Direct Quantum Dynamics Using Variational Gaussian Wavepackets and Gaussian Process Regression: Supplementary Material

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I. POTENTIAL ENERGY OPERATOR MATRIX ELEMENTS

Below we provide the derivation and full expressions for the potential energy operator matrix elements used in the GAP-vMCG method, both for $k^{\mathrm{Full}}(\mathbf{q},\mathbf{q}_k)$ and $k^{\mathrm{Add}}(\mathbf{q},\mathbf{q}_k)$. Since we use vMCG within the frozen-width approximation, with only the position and momentum of fixed-width GWPs being propagated, we only provide formulas relevant to this approximation here, with extension to the time-dependent width parameter being straightforward.

With $k^{\mathrm{Full}}(\mathbf{q},\mathbf{q}_k)$, the GAP-vMCG potential energy ME reads

$$\mathcal{V}_{ij} = \langle g_i|\hat{\mathcal{V}}^{\mathrm{Full}}|g_j\rangle = \langle g_i|\sum_{k=1}^{M}\omega_k k^{\mathrm{Full}}(\mathbf{q},\mathbf{q}_k)|g_j\rangle = \kappa^2\sum_{k=1}^{M}\omega_k\prod_{m=1}^{f}\langle g_i^m|e^{-\gamma(q^m-q_k^m)^2}|g_j^m\rangle\,. \quad \text{(S1)}$$

With the f-dimensional GWP given in the Heller form

$$g_i(\mathbf{q},t) = \prod_{m=1}^{f}\left(\frac{2\alpha_i^m}{\pi}\right)^{1/4}\exp[-\alpha_i^m(\hat{q}^m - q_i^m(t))^2 + ip_i^m(t)(\hat{q}^m - q_i^m(t))], \quad \text{(S2)}$$

the one-dimensional, one-point term from the full matrix element expression in Eq. (S1) can be further expanded as follows:

$$\begin{aligned}\langle g_i^m|e^{-\gamma(q^m-q_k^m)^2}|g_j^m\rangle = &\left(\frac{2\alpha_i^{*m}}{\pi}\right)^{1/4}\left(\frac{2\alpha_j^m}{\pi}\right)^{1/4}\int \mathrm{d}q^m\,\exp[-(\alpha_i^{*m}+\alpha_j^m+\gamma)(\hat{q}^m)^2]\\ &\times\int \mathrm{d}\hat{q}^m\,\exp[(2\alpha_i^{*m}q_i^m + 2\alpha_j^m q_j^m + 2\gamma q_k^m + i(p_j^m - p_i^m))q^m]\\ &\times\exp[-(\alpha_i^{*m}(q_i^m)^2 + \alpha_j^m(q_j^m)^2 + \gamma(q_k^m)^2) + i(p_i^m q_i^m - p_j^m q_j^m)], \quad \text{(S3)}\end{aligned}$$

where the asterisk symbol means complex conjugate. Applying the standard Gaussian integral formula $\int dx\, e^{-ax^2+bx+c} = \sqrt{\frac{\pi}{a}}e^{\frac{b^2}{4a}+c}$ to Eq. (S3), we obtain the final expression:

$$\begin{aligned}\langle g_i^m|e^{-\gamma(q^m-q_k^m)^2}|g_j^m\rangle = &\left(\frac{2\alpha_i^{*m}}{\pi}\right)^{1/4}\left(\frac{2\alpha_j^m}{\pi}\right)^{1/4}\left(\frac{\pi}{\alpha_i^{*m}+\alpha_j^m+\gamma}\right)^{1/2} \quad \text{(S4)}\\ &\times\exp\left[\frac{(2\alpha_i^{*m}q_i^m + 2\alpha_j^m q_j^m + 2\gamma q_k^m + i(p_j^m - p_i^m))^2}{4(\alpha_i^{*m}+\alpha_j^m+\gamma)}\right]\\ &\times\exp\left[-(\alpha_i^{*m}(q_i^m)^2 + \alpha_j^m(q_j^m)^2 + \gamma(q_k^m)^2) + i(p_i^m q_i^m - p_j^m q_j^m)\right],\end{aligned}$$

which is equivalent to Eqs. (27-28) from Ref. [1].

It is convenient to write (and implement) the vMCG equations-of-motion (EOM) in terms of the following parameters:[2]

$$\varsigma_i^m = -\alpha_i^m, \quad \text{(S5)}$$

$$\xi_i^m = 2\alpha_i^m q_i^m + ip_i^m, \tag{S6}$$

$$\eta_i^m = -\alpha_i^m (q_i^m)^2 - ip_i^m q_i^m - \frac{1}{2}\ln\left(\frac{\pi}{2\alpha_i^m}\right)^{1/2}, \tag{S7}$$

in which Eq. (S2) takes a simple form:

$$g_i(\mathbf{q},t) = \exp\left[\sum_{m=1}^{f} \varsigma_i^m (q^m)^2 + \xi_i^m q^m + \eta_i^m\right]. \tag{S8}$$

One should note that Eq. (S8) only describes separable GWPs - in the fully thawed formalism one needs to adopt a matrix form such as in Eq. (10) from Ref. [2] with the widths of the 1D Gaussians being coupled to each other within a given GWP. In terms of those new parameters defined in Eqs. (S5-S7), the formula for the 1D matrix element becomes:

$$\langle g_i^m | e^{-\gamma(q^m - q_k^m)^2} | g_j^m \rangle = \left(\frac{\pi}{-\varsigma_i^{*m} - \varsigma_j^m + \gamma}\right)^{1/2} \exp\left[\frac{(\xi_i^{*m} + \xi_j^m + 2\gamma q_k^m)^2}{4(-\varsigma_i^{*m} - \varsigma_j^m + \gamma)} - \gamma (q_k^m)^2 + \eta_i^{*m} + \eta_j^m\right]. \tag{S9}$$

Plugging Eq. (S9) into Eq. (S1) we obtain the full expression for GAP-vMCG potential energy matrix element when using $k^{\text{Full}}(\mathbf{q}, \mathbf{q}_k)$.

Apart from the usual Hamiltonian matrix elements, fully-variational vMCG EOMs also require the derivative matrix elements:[2]

$$\mathcal{H}_{ij}^{\beta 0} = \langle \frac{\partial g_i}{\partial \lambda_i^\beta} | \hat{\mathcal{H}} | g_j \rangle \,, \tag{S10}$$

where λ_i^β is the βth parameter of the ith GWP being propagated. In the frozen-width approximation only the $\boldsymbol{\xi}$ parameters (the number of which is equal to the number of degrees of freedom) are propagated, so we will only consider the $\mathcal{V}_{ij}^{\xi^n 0}$ matrix element, which is just:

$$\langle \frac{\partial g_i}{\partial \xi_i^n} | \hat{\mathcal{V}} | g_j \rangle = \langle g_i | q^n \hat{\mathcal{V}} | g_j \rangle \,. \tag{S11}$$

The analytic expression for the corresponding 1D, one-point $k^{\text{Full}}(\mathbf{q}, \mathbf{q}_k)$ matrix element can be straightforwardly obtained from Eq. (S3) by applying the standard formula for the first-order Gaussian moment integral, $\int dx\, x e^{-ax^2+bx+c} = \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}+c} \frac{b}{2a}$:

$$\begin{aligned}\langle \frac{\partial g_i^m}{\partial \xi_i^m} | e^{-\gamma(q^m - q_k^m)^2} | g_j^m \rangle &= \frac{2\alpha_i^{*m} q_i^m + 2\alpha_j^m q_j^m + 2\gamma q_k^m + i(p_j^m - p_i^m)}{2(\alpha_i^{*m} + \alpha_j^m + \gamma)} \langle g_i^m | e^{-\gamma(q^m - q_k^m)^2} | g_j^m \rangle \\ &= \frac{\xi_i^{*m} + \xi_j^m + 2\gamma q_k^m}{2(-\varsigma_i^{*m} - \varsigma_j^m + \gamma)} \langle g_i^m | e^{-\gamma(q^m - q_k^m)^2} | g_j^m \rangle \,, \end{aligned} \tag{S12}$$

where on the second line we used the parameters defined in Eqs. (S5-S7). The full multi-dimensional expression therefore reads:

$$\langle \frac{\partial g_i}{\partial \xi_i^n} | \hat{\mathcal{V}}^{\text{Full}} | g_j \rangle = \kappa^2 \sum_{k=1}^{M} \omega_k \prod_{m=1}^{f} \frac{\xi_i^{*n} + \xi_j^n + 2\gamma q_k^n}{2(-\varsigma_i^{*n} - \varsigma_j^n + \gamma)} \langle g_i^m | e^{-\gamma (q^m - q_k^m)^2} | g_j^m \rangle \,. \tag{S13}$$

The form of $k^{\text{Add}}(\mathbf{q}, \mathbf{q}_k)$ somewhat complicates the expressions for matrix elements. For the second-order additive kernel, used in the current work, they take the following forms:

$$\begin{aligned} \langle g_i | \hat{\mathcal{V}}^{\text{Add}} | g_j \rangle = \kappa^2 \sum_{k=1}^{M} \omega_k \Bigg(& \sum_{m=1}^{f} \langle g_i^m | e^{-\gamma (q^m - q_k^m)^2} | g_j^m \rangle \prod_{n \neq m}^{f} \langle g_i^n | g_j^n \rangle \\ & + \sum_{m<n}^{f} \langle g_i^m | e^{-\gamma (q^m - q_k^m)^2} | g_j^m \rangle \langle g_i^n | e^{-\gamma (q^n - q_k^n)^2} | g_j^n \rangle \prod_{o \neq m,n}^{f} \langle g_i^o | g_j^o \rangle \Bigg) \,, \end{aligned} \tag{S14}$$

$$\begin{aligned} \langle \frac{\partial g_i}{\partial \xi_i^n} | \hat{\mathcal{V}}^{\text{Add}} | g_j \rangle = \kappa^2 \sum_{k=1}^{M} \omega_k \Bigg(& \sum_{m \neq n}^{f} \langle g_i^m | e^{-\gamma (q^m - q_k^m)^2} | g_j^m \rangle \prod_{o \neq m}^{f} \langle g_i^o | g_j^o \rangle \frac{\xi_i^{*n} + \xi_j^n}{2(-\varsigma_i^{*n} - \varsigma_j^n)} \\ & + \langle g_i^n | e^{-\gamma (q^n - q_k^n)^2} | g_j^n \rangle \prod_{m \neq n}^{f} \langle g_i^m | g_j^m \rangle \frac{\xi_i^{*n} + \xi_j^n + 2\gamma q_k^n}{2(-\varsigma_i^{*n} - \varsigma_j^n + \gamma)} \\ & + \sum_{o<m \neq n}^{f} \langle g_i^o | e^{-\gamma (q^o - q_k^o)^2} | g_j^o \rangle \langle g_i^m | e^{-\gamma (q^m - q_k^m)^2} | g_j^m \rangle \prod_{p \neq o,m}^{f} \langle g_i^p | g_j^p \rangle \frac{\xi_i^{*n} + \xi_j^n}{2(-\varsigma_i^{*n} - \varsigma_j^n)} \\ & + \sum_{m \neq n}^{f} \langle g_i^m | e^{-\gamma (q^m - q_k^m)^2} | g_j^m \rangle \langle g_i^n | e^{-\gamma (q^n - q_k^n)^2} | g_j^n \rangle \prod_{o \neq m}^{f} \langle g_i^o | g_j^o \rangle \frac{\xi_i^{*n} + \xi_j^n + 2\gamma q_k^n}{2(-\varsigma_i^{*n} - \varsigma_j^n + \gamma)} \Bigg) \,, \end{aligned} \tag{S15}$$

which can be trivially obtained by using Eqs. (S9) and (S13) as well as the formula for the first-order Gaussian moment:

$$\langle \frac{\partial g_i}{\partial \xi_i^n} | g_j \rangle = \frac{\xi_i^{*n} + \xi_j^n}{2(-\varsigma_i^{*n} - \varsigma_j^n)} \prod_{m=1}^{f} \langle g_i^m | g_j^m \rangle \,. \tag{S16}$$

II. ADJUSTMENT OF KERNEL PARAMETERS

Values for parameters γ and κ have been gradually lowered from their default values of 0.5 and 1.0 (used in previous work) correspondingly with steps of 0.1 until the quality of the flux started to visually deteriorate compared to the exact result or otherwise the wavepacket propagation became less stable; then finer steps of 0.05 were used for fine-tuning. The value

for λ has been used as in previous work. Parameters obtained in this fashion should not be considered to be general for arbitrary molecular system and a proper optimization should become part of the GAP-vMCG algorithm, as we point out in the main text.

REFERENCES

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