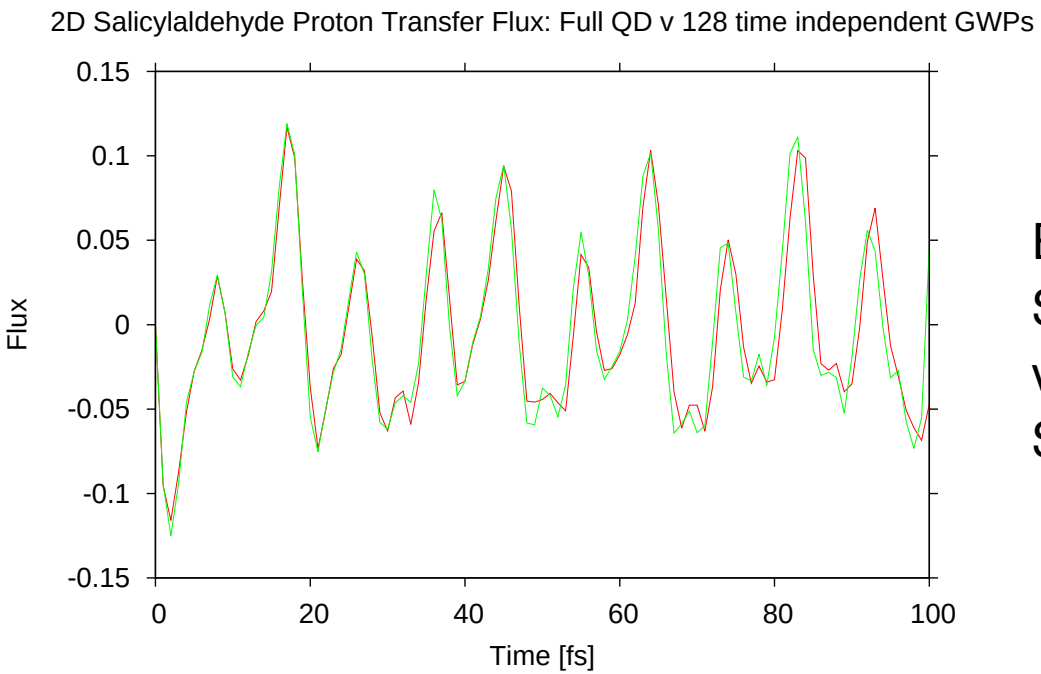

Exact (red).
Size: 2542 Time 16 s
vMCG 128 t-ind (green).
Size: 512 Time: 2294 s

Flux through barrier

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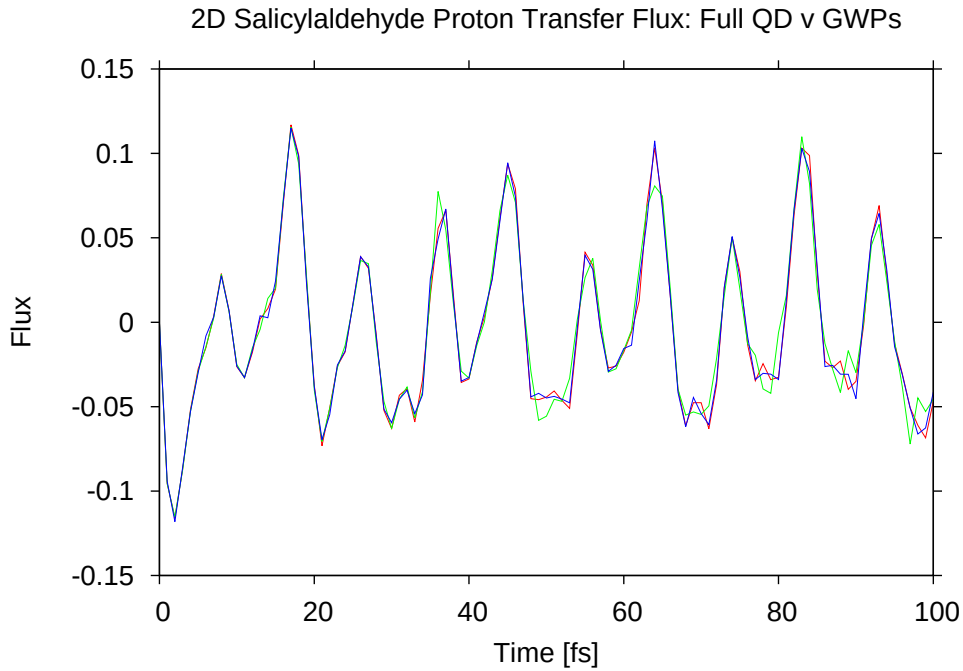

Exact (red).
Size: 2542. Time: 16 s
vMCG 16 (green).
Size: 64. Time: 68 s
vMCG 32 (blue).
Size: 128. Time: 205 s

Flux through barrier

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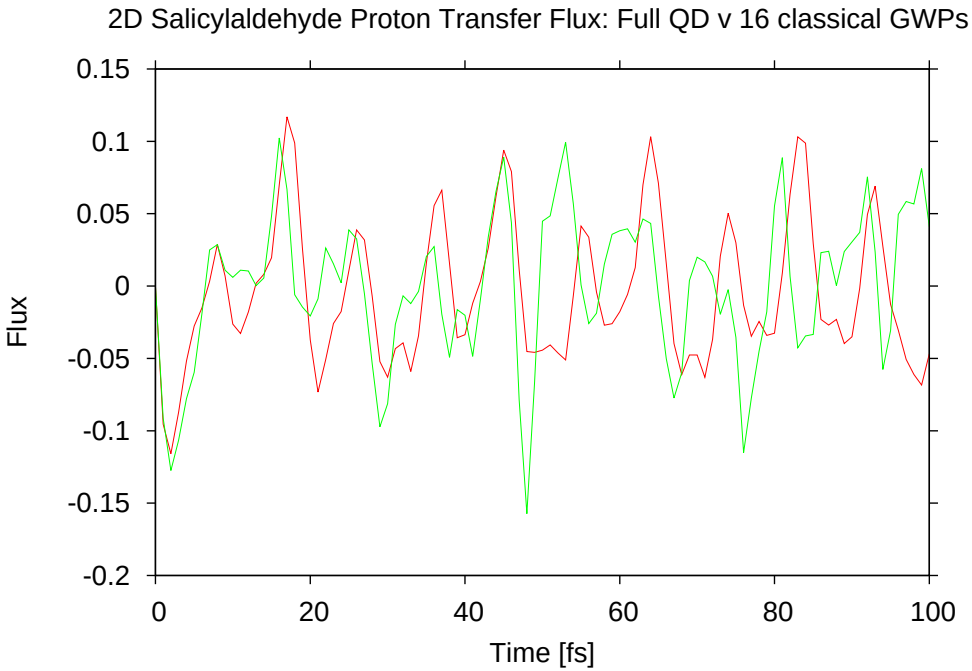
4th order integrals.



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.

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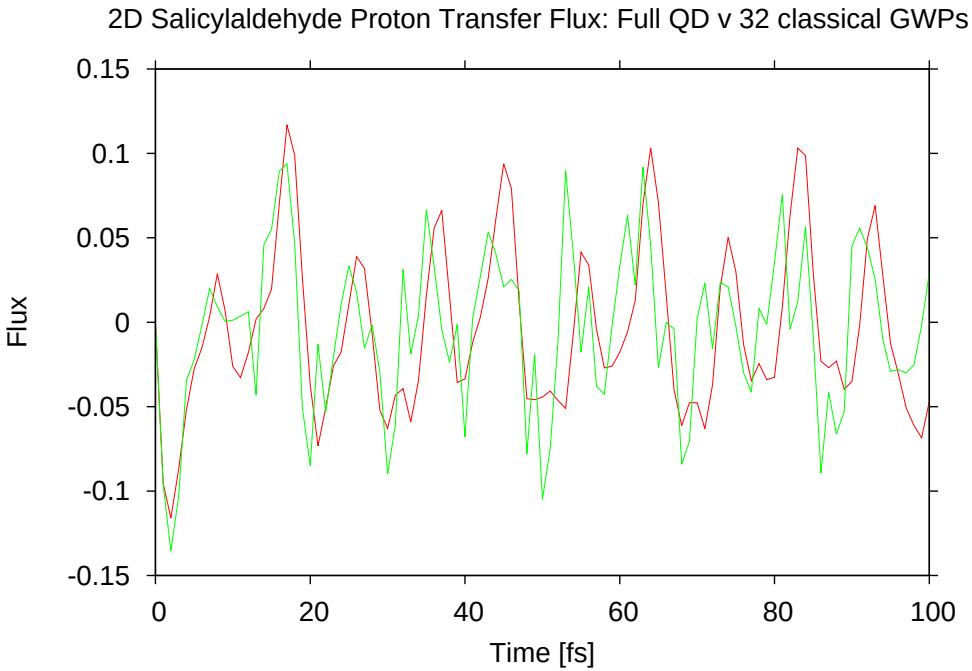
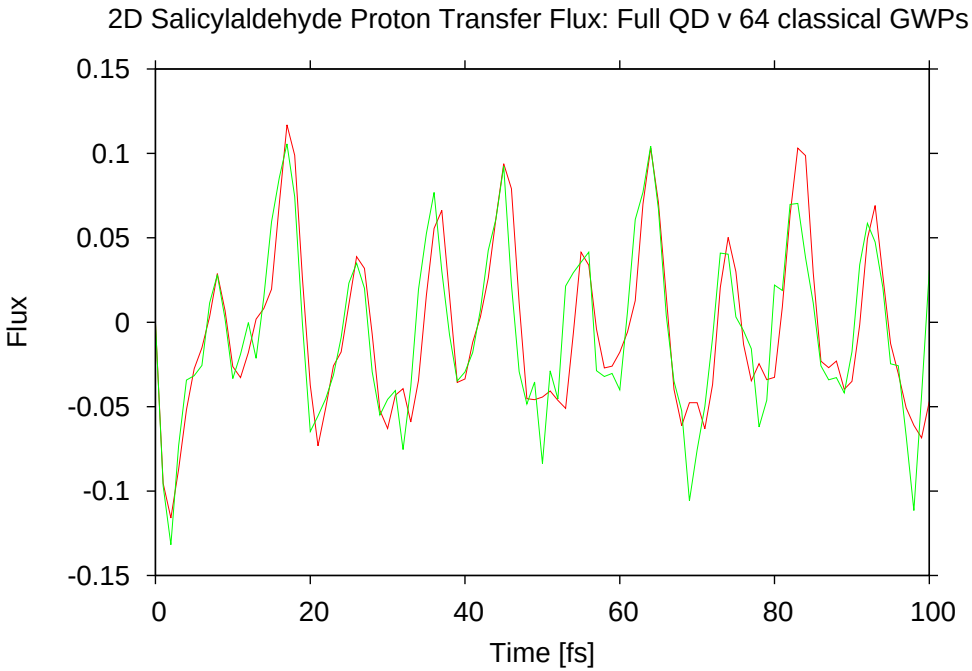


Exact (red). Time: 16 s
32 class GWPs (green).
Size: 128 Time: 24 s

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.

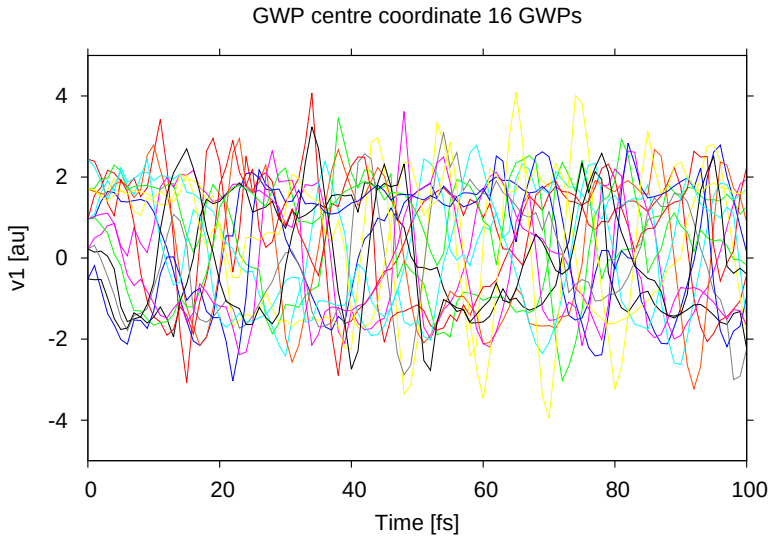
4th order integrals.

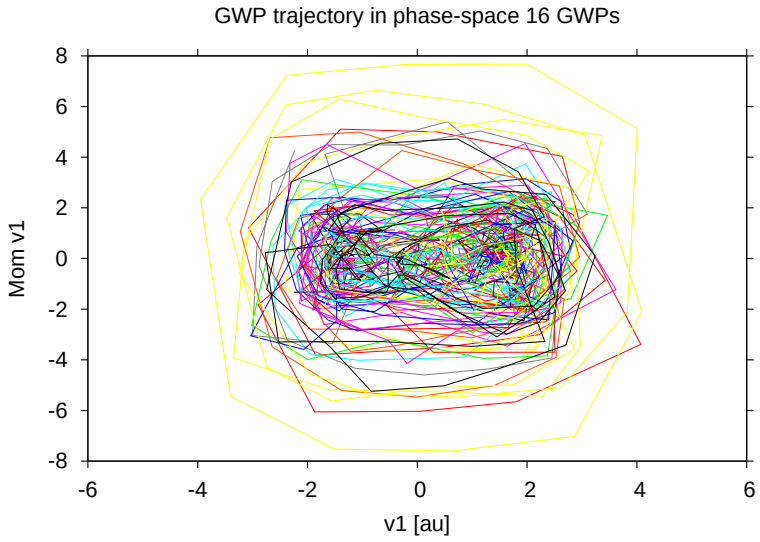


Exact (red). Time: 161 s
64 class GWPs (blue).
Size: 256 Time: 161 s

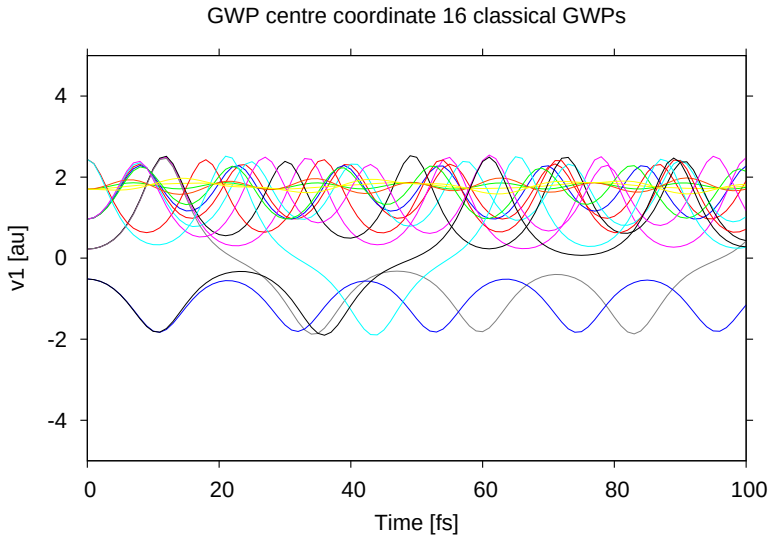
Trajectories with 16 GWPs

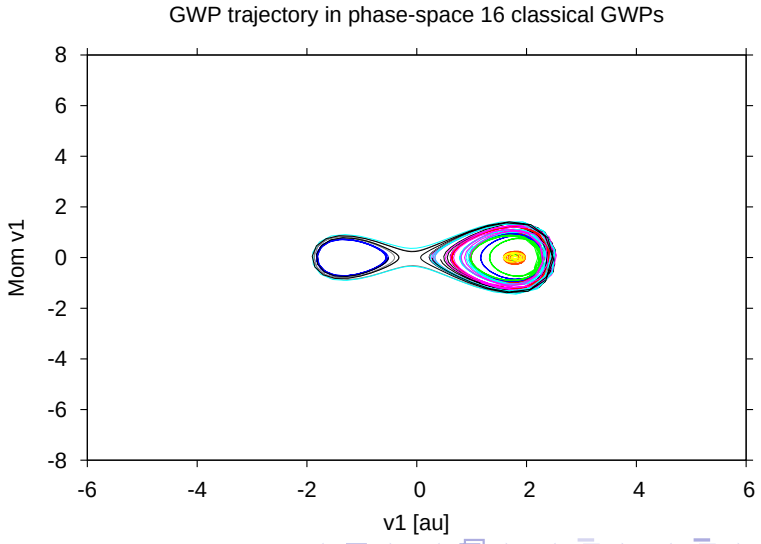
vMCG





Classical





Local Harmonic Approximation

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

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

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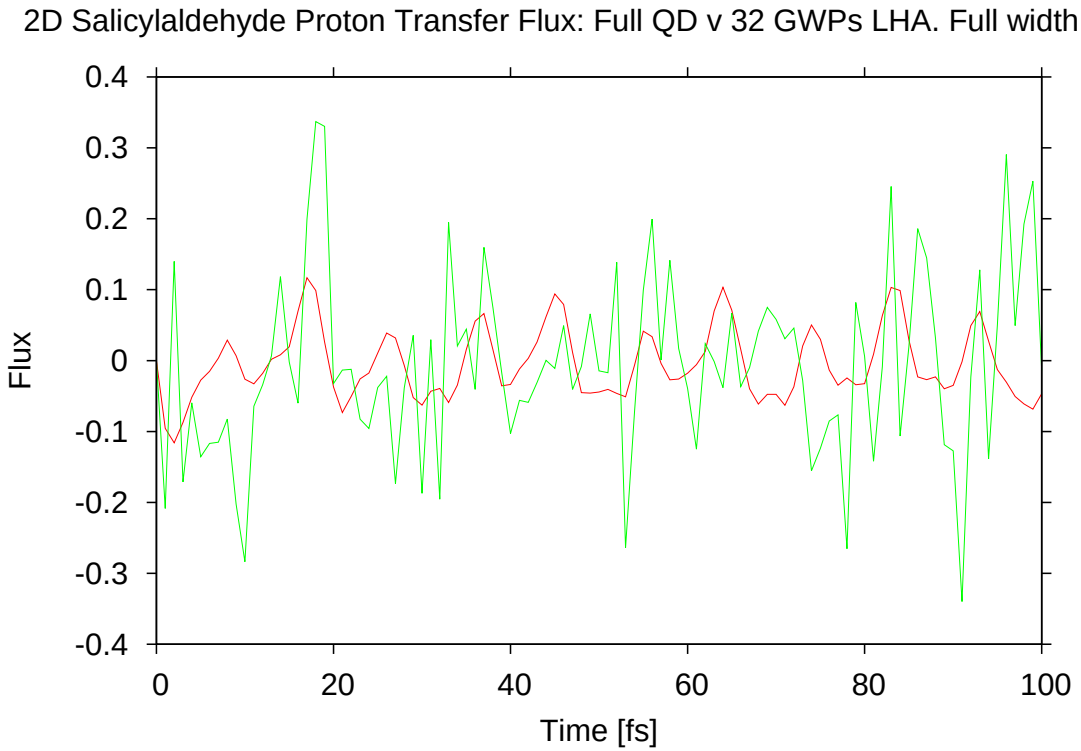

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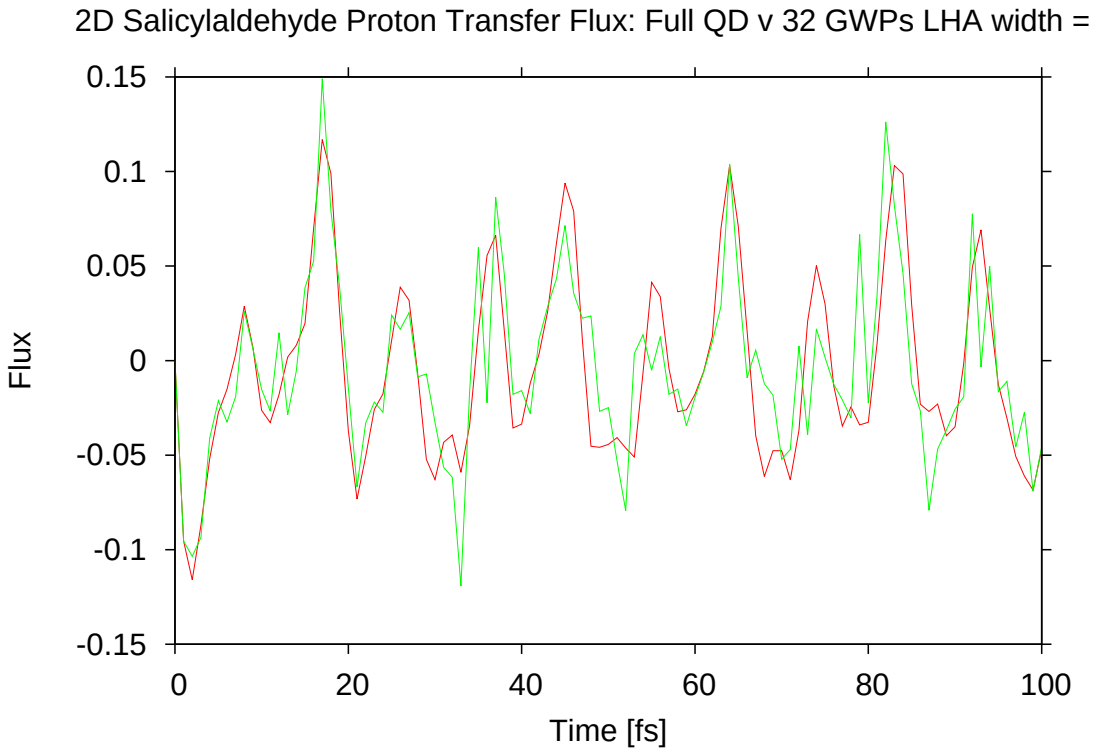
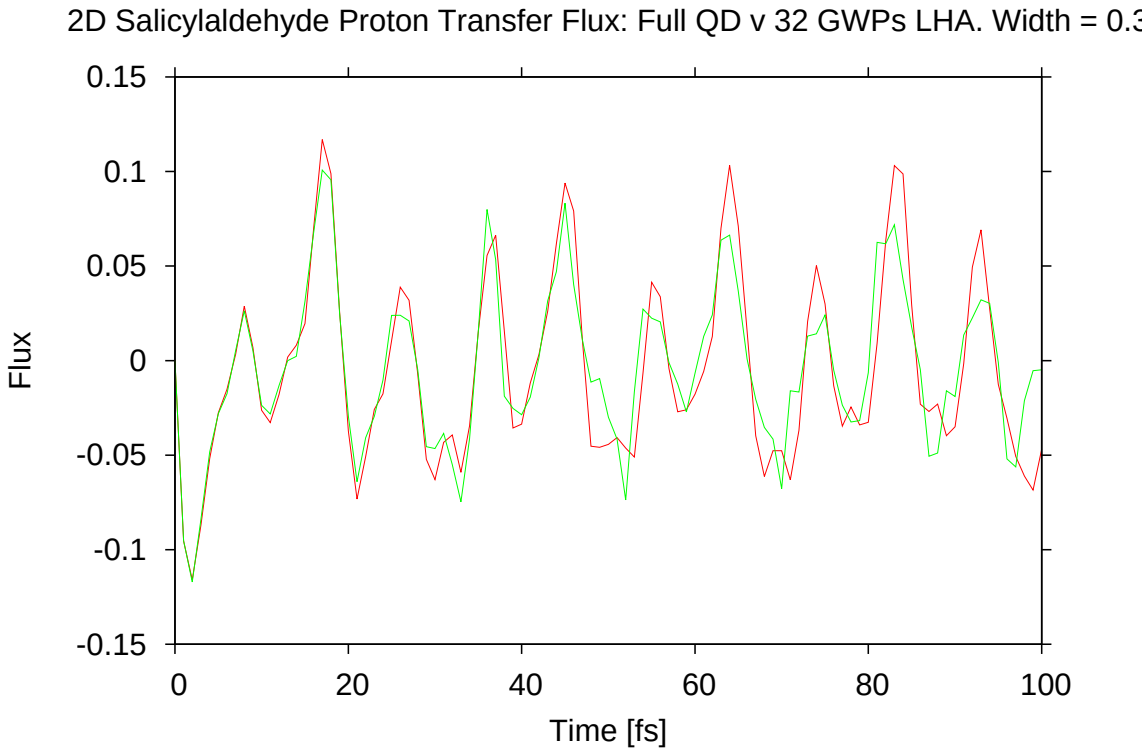


Local Harmonic Approximation

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

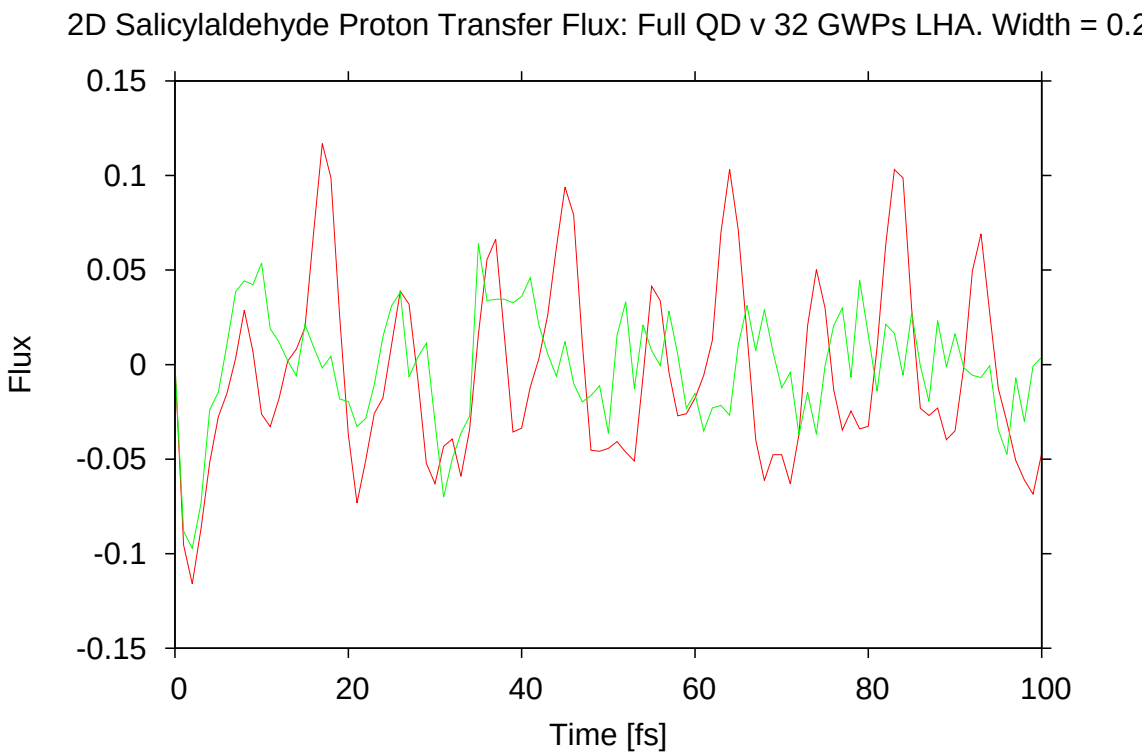
$$V_l(\mathbf{x}) = V_{0\alpha} + \sum_{\alpha} V'_{\alpha}(x_\alpha - q_{l\alpha}) + \frac{1}{2}\sum_{\alpha\beta} V''_{\alpha\beta}(x_\alpha - q_{l\alpha})(x_\beta - q_{l\beta})$$



Local Harmonic Approximation

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

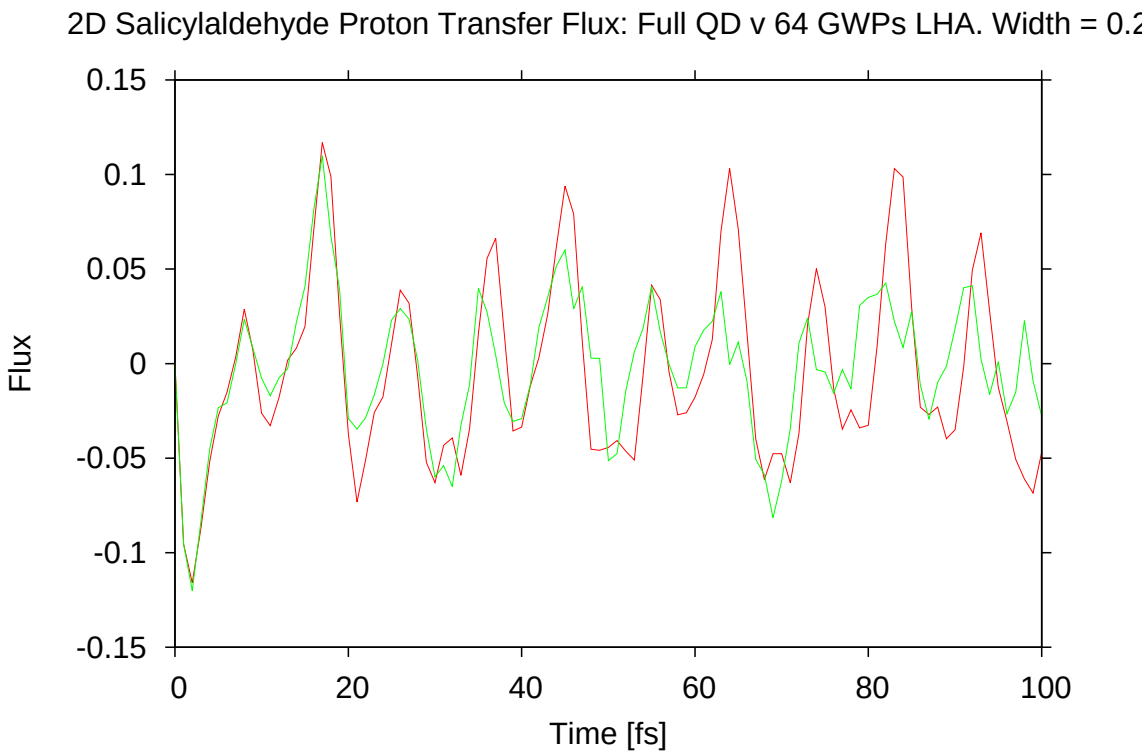
$$V_l(\mathbf{x}) = V_{0\alpha} + \sum_{\alpha} V'_{\alpha}(x_\alpha - q_{l\alpha}) + \frac{1}{2}\sum_{\alpha\beta} V''_{\alpha\beta}(x_\alpha - q_{l\alpha})(x_\beta - q_{l\beta})$$



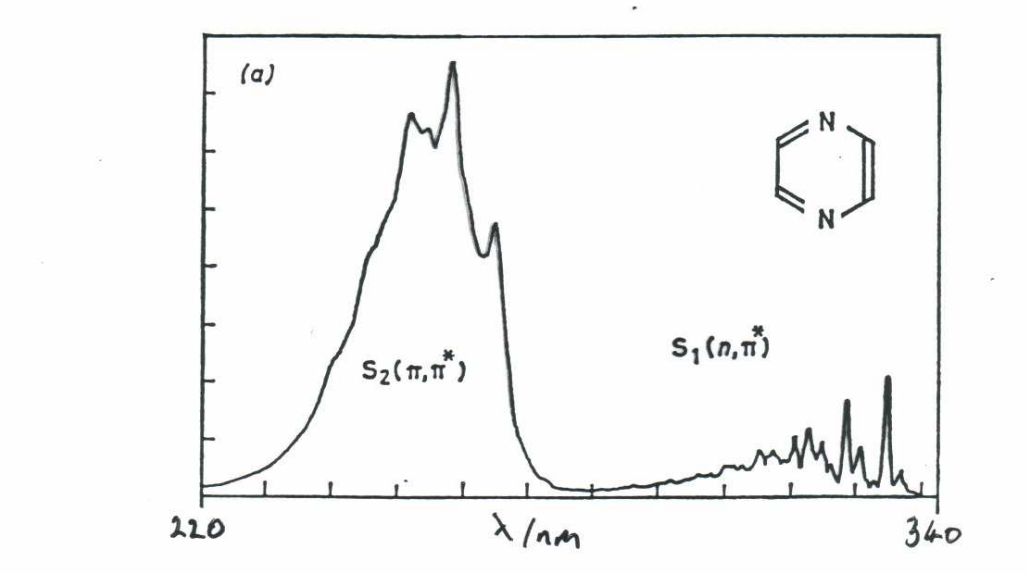
Local Harmonic Approximation

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

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



Pyrazine Excitation: Model Hamiltonian



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

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

$$\mathbf{H} = \sum_i \frac{\omega_i}{2}\left(-\frac{\partial^2}{\partial Q_i^2} + Q_i^2\right)\mathbf{1} + \begin{pmatrix} -\Delta & 0 \\ 0 & \Delta \end{pmatrix} + \sum_{i\in G_1} \begin{pmatrix} \kappa_i^{(1)} & 0 \\ 0 & \kappa_i^{(2)} \end{pmatrix} Q_i +$$

$$\sum_{(i,j)\in G_2} \begin{pmatrix} \gamma_{i,j}^{(1)} & 0 \\ 0 & \gamma_{i,j}^{(2)} \end{pmatrix} Q_i Q_j + \sum_{i\in G_3} \begin{pmatrix} 0 & \lambda_i \\ \lambda_i & 0 \end{pmatrix} Q_i + \sum_{(i,j)\in G_4} \begin{pmatrix} 0 & \mu_{i,j} \\ \mu_{i,j} & 0 \end{pmatrix} Q_i Q_j \,.$$

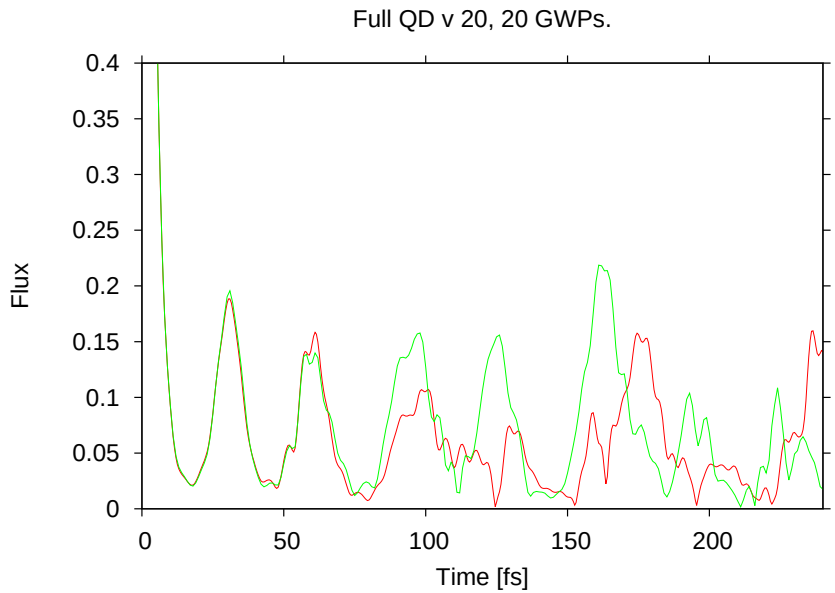
4D model: Linear Coupling

Autocorrelation function:

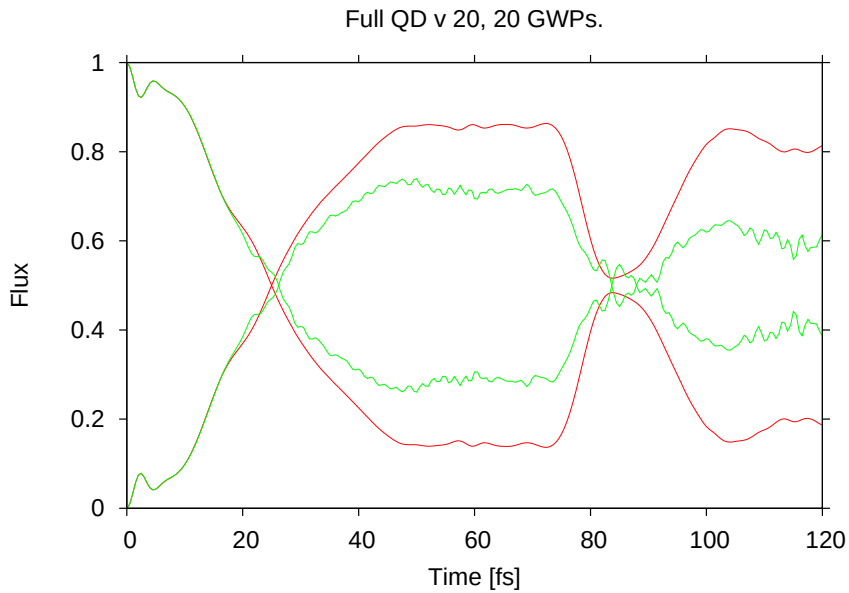
State Populations:

4D model: Linear Coupling

Autocorrelation function:



State Populations:



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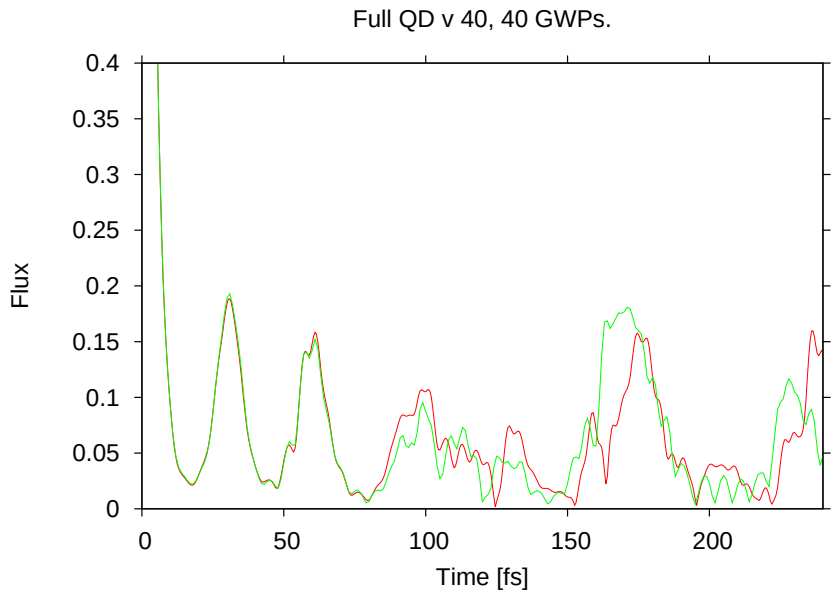

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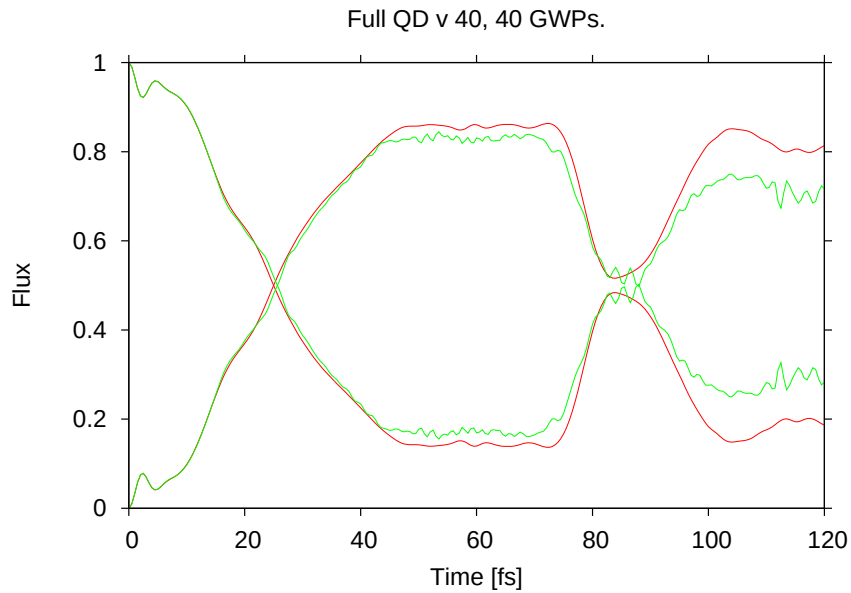

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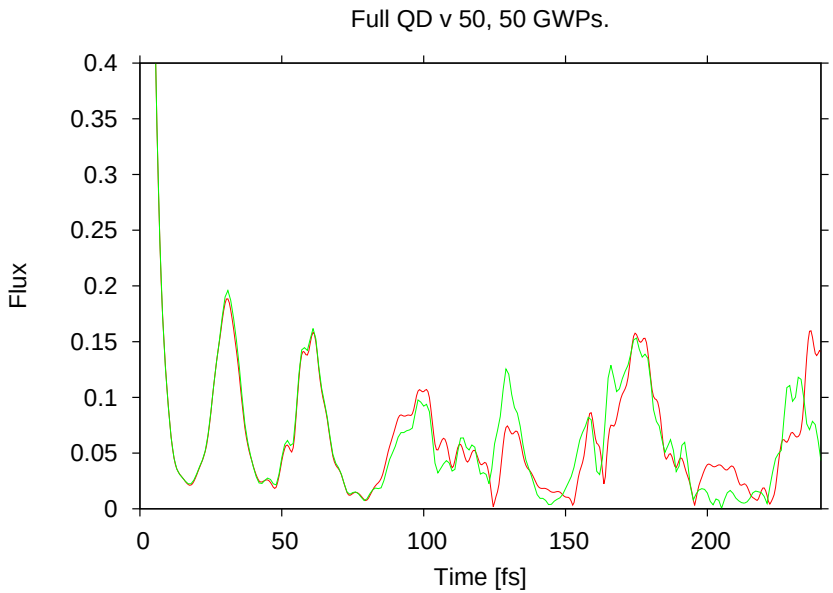

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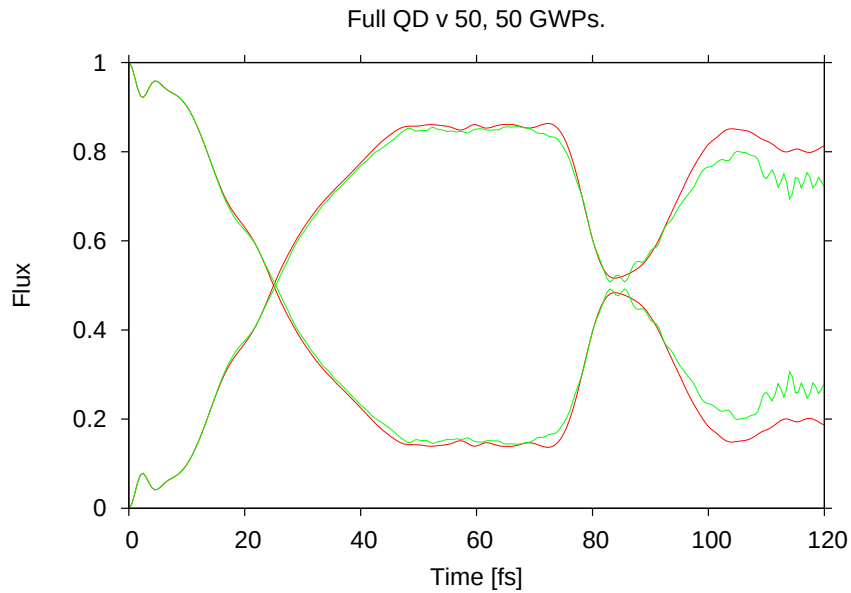

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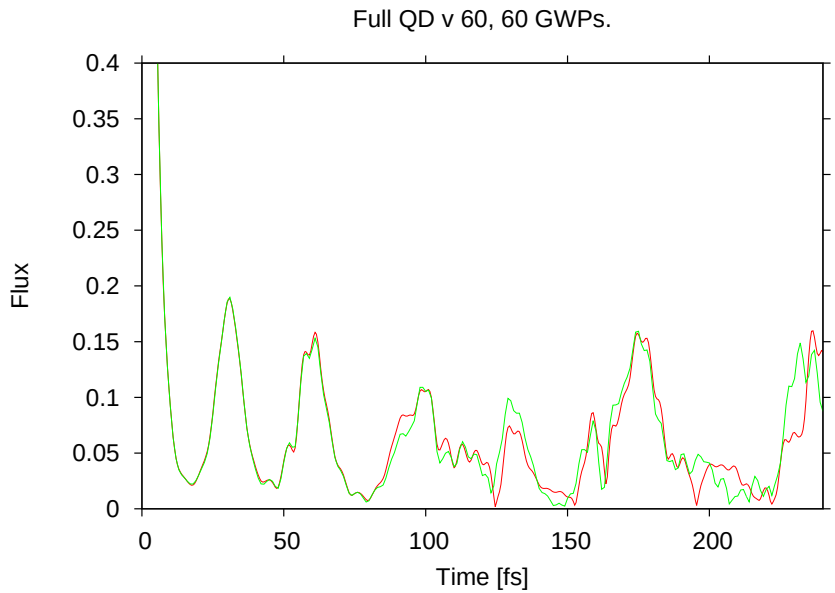

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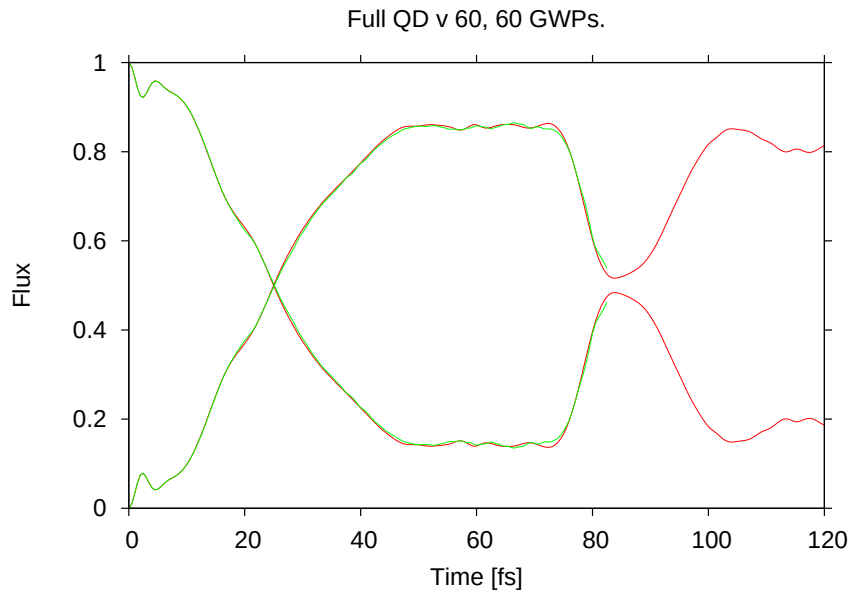

Conclusions

- 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.