Time-Sliced Thawed Gaussian Propagation Method for Simulations of Quantum Dynamics

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ABSTRACT: A rigorous method for simulations of quantum dynamics is introduced on the basis of concatenation of semiclassical thawed Gaussian propagation steps. The time-evolving state is represented as a linear superposition of closely overlapping Gaussians that evolve in time according to their characteristic equations of motion, integrated by fourth-order Runge—Kutta or velocity Verlet. The expansion coefficients of the initial superposition are updated after each semiclassical propagation period by implementing the Husimi Transform analytically in the basis of closely overlapping Gaussians. An advantage of the resulting time-sliced thawed Gaussian (TSTG) method is that it allows for full-quantum dynamics propagation without any kind of multidimensional integral calculation, or inversion of overlap matrices. The accuracy of the TSTG method is demonstrated as applied to simulations of quantum tunneling, showing quantitative agreement with benchmark calculations based on the splitoperator Fourier transform method.



INTRODUCTION

An outstanding challenge in chemical dynamics is the development of rigorous methods for simulations of quantum dynamics in complex molecular systems, including accurate descriptions of tunneling and coherences.¹ The main difficulty is the efficient integration of the time-dependent Schrödinger equation (TDSE). For systems with a few degrees of freedom, numerically exact methods are available, including the splitoperator Fourier transform $(SOFT)^{2-4}$ and a variety of other wavepacket propagation methods⁵⁻⁸ which have been applied for studies of collision processes 9^{-11} and femtosecond laserinduced processes.¹² However, the study of systems with more than six degrees of freedom (DOF) typically requires problemspecific Hamiltonians that partition DOFs into weakly correlated components. In particular, pseudoharmonic potentials (e.g., reaction surface Hamiltonians) with a few largeamplitude DOFs weakly coupled to a bath of harmonic oscillators, enable simulations based on MP/SOFT,¹³⁻¹⁵ or the multiconfigurational time-dependent Hartree methods (MCTDH)^{1,16,17} and its multilayer variant¹⁸ that treats correlations between tens^{19–22} or hundreds of DOFs^{23,24} by employing multiple configurations.

Approximate semiclassical methods have been developed to include quantum effects in simulations of dynamics of systems with many degrees of freedom.²⁵ One of the these approaches is the so-called *thawed Gaussian* propagation scheme also called the *Gaussian beam method*,^{26–34} based on Gaussians that evolve according to semiclassical equations of motion.^{35–37} A recent application of that methodology is the study of ultrashort electron dynamics in plasmas.³⁸ Several quantum propagation methods have been developed inspired by the thawed Gaussian wavepacket propagation scheme, including the multiple spawning approach,^{39–42} the coupled coherent states method,^{43–45} and the multiconfigurational Ehrenfest method,^{46,47}

recently combined with the spawning approach to form the multiple cloning method. 48

Quantum propagation methods that exploit re-expansion of the time-dependent state into Gaussian representations have been developed in conjunction with semiclassical⁴⁹ and splitoperator^{13–15,50,51} propagators, where the stability of the resulting propagation can be enhanced by removal of linearly dependent Gaussian components.⁵² Re-expansion has also been exploited by the basis expansion leaping algorithm,⁵³ and the Gaussian MCTDH method⁵⁴ aimed at system-bath problems.^{55,56} Its multilayer variant⁵⁷ established equations of motion for Gaussian basis functions in the MCTDH formalism, related to the local coherent state approximation approach.⁵⁸ Elimination of grid-based functions from G-MCTDH has led to the variational multiconfiguration Gaussian wavepacket (vMCG) method.^{59–64}

In this paper, we introduce a rigorous method for the simulation of quantum dynamics based on concatenation of semiclassical thawed Gaussian propagation steps. The timeevolving state is represented as a linear superposition of overlapping Gaussians that evolve in time along characteristic curves integrated by fourth-order Runge–Kutta or velocity Verlet. The expansion coefficients of the initial superposition are updated analytically after each semiclassical propagation period by implementing the Husimi transform in the basis of closely overlapping Gaussians.

An advantage of the resulting time-sliced thawed Gaussian (TSTG) method is that it allows for full-quantum dynamics

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Figure 1. Weighting function $S(p) = \sum g_i^2(p)$ (black) as a function of p, obtained with Gaussian basis elements g_i (blue) spaced by $\Delta p = \sigma$ (left), and $\Delta p = \sigma/2$ (right). We note that S(p) changes by about $\pm 1\%$ (left) whereas it only varies by $5 \times 10^{-7}\%$ (right) as a function of p within the support range of any basis function g_i .

propagation for arbitrary potential energy surfaces and avoids the need of calculating numerical multidimensional integrals, inversion of overlap matrices, or Fourier transform calculations. The method can be trivially parallelized with efficient matrix multiplication algorithms and is shown to yield accurate simulations of quantum tunneling in model systems that allow for direct comparisons to benchmark SOFT calculations. A drawback of the method when implemented with overcomplete basis sets arranged on equally spaced grids of basis Gaussians is the exponential scaling with dimensionality. However, implementations based on time-adaptive subsets of basis functions can reduce the computational effort necessary for propagation of states that remain sufficiently localized in phase space.

The paper is organized as follows. First, we introduce the derivation of the Husimi transform expansion for representation of the time-dependent wave function as well as the equations of motion for the basis Gaussians and reinitialization procedure of the TSTG method. Then, we illustrate the application of the TSTG propagation as applied to the description of tunneling dynamics including a 2-dimensional model system with strongly correlated DOF that allow for direct comparisons with benchmark calculations.

METHODS

Husimi Transform Expansion. We introduce the TSTG method as applied to the propagation of an initial state,

$$\Psi(x) = \pi^{-1/4} \alpha^{1/4} e^{-\alpha/2(x-x_0)^2 + ip_0(x-x_0)}$$
(1)

describing a 1-dimensional system, initially placed at x_0 with momentum p_0 . The Fourier transform $\hat{\Psi}$ can be represented according to the Fast Gaussian Wavepacket Transform approach,^{65,66} as follows:

$$\hat{\Psi}(p) = \sum_{i,k} c_{i,k} \hat{\phi}_{i,k}(p)$$
(2)

where

$$\hat{\phi}_{j,k}(p) = \frac{\sqrt{\Delta x}}{\sqrt{2\pi}} g_j(p) \mathrm{e}^{-ipx_k} \tag{3}$$

with

$$g_j(p) = e^{-(p-p_j)^2/\sigma^2}$$
 (4)

and expansion coefficients

$$c_{j,k} = \int \mathrm{d}p \; \hat{\psi}_{j,k}^*(p) \; \hat{\Psi}(p) \tag{5}$$

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where

$$\hat{\psi}_{j,k}(p) = \frac{\hat{\phi}_{j,k}(p)}{S(p)}$$
(6)

with

$$S(p) = \sum_{j} g_j^2(p) \tag{7}$$

We note that p_j defines the center of Gaussian $\hat{\phi}_{j,k}(p)$, in momentum space, whereas x_k corresponds to the center of the inverse Fourier transform basis functions,

$$\phi_{j,k}(x) = \frac{1}{\sqrt{2\pi}} \int \hat{\phi}_{j,k}(p) \mathrm{e}^{ipx} \,\mathrm{d}p \tag{8}$$

$$=\frac{\sqrt{\Delta x}}{\sqrt{\pi}}\frac{\sigma}{2}e^{-(\sigma^2/4)(x-x_k)^2+ip_j(x-x_k)}$$
(9)

that represent $\Psi(x)$ in the space of coordinates x,

$$\Psi(x) = \sum_{j,k} c_{j,k} \phi_{j,k}(x)$$
(10)

as obtained by the inverse Fourier transform of both sides of eq 2.

According to eq 10, the expansion coefficient can also be obtained as follows:

$$c_{i,k} = \int \mathrm{d}x \, \psi_{i,k}^*(x) \, \Psi(x) \tag{11}$$

with

$$\psi_{i,k}(x) = \frac{1}{\sqrt{2\pi}} \int \mathrm{d}p \ \mathrm{e}^{i/\hbar p x} \hat{\psi}_{i,k}(p) \tag{12}$$

Appendix A shows that any target state Ψ can be represented exactly, according to eq 2, as a linear superposition of Gaussians $\hat{\phi}_{j,k}(p)$ defined by eq 3, with expansion coefficients $c_{j,k}$ defined by eq 5. For simplicity, the basis Gaussians are equally spaced with $\Delta x = (x_k - x_{k-1})$ and $\Delta p = (p_i - p_{i-1})$, although nonuniform phase-space distributions of basis functions are also possible.

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To obtain the Husimi transform expansion, we depart from the original implementation of the fast Gaussian wavepacket transform based on $\Delta p = \sigma$,⁶⁵ because such a spacing makes $S(p) = \sum g_i^2(p)$ a complicated function of p (Figure 1a). Calculations of $c_{i,k}$ based on eq 5 thus require numerical integration, making the fast Gaussian wavepacket transform expansion numerically impractical for high dimensional problems. Instead, we construct a basis set with $\Delta p = \sigma/2$ that makes $S = \sum g_i^2(p)$ approximately constant (i.e., independent of p) within the support of any basis function g_i (Figure 1b).

In our representation with $\Delta p = \sigma/2$,

$$\hat{\psi}_{i,k}(p) = \frac{\sqrt{\Delta x}}{\sqrt{2\pi}S} e^{-(p-p_i)^2/\sigma^2 - \iota p x_k}$$
(13)

and

$$\psi_{i,k}(x) = \frac{1}{S} \frac{\sqrt{\Delta x}}{\sqrt{2\pi}} \sqrt{\frac{\sigma^2}{2}} e^{-(\sigma^2/4)(x-x_k)^2 + \iota p(x-x_k)}$$
(14)

where S is constant, allowing for *analytic* calculations of $c_{j,k\sigma}$ according to eq 11, when Ψ is defined according to eq 1. Evaluation of those Husimi transform Gaussian integrals, after substitution of eq 13 or 14 into eq 11, gives

$$c_{j,k} = \frac{\sqrt{\Delta x}}{(\alpha \pi)^{1/4}} \frac{1}{S} \sqrt{\frac{\sigma^2 \alpha}{2\alpha + \sigma^2}} e^{-(p_j - p_0)^2 / (2\alpha + \sigma^2)} \\ \times e^{-\alpha \sigma^2 (x_0 - x_k)^2 / 2(2\alpha + \sigma^2)} e^{-\iota (x_0 - x_k)(2\alpha p_j + \sigma^2 p_0) / (2\alpha + \sigma^2)}$$
(15)

We refer to the resulting Gaussian representation, introduced by eq 10 with $c_{j,k}$ defined by eq 15, as the *Huisimi transform expansion* of the TSTG propagation scheme.

TSTG Equations of Motion. $\Psi(x)$ is expanded according to eq 10 and it is evolved in time by moving the basis functions,

$$\phi_{i,k}(x) = \frac{\sqrt{\Delta x}}{\sqrt{2\pi Q_k}} e^{-P_k/2Q_k(x-x_k)^2 + \iota p_k(x-x_k) + \iota S_k}$$
(16)

according to the thawed Gaussian equations of motion (Appendix B), ^{26,30,34,67,68}

$$\begin{aligned} \dot{x}_{k} &= \frac{p_{k}}{m} \\ \dot{p}_{k} &= -V'(x_{k}) \\ \dot{S}_{k} &= p\dot{x}_{k} - \left(V(x_{k}) + \frac{p_{k}^{2}}{2m}\right) \\ \dot{Q}_{k} &= i\frac{p_{k}}{m} \\ \dot{P}_{k} &= iV''(x_{k})Q_{k} \end{aligned}$$
(17)

which can be accurately integrated by fourth-order Runge– Kutta, or velocity Verlet algorithms.

The evolution of the basis set parameters, according to eq 17, ensures that $\phi_{i,k}(x)$ evolves according to the TDSE so long as V(x) is harmonic within the support of $\phi_{i,k}(x,t)$ (Appendix B). Such a propagation scheme, known as the *thawed Gaussian* (or *Gaussian beam*) method,^{26,30,34,67,68} is usually accurate only for a short propagation period τ . Beyond that time, $\phi_{i,k}(x,t)$ typically gets wider and eq 17 no longer reproduce the TDSE because V(x) can no longer be approximated as harmonic throughout the whole support of $\phi_{i,k}(x,t)$.

To bypass the limitations of the thawed Gaussian method and perform accurate long-time simulations, we interrupt the semiclassical propagation after a short time τ , as proposed before,^{49,65} and we reinitialize the state by re-expanding the time-evolved basis functions $\phi_{i,k}(x,\tau)$ in terms of the original functions $\phi_{i,k}(x,0)$, using the Husimi transform:

$$\phi_{j,k}(x,\tau) = \sum_{j',k'} \tilde{c}_{j',k'}^{j,k}(\tau) \phi_{j',k'}(x,0)$$
(18)

where

$$\tilde{c}_{j',k'}^{j,k}(\tau) = \frac{\Delta x}{S\sqrt{2\pi}} \sqrt{\frac{\gamma_{\tau}\gamma}{(\gamma_{\tau}+\gamma)}} \\ \times e^{-1/2(\gamma_{\tau}+\gamma)[(p_{j'}-p_{j}(\tau;k))^{2}+\gamma_{\tau}\gamma(x_{k}(\tau;j)-x_{k'})^{2}]} \\ \times e^{i(S_{\tau}^{j,k}-(x_{k}(\tau;j)-x_{k'})(\gamma_{\tau}p_{j'}+\gamma p_{j}(\tau;k))/(\gamma_{\tau}+\gamma))}$$
(19)

with $\gamma_{\tau} = P_{\tau}^{j,k}/Q_{\tau}^{j,k}$ and $\gamma = \sigma^2/2$. According to eq 19, the timeevolved wave function is represented in the original basis set, as follows:

$$\Psi(x,\tau) = \sum_{j,k} c_{j,k} (\sum_{j',k'} \tilde{c}_{j',k'}^{j,k}(\tau) \phi_{j',k'}(x))$$

=
$$\sum_{j',k'} c_{j',k'}(\tau) \phi_{j',k'}(x)$$
 (20)

where

$$c_{j',k'}(\tau) = \sum_{j,k} c_{j,k} \tilde{c}_{j',k'}^{j,k}(\tau)$$
(21)

The re-expansion after semiclassical propagation completes a TSTG propagation step for time τ , which is then repeated N times to evolve the system for time $t = N \times \tau$. As presented in this section, it is clear that the resulting propagation scheme avoids the need of computing any kind of multidimensional integrals, inversion of overlap matrices, or numerical Fourier transform. Computations can be trivially parallelized with efficient matrix multiplication algorithms.

Multidimensional Systems. We implement the TSTG method for multidimensional systems, with n coupled DOFs, assuming that the initial state is a Gaussian,

$$\Psi(\mathbf{x}) = e^{i[(\mathbf{x}-\mathbf{x}_0)\cdot\mathbf{A}_0\cdot(\mathbf{x}-\mathbf{x}_0)+\mathbf{p}_0\cdot(\mathbf{x}-\mathbf{x}_0)+\gamma_0]}$$
(22)

where \mathbf{x}, \mathbf{x}_0 , and \mathbf{p}_0 are real *n*-dimensional vectors, and \mathbf{A}_0 is an $n \times n$ complex symmetric matrix. γ_0 is a complex number that includes the phase and normalization variables. More general initial states can be defined as linear combinations of Gaussians.

To solve the TDSE, we expand the initial state as a linear superposition of products of one-dimensional Gaussians,

$$\Psi(\mathbf{x}) = \sum_{\mathbf{i},\mathbf{k}} c_{\mathbf{i},\mathbf{k}} \phi_{\mathbf{i},\mathbf{k}}(\mathbf{x})$$
(23)

with

$$\phi_{\mathbf{i},\mathbf{k}}(\mathbf{x}) = \prod_{d=1}^{n} \phi_{i_d,k_d}(x_d)$$
(24)

where $\mathbf{i} = (i_1, ..., i_n)$ and $\mathbf{k} = (k_1, ..., k_n)$ are *n*-dimensional indices that enumerate the basis functions $\phi_{i_d,k_d}(\mathbf{x}_d)$. Using a Gaussian basis lends itself naturally to on-the-fly computions, using quantum chemistry algorithms that include the analytical Hessians.

The expansion coefficients $c_{i,k}$ are defined, according to eq 11, as follows:

$$c_{i,k} = \int dx_1 \cdots dx_n \prod_{d=1}^n \psi_{i_d,k_d}^*(x_d) \Psi(x_1,...,x_n)$$
(25)

where the weighted basis functions $\psi_{i_d,k_d}(x_d)$ are defined, according to eq 14, as follows:

$$\Psi_{i_d,k_d}(x_d) = \frac{1}{S_d} \frac{\sqrt{\Delta x_d}}{\sqrt{2\pi}} \sqrt{\frac{\sigma_d^2}{2}} e^{-\sigma_d^2/4(x_d - x_{kd})^2 + \iota p_d(x_d - x_{kd})}$$
(26)

Expansion Coefficients. We note that the *n*-dimensional integral, introduced by eq 25, is not factorable when A_0 has off-diagonal elements different from zero. To integrate eq 25 analytically, we implement a coordinate transformation, as described below. First, we substitute Ψ and $\psi_{i_dk_d}(x_d)$ as defined by eqs 23 and 26, respectively, and we group terms of the same order of **x**, as follows:

$$\begin{aligned} c_{\mathbf{i},\mathbf{k}} &= \int dx_{1} \cdots dx_{n} \left(\prod_{d=1}^{n} \frac{\sigma_{d} \sqrt{\Delta} x_{d}}{2S_{d} \sqrt{\pi}} \right) \\ &\times \exp \left[- (x_{1} - x_{k_{1}}, \dots, x_{n} - x_{k_{n}}) \left(\frac{\sigma_{1}^{2}}{4} & 0 \\ \vdots \\ 0 & \frac{\sigma_{n}^{2}}{4} \right) \left(x_{1} - x_{k_{1}} \\ \vdots \\ x_{n} - x_{k_{n}} \right) - \iota(p_{1}, \dots, p_{n}) \left(\frac{x_{1} - x_{k_{1}}}{x_{n} - x_{k_{n}}} \right) \right] \\ &\times \exp \left[\iota \left[(x_{1} - x_{01}, \dots, x_{n} - x_{0n}) \left(\frac{A_{011}}{5} & \dots & A_{01n} \\ \vdots \\ A_{0n1} & \dots & A_{0nn} \right) \left(\frac{x_{1} - x_{01}}{s_{n} - x_{0n}} \right) + (p_{01}, \dots, p_{0n}) \left(\frac{x_{1} - x_{01}}{s_{n} - x_{0n}} \right) + \gamma_{0} \right] \\ &= N_{c} \int dx_{1} \cdots dx_{n} \exp \left[-(x_{1} - x_{01}, \dots, x_{n} - x_{0n}) A_{0} \left(\frac{x_{1} - x_{01}}{s_{N} - x_{0n}} \right) + B \left(\frac{x_{1} - x_{01}}{s_{n} - x_{0n}} \right) + \gamma \right] \end{aligned}$$

$$\tag{27}$$

where

$$\begin{split} N_{c} &= \prod_{d=1}^{n} \frac{\sigma_{d} \sqrt{\Delta x_{d}}}{2S_{d} \sqrt{\pi}} \\ \gamma &= i\gamma_{0} - \sum_{d=1}^{n} \frac{\sigma_{d}^{2}}{4} (x_{0d} - x_{kd})^{2} - i \sum_{d=1}^{n} p_{id} (x_{0d} - x_{kd}) \\ \mathbf{B} &= \begin{pmatrix} ip_{01} - ip_{i1} - \frac{\sigma_{1}^{2}}{2} (x_{01} - x_{k1}) \\ \vdots \\ ip_{0n} - ip_{in} - \frac{\sigma_{n}^{2}}{2} (x_{0n} - x_{kn}) \end{pmatrix} \\ \mathbf{A}_{0}' &= \begin{pmatrix} \frac{\sigma_{1}^{2}}{4} - iA_{011} & -iA_{012} & \dots & -iA_{01n} \\ -iA_{012} & \frac{\sigma_{2}^{2}}{4} - iA_{022} & \dots & -iA_{02n} \\ \vdots & \vdots & \ddots & \vdots \\ -iA_{0n1} & -iA_{0n2} & \dots & \frac{\sigma_{n}^{2}}{4} - iA_{0nn} \end{pmatrix} \end{split}$$

 A'_0 is a complex symmetric matrix that can be diagonalized by using an orthogonal coordinate transformation defined by the unitary matrix U, described in Appendix C. Therefore,

$$c_{i,k} = N_{c} \int dx_{1} \cdots dx_{n} \exp \left[-(x_{1} - x_{01}) \dots x_{n} - x_{0n}) \mathbf{A}_{0} \begin{pmatrix} x_{1} - x_{01} \\ \vdots \\ x_{n} - x_{0n} \end{pmatrix} \right] \\ + \mathbf{B} \begin{pmatrix} x_{1} - x_{01} \\ \vdots \\ x_{n} - x_{0n} \end{pmatrix} + \gamma \\ = N_{c} \left| \frac{\partial(x_{1}, \dots, x_{n})}{\partial(\xi_{1}, \dots, \xi_{n})} \right| \int d\xi_{1} \cdots d\xi_{n} \exp \left[(\xi_{1}, \dots, \xi_{n}) \begin{pmatrix} a_{1} & 0 \\ \ddots \\ 0 & a_{3}4 \end{pmatrix} \begin{pmatrix} \xi_{1} \\ \vdots \\ \xi_{n} \end{pmatrix} \right] \\ + (b_{1}, \dots, b_{n}) \begin{pmatrix} \xi_{1} \\ \vdots \\ \xi_{n} \end{pmatrix} + \gamma \\ = N_{c} \pi^{n/2} e^{\gamma} \prod_{d=1}^{n} a_{d}^{-1/2} e^{b_{d}^{2}/4a_{d}}$$
(29)

where we have introduced the substitutions $\left|\frac{\partial(x_1,...,x_n)}{\partial(\xi_1,...,\xi_n)}\right| = 1$ and **BU** = $(b_1, ..., b_n)$.

Propagation. The basis functions are initialized as follows

$$\phi_{\mathbf{i},\mathbf{k}}(\mathbf{x}) = e^{i[(\mathbf{x}-\mathbf{x}_k)\mathbf{A}(\mathbf{x}-\mathbf{x}_k)+\mathbf{p}_i(\mathbf{x}-\mathbf{x}_k)+\gamma]}$$
(30)

with

D

(28)



Figure 2. Comparison of |C(t)| (a) and Re[C(t)] (b) calculated by the weighted Gaussian method (black) and the reference SOFT method (blue).

$$\mathbf{A} = \begin{pmatrix} \frac{\sigma_1^2}{4} & 0\\ & \ddots & \\ 0 & \frac{\sigma_n^2}{4} \end{pmatrix}$$
$$\mathbf{p}_i = (p_{i_1}, p_{i_2}, \dots, p_{i_n})$$
$$\mathbf{x}_k = (x_{k_1}, x_{k_2}, \dots, x_{k_n})$$
$$\gamma = -\iota \sum_{d=1}^n \ln \left(\frac{\sigma_d \sqrt{\Delta x_d}}{2\sqrt{\pi}} \right)$$
(31)

and propagated by integration of the following equations of motion: 69

$$\dot{x}_{k} = \mathbf{p}_{i} \cdot \mathbf{m}^{-1}$$

$$\dot{\mathbf{p}}_{i} = -\mathbf{V}_{k}'$$

$$\dot{A} = -2 \operatorname{Am}^{-1} \mathbf{A} - \frac{1}{2} \mathbf{V}_{k}''$$

$$\dot{\gamma} = \iota \operatorname{Tr}[\operatorname{Am}^{-1}] + \frac{1}{2} \mathbf{p}_{i} \mathbf{m}^{-1} \mathbf{p}_{i} - V_{k} \qquad (32)$$

where V_k is the potential, \mathbf{V}'_k the gradient of the potential, and \mathbf{V}''_k the $n \times n$ matrix of second derivatives of the potential evaluated at $\mathbf{x} = \mathbf{x}_k$.

The integration of the equations of motion, introduced by eq 32, is performed by using velocity Verlet, or fourth-order Runge–Kutta algorithms. The evolution is interrupted after a short time τ and the time-evolved basis functions are re-expanded in the original basis, as follows:

$$\phi_{\mathbf{j},\mathbf{k}}(\mathbf{x},\tau) = \sum_{\mathbf{j}',\mathbf{k}'} \tilde{c}_{\mathbf{j}',\mathbf{k}'}^{\mathbf{j},\mathbf{k}'}(\tau) \ \phi_{\mathbf{j}',\mathbf{k}'}(x,0)$$
(33)

where $\tilde{c}_{j',k'}^{j,k}(\tau)$ are defined analogously to eq 29, allowing for reexpansion of the time-evolved wavepacket, as follows:

$$\Psi(\mathbf{x};\tau) = \sum_{\mathbf{i},\mathbf{k}} c_{\mathbf{i},\mathbf{k}} \phi_{\mathbf{i},\mathbf{k}}(t)$$

=
$$\sum_{\mathbf{i},\mathbf{k}} c_{\mathbf{i},\mathbf{k}} (\sum_{\mathbf{i}',\mathbf{k}'} \tilde{c}_{\mathbf{i}',\mathbf{k}'}^{\mathbf{i},\mathbf{k}}(\tau) \prod_{d=1}^{n} \phi_{i_{d}'},k_{d}'}(x_{d}))$$

=
$$\sum_{\mathbf{i},\mathbf{k}} c_{\mathbf{i},\mathbf{k}}(\tau) \prod_{d=1}^{n} \phi_{i_{d},k_{d}}(x_{d})$$
(34)

which completes the propagation for a time slice τ . The procedure is then repeated *N* times until reaching the final propagation time $t = N \times \tau$.

To parallelize the program, we distribute the propagation and re-expansion of basis functions equally among processors. To reduce the computational cost, only basis functions with coefficients above a certain threshold are to be propagated and re-expanded. Re-expansion can be greatly accelerated by evaluating only Husimi transforms with basis functions within a limited range in phase space.

RESULTS

One Dimensional Double-Well Potential. We consider modeling tunneling in a 1-dimensional double-well potential that allows for direct comparisons with benchmark calculations based on the split operator Fourier transform (SOFT) method.

The double-well model system is described by the Hamiltonian

$$H = \frac{p^2}{m} + V \tag{35}$$

with

$$V(x) = \frac{x^4}{16\eta} - \frac{x^2}{2}$$
(36)

which is expressed in atomic units, with $\hbar = 1$, m = 1, and $\eta = 1.3544$. Though simple, this 1-dimensional model has been shown to defeat the capabilities of rigorous semiclassical methods such as the Herman–Kluk semiclassical initial value representation.⁴⁹

The initial wave function is defined, as follows:

$$\Psi(x,0) = \pi^{-1/4} e^{-(1/2)(x+2\sqrt{\eta})^2}$$
(37)

corresponding to an electron with energy E = -1.576 au, far below the double-well energy barrier at E = 0 au.

SOFT simulations are implemented with a 256 point grid in the range $x \in (-8, +8)$. Husimi transform expansions for



Figure 3. Comparison of 2D simulations in a quartic double-well potential (top left, and gray background, black contours). Quantum density determined with SOFT (blue contours) and TSTG (white contours) show good agreement in the description of tunneling dynamics.

TSTG propagation are based on 64 values of x_k in the range (-8, +8) and 32 values of p_i spanning over the range $(-8\pi, +8\pi)$. The integration time increment dt = 0.02 au is used for both SOFT and velocity Verlet propagation. Re-expansion is performed at time increments $\tau = 5 \times dt$.

Figure 2 compares SOFT and TSTG results for the survival amplitude,

$$C(t) = \int dx \ \Psi^{*}(-x,0) \ \Psi(x,t)$$
(38)

computed as the overlap between the time-dependent wave function $\Psi(x,t)$ and the mirror image of the initial state on the opposite side of the double-well, $\Psi(-x,0)$.

The comparison of Figure 2 shows that both the tunneling amplitude and period are accurately reproduced by the TSTG method, as compared to benchmark SOFT calculations.

Tunneling in a Two-Dimensional Double-Well. To illustrate the capabilities of the TSTG method as applied to the description of tunneling in a multidimensional potential energy surface that allows for comparisons with benchmark SOFT calculations, we consider the following model potential:

$$V(x_1, x_2) = \frac{x_1^4}{16\eta} - \frac{x_1^2}{2} + \frac{x_2^2}{2} + \frac{x_1 x_2}{2}$$
(39)

describing two strongly correlated DOF. Figure 3 shows contour lines of $V(x_1,x_2)$, as well as contour lines for the timedependent probability density described by the SOFT and TSTG methods.

The initial wave function was defined as follows:

$$\Psi(\mathbf{x},0) = \frac{1}{\sqrt{\pi}} e^{-(1/2)(x_1 + 2\sqrt{\eta})^2 + (1/2)x_2^2}$$
(40)

centered at $(-2\sqrt{\eta}, 0)$, which corresponds to the system in one of the double-well minima and displaced relative to the minimum along the other coordinate.

SOFT calculations were based on a 64 \times 64 grid representation with $x_1 \in (-8, +8)$, $x_2 \in (-8, +8)$, whereas the TSTG simulations were based on 48 \times 48 weighted Gaussians in the same range of coordinates, and 24 \times 24 basis functions in momentum space. The time step propagation increment dt = 0.02 au and re-expansion period $\tau = 0.1$ were chosen as for the 1-dimensional simulations.

Figure 4 compares the time-dependent tunneling probability calculated by SOFT and TSTG by integrating the probability density for $x_1 < 0$. The results show excellent quantitative agreement even for simulations of tunneling dynamics with strongly correlated reaction coordinates.



Figure 4. Plot of the tunneling population over time in twodimensional double well simulations computed with SOFT (light blue) and TSTG (black).

CONCLUSIONS

We have introduced the TSTG propagation method for accurate simulations of quantum dynamics. The method is essentially a time-sliced implementation of the semiclassical thawed Gaussian propagation scheme, with analytic concatenation of short-time propagation periods based on the Husimi transform, implemented in the limit of highly overlapping Gaussians. An advantage of the TSTG method is that it allows for full-quantum dynamics propagation without having to compute numerically any kind of multidimensional integral, inversion of overlap matrices, or numerical Fourier transforms. The efficiency of the propagation can be optimized by keeping only the Gaussians with significant contributions to the expansion and a linked list of neighboring Gaussians with significant overlap that is updated after each propagation step. When the state remains localized, such an approach can avoid the "curse of dimensionality", even when the Gaussians are kept equally spaced in phase-space. As implemented, we have demonstrated the accuracy of the TSTG method, showing quantitative agreement with full quantum mechanical SOFT simulations in the description of tunneling dynamics even in a two-dimensional model system with strongly correlated coordinates.

APPENDICES

A. Gaussian Expansion

We show that any function $\Psi(p)$ can be expanded according to eq 2, as follows:

$$\hat{\Psi}(p) = \sum_{i} g_{i}(p) \frac{g_{i}(p)}{\sum_{j} g_{j}^{2}(p)} \hat{\Psi}(p)
= \sum_{i} g_{i}(p) \int dp' \, \delta(p'-p) \frac{g_{i}(p')}{\sum_{j} g_{j}^{2}(p')} \hat{\Psi}(p')$$
(41)

We note that eq 41 is completely general. It is valid not only for functions $g_i(p)$ defined as Gaussians according to eq 4 but also for any other type of basis functions. Furthermore, the sum \sum_i could include any arbitrary set of functions $g_i(p)$ that might be uniformly (or nonuniformly) distributed.

Substituting the delta function by its discrete Fourier expansion into eq 41, we obtain

$$\begin{split} \hat{\Psi}(p) &= \sum_{i} g_{i}(p) \int \mathrm{d}p' \left(\sum_{k} \frac{\Delta x}{2\pi} \mathrm{e}^{-i(p-pr)x_{k}} \right) \frac{g_{i}(p')}{\sum_{j} g_{j}^{2}(p')} \hat{\Psi}(p') \\ &= \sum_{i,k} \frac{\sqrt{\Delta x}}{\sqrt{2\pi}} g_{i}(p) \mathrm{e}^{-ipx_{k}} \left(\int \frac{\sqrt{\Delta x}}{\sqrt{2\pi}} \frac{g_{i}(p') \mathrm{e}^{ip'x_{k}}}{\sum_{j} g_{j}^{2}(p')} \hat{\Psi}(p') \mathrm{d}p' \right) \\ &= \sum_{i,k} \hat{\phi}_{i,k}(p) c_{i,k} \end{split}$$

$$(42)$$

where $c_{i,k}$ and $\hat{\phi}_{i,k}(p)$ can be readily identified as follows:

$$c_{i,k} = \int \frac{\sqrt{\Delta x}}{\sqrt{2\pi}} \frac{g_i(p') e^{ip' x_k}}{\sum_j g_j^2(p')} \hat{\Psi}(p') \, \mathrm{d}p'$$
(43)

and

$$\hat{\phi}_{i,k}(p) = \frac{\sqrt{\Delta x}}{\sqrt{2\pi}} g_i(p) \mathrm{e}^{-\iota p x_k} \tag{44}$$

which completes the demonstration.

B. Semiclassical Equations of Motion. This section describes the integration of the time-dependent Schrödinger equation,

$$G(x) = i\hbar \frac{\partial \phi}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} - V(x,t)\phi = 0$$
(45)

according to the *thawed Gaussian* method, ^{26,30,67,68} based on the Gaussian-beam ansatz,

$$\phi(x,t) = \pi^{-1/4} \hbar^{-1/4} Q^{-1/2} e^{-\gamma(x-q)^2/(2\hbar) + i/\hbar p(x-q) + \iota S/\hbar}$$
(46)

with $\gamma = PQ^{-1}$.

We look for the equations of motion of the parameters that define $\phi(x)$ and ensure that G(x) vanishes to second order near the center of the Gaussian x = q. A Taylor expansion gives

$$G(x) = G(q) + G'(q)(x - q) + \frac{1}{2}G''(q)(x - q)^{2} + \dots$$
(47)

and making G(q) = G'(q) = G''(q) = 0, we obtain a solution to third-order accuracy (i.e., $G = O(|x - q|^3)$).

Considering that

$$i\hbar \frac{\partial \phi}{\partial t} = \left(-\dot{S} - \frac{i\hbar}{2} \frac{\dot{Q}}{Q} - i(\dot{P}Q^{-1} - PQ^{-2}\dot{Q})(x-q)^2/2 + iPQ^{-1}(x-q)\dot{q} - \dot{p}(x-q) + p\dot{q} \right) \phi$$
(48)

and

$$\frac{\hbar^2}{2m}\frac{\partial^2\phi}{\partial x^2} = \frac{\hbar^2}{2m} \left(\left[-PQ^{-1}(x-q)/\hbar + \frac{i}{\hbar}p \right]^2 - PQ^{-1}/\hbar \right) \phi$$
(49)

we obtain

$$G(x) = \left(-\dot{S} - \frac{i\hbar}{2}\frac{\dot{Q}}{Q} - i(\dot{P}Q^{-1} - PQ^{-2}\dot{Q})(x-q)^2/2 + iPQ^{-1}(x-q)\dot{q} - \dot{p}(x-q) + p\dot{q} + \frac{\hbar^2}{2m} \left[-PQ^{-1}(x-q)/\hbar + \frac{i}{\hbar}p\right]^2 - \frac{\hbar}{2m}PQ^{-1} - V(x)\psi$$
(50)

Therefore,

$$g'(x) = G(x)\frac{\phi'}{\phi} + (-i(\dot{P}Q^{-1} - PQ^{-2}\dot{Q})(x - q) + iPQ^{-1}\dot{q} - \dot{p} - \frac{\hbar}{m} \bigg[-PQ^{-1}(x - q)/\hbar + \frac{i}{\hbar}p \bigg] PQ^{-1} - V'(x))\phi$$
(51)

and

$$G''(x) = G(x)\frac{\phi''}{\phi} + G'(x)\frac{\phi'}{\phi} - G(x)\frac{{\phi'}^2}{\phi^2} + \left[G'(x)\frac{1}{\phi} - G(x)\frac{\phi'}{\phi^2}\right]\phi' + (-i(\dot{P}Q^{-1} - PQ^{-2}\dot{Q}) + \frac{1}{m}[PQ^{-1}]^2 - V''(x))\phi$$
(52)

Making G(q) = G'(q) = 0, we obtain

$$G'(q) = \left(iPQ^{-1}\dot{q} - \dot{p} - i\frac{p}{m}PQ^{-1} - V'(q)\right)\phi(q) = 0$$
(53)

This equation must be satisfied even when $\gamma = PQ^{-1}$ is real. Therefore, because the real and imaginary parts of the bracket must be zero,

$$\dot{q} = \frac{p}{m}$$
$$\dot{p} = -V'(q) \tag{54}$$

In addition,

$$G(q) = \left(-\dot{S} - \frac{i\hbar}{2}\frac{\dot{Q}}{Q} - PQ^{-1}\frac{\hbar}{2m} - V(q) - \frac{p^2}{2m} + p\dot{q}\right)\phi(q) = 0$$
(55)

which must hold true even when $\gamma = PQ^{-1}$ is imaginary. Therefore,

$$\dot{S} = p\dot{q} - \left(V(q) + \frac{p^2}{2m}\right)$$
$$\dot{Q} = i\frac{P}{m}$$
(56)

Finally,

$$G''(q) = \left(-i(\dot{P}Q^{-1} - PQ^{-2}\dot{Q}) + \frac{1}{m}[PQ^{-1}]^2 - V''(q)\right)\phi(q) = 0$$
(57)

which is verified when

$$\dot{P} = iV''(q)Q \tag{58}$$

C. Coordinate Transformation for Multi-Dimension Systems. This section describes an algorithm for diagonalizing a complex symmetric $n \times n$ matrix A with real and imaginary parts A_1 and A_2 , respectively, so that $A = A_1 + \iota A_2$. Because A is symmetric, both A_1 and A_2 are real symmetric matrices which can be diagonalized by a unitary matrix. Accordingly, we note that

$$\mathbf{R} = \begin{pmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{A}_2 & -\mathbf{A}_1 \end{pmatrix}$$
(59)

is a real symmetric matrix. Denote one of its eigenvectors as $(uv)^{T}$ where both u and v are vectors of length n. And $|(uv)^{T}| = 1$. Thus,

$$\begin{pmatrix} \mathbf{A}_1 & \mathbf{A}_2 \\ \mathbf{A}_2 & -\mathbf{A}_1 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} u\mathbf{A}_1 + v\mathbf{A}_2 \\ u\mathbf{A}_2 - v\mathbf{A}_1 \end{pmatrix} = \epsilon \begin{pmatrix} u \\ v \end{pmatrix}$$
(60)

It can be shown that U = u + iv is an eigenvector of A because

$$\mathbf{U}^{\mathrm{T}}\mathrm{A}\mathrm{U} = \mathbf{U}^{\mathrm{T}}[(\mathbf{A}_{1} + \iota\mathbf{A}_{2})(u + \iota\nu)]$$

= $\mathbf{U}^{\mathrm{T}}[(u\mathbf{A}_{1} + \nu\mathbf{A}_{2}) + \iota(u\mathbf{A}_{2} - \nu\mathbf{A}_{1})]$
= $(u + \iota\nu)^{\mathrm{T}}\epsilon(u + \iota\nu)$
= ϵ (61)

We note that (v - u) is also an eigenvector of **R** with eigenvalue $-\epsilon$. Therefore, the eigenvalues of **R** appear in pairs and the eigenvectors with positive eigenvalues form one orthonormal basis set for **A** whereas the negative form the other. The former is used for diagonalization. Applying **U** to the original coordinates, we get

$$\begin{pmatrix} \xi_1 \\ \vdots \\ \xi_n \end{pmatrix} = \mathbf{U}^{\dagger} \begin{pmatrix} x_1 - x_{01} \\ \vdots \\ x_2 - x_{02} \end{pmatrix}$$
(62)

and

$$\mathbf{U}^{\dagger}\mathbf{A}_{0}^{\prime}\mathbf{U} = \begin{pmatrix} a_{11} & 0 \\ & \ddots & \\ 0 & & a_{nn} \end{pmatrix} \qquad \mathbf{U}^{\dagger}\mathbf{U} = 1$$
(63)

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Notes

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