Quantum tunneling dynamics in multidimensional systems: A matching-pursuit description

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Rigorous simulations of quantum tunneling dynamics in model systems with up to 20 coupled degrees of freedom are reported. The simulations implement an extension of the recently developed matching-pursuit/split-operator Fourier-transform method to complex-valued coherent-state representations. The resulting method recursively applies the time-evolution operator, as defined by the Trotter expansion to second order accuracy, in dynamically adaptive coherent-state representations generated by an approach that combines the matching-pursuit algorithm with a gradient-based optimization method. © *2004 American Institute of Physics.*
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I. INTRODUCTION

Studies of atomic and molecular quantum process at the most fundamental level of theory require solving the time-dependent Schrödinger equation. In recent years, there has been significant progress in the development and application of numerically exact methods[1–13] based on the split-operator Fourier-transform (SOFT) approach,[14–16] the Chebyshev expansion,[17] or the short iterative Lanczos[18] algorithms. Unfortunately, these rigorous approaches are still limited to systems with very few degrees of freedom (e.g., molecular systems with less than three or four atoms). The major stumbling block that hinders applications to larger systems, however, is not intrinsic to the nature of these powerful integrators but rather to the typical representation of time-dependent wave functions in basis sets of orthogonal functions (or grid points). Such conventional representations require computational effort that scales exponentially with the dimensionality of the system.

Due to the limitations of rigorous approaches, studies of quantum processes in multidimensional systems are currently based on approximate methods built around mixed quantum-classical, variational, semiclassical, or path-integral ideas. However practical, these approaches require a compromise between accuracy and feasibility and rely on *ad hoc* approximations whose resulting consequences are often difficult to quantify in applications to complex (nonintegrable) dynamics. Establishing rigorous, yet practical, computational methods to integrate the time-dependent Schrödinger equation is therefore one of the important challenges in theoretical chemistry.

The matching-pursuit/split-operator Fourier-transform (MP/SOFT) method[19,20] has been recently introduced in an effort to develop a simple and rigorous time-dependent method for simulations of quantum processes in multidimensional systems, based on nonorthogonal representations. To date, however, the efficiency and accuracy of the method have been demonstrated only for the description of quantum dynamics in a one-dimensional model system.[19] The goal of this paper is to introduce a generalization of the MP/SOFT method and demonstrate its capabilities for simulations of quantum dynamics in systems with many coupled degrees of freedom.

The MP/SOFT method is based on the recursive application of the time-evolution operator, as defined by the Trotter expansion to second order accuracy, in dynamically adaptive and nonorthogonal coherent-state representations generated according to the matching-pursuit algorithm.[21] The main advantage of this approach relative to the standard grid-based SOFT method is that the coherent-state expansions allow for an *analytic* implementation of the Trotter expansion, bypassing the exponential scaling problem associated with the usual fast-Fourier-transform implementation of the propagator.

When compared to other time-dependent methods based on coherent-state expansions,[22–32] the MP/SOFT approach has the advantage of avoiding the usual need of solving a coupled system of differential equations for propagating expansion coefficients. In addition, the method overcomes the usual numerical difficulties caused by the underlying overcompleteness, introduced by nonorthogonal basis functions,[5] by implementing a successive orthogonal decomposition scheme.

As formulated in Ref. 19, however, there are two caveats worth mentioning. First, the method requires the recursive construction of overcomplete basis sets for each propagation time slice. This involves a computational effort that becomes increasingly difficult as the number of coupled degrees of freedom in the system increases. Second, the efficiency of the method is limited to the capabilities of representations based on real-valued coherent states (i.e., coherent state with real-valued coordinates, momenta, and fixed scaling parameters). The generalization of the MP/SOFT method, introduced in this paper, avoids the need of constructing overcomplete basis sets and generalizes the representations to expansions based on complex-valued coherent states (i.e., coherent state with complex-valued coordinates, momenta, and variable scaling parameters).

The capabilities of the method for efficiently describing

quantum dynamics in multidimensional model systems are demonstrated in terms of simulations of deep-tunneling quantum dynamics in model systems with up to 20 coupled degrees of freedom. Considering the limitations of numerically exact methods and the crucial roles that quantum processes play in a wide range of atomic and molecular processes (e.g., electron and proton transfer in chemical and biological reactions), this approach provides a simple computational technique to advance our understanding of a wide range of quantum processes in systems that are beyond the state-of-the-art in numerically exact time-dependent methods.

The paper is organized as follows. Section II describes the generalization of the MP/SOFT method to complex-valued coherent-state representations generated according to a computational approach that combines the matching-pursuit algorithm with a gradient-based optimization method. Section III describes the implementation of the generalized MP/SOFT method introduced in Sec. II to the description of deep tunneling in multidimensional model systems. Section IV summarizes and concludes.

II. METHODS

Consider the propagation of the N-dimensional wave function $\langle \mathbf{x}|\Psi_t\rangle$ by recursively applying the short-time approximation to the time-evolution operator defined by the Trotter expansion

$$e^{-i\hat{H}\tau} \approx e^{-iV(\hat{\mathbf{x}})\tau/2} e^{-i(\hat{\mathbf{p}}^2/2m)\tau} e^{-iV(\hat{\mathbf{x}})\tau/2}. \tag{1}$$

Here, τ is a short propagation period for the time evolution of the system as described by the Hamiltonian $\hat{H} = \hat{\mathbf{p}}^2/(2m) + V(\hat{\mathbf{x}})$. To keep the notation as simple as possible, all expressions are written in mass-weighted coordinates and atomic units, so that all degrees of freedom have the same mass m and $\hbar = 1$.

The implementation of Eq. (1) according to the generalization of the MP/SOFT method introduced in this paper can be described by the following steps.

Step 1. Decompose $\langle \mathbf{x}|\tilde{\Psi}_t\rangle \equiv \langle \mathbf{x}|e^{-iV(\hat{\mathbf{x}})\tau/2}|\Psi_t\rangle$ in a matching-pursuit coherent-state expansion,

$$\langle \mathbf{x}|\tilde{\Psi}_t\rangle \approx \sum_{j=1}^{n} c_j \langle \mathbf{x}|j\rangle. \tag{2}$$

Here, $\langle \mathbf{x}|j\rangle$ are N-dimensional coherent states,

$$(\mathbf{x}|j\rangle \equiv \prod_{k=1}^{N} A_j(k) e^{-\gamma_j(k)[x(k)-x_j(k)]^2/2} e^{ip_j(k)[x(k)-x_j(k)]}, \tag{3}$$

with *complex-valued* coordinates $x_j(k) \equiv r_j(k) + id_j(k)$, momenta $p_j(k) \equiv g_j(k) + if_j(k)$, and scaling parameters $\gamma_j(k) \equiv a_j(k) + ib_j(k)$. The normalization constants are $A_j(k) \equiv [a_j(k)/\pi]^{1/4} \exp(-1/2 a_j(k) d_j(k)^2 - d_j(k) g_j(k) - [b_j(k) d_j(k) + f_j(k)]^2/[2a_j(k)])$ and the expansion coefficients, introduced by Eq. (2), are defined as follows: $c_1 \equiv \langle 1|\tilde{\Psi}_t\rangle$ and $c_j \equiv \langle j|\tilde{\Psi}_t\rangle - \Sigma_{k=1}^{j-1} c_k \langle j|k\rangle$ for $j = 2-N$.

Step 2. Analytically Fourier transform the coherent-state expansion to the momentum representation, apply the kinetic energy part of the Trotter expansion and analytically inverse Fourier transform the resulting expression back to the coordinate representation to obtain the time evolved wave function

$$\langle \mathbf{x}|\Psi_{t+\tau}\rangle = \sum_{j=1}^{n} c_j e^{-iV(\mathbf{x})\tau/2} \langle \mathbf{x}|\tilde{j}\rangle, \tag{4}$$

where

$$\langle \mathbf{x}|\tilde{j}\rangle \equiv \prod_{k=1}^{N} A_j(k) \sqrt{\frac{m}{m + i\tau\gamma_j(k)}} \times \exp\left(\frac{\left(\frac{p_j(k)}{\gamma_j(k)} - i[x_j(k) - x(k)] \right)^2}{\left(\frac{2}{\gamma_j(k)} + \frac{i2\tau}{m} \right)} - \frac{p_j(k)^2}{2\gamma_j(k)} \right). \tag{5}$$

Note that the computational task necessary for quantum propagation, according to this approach, is completely reduced to the problem of recursively generating the coherent-state expansions introduced by Eq. (2). These expansions are obtained by combining the matching pursuit with a gradient-based optimization method as follows.

Step 1.1. Starting from an initial trial coherent state $|j\rangle$ evolve the real and imaginary components of its complex parameters $x_j(k)$, $p_j(k)$, and $\gamma_j(k)$ and locally maximize the norm of its overlap with the target state $|\langle j|\tilde{\Psi}_t\rangle|$ (the results reported in Sec. III were obtained by implementing a gradient-based optimization scheme that combines the steepest descent algorithm with the parabolic search approach.[33] The parameters $x_1(k)$, $p_1(k)$, and $\gamma_1(k)$ of the local maximum define the first coherent state $|1\rangle$ in the expansion and its corresponding expansion coefficient c_1 as follows: $|\tilde{\Psi}_t\rangle = c_1|1\rangle + |\epsilon_1\rangle$, where $c_1 \equiv \langle 1|\tilde{\Psi}_t\rangle$. Note that the residual vector $|\epsilon_1\rangle$ is orthogonal to $|1\rangle$ due to the definition of c_1.

Step 1.2. Goto step 1.1, replacing $|\tilde{\Psi}_t\rangle$ by $|\epsilon_1\rangle$, i.e., subdecompose $|\epsilon_1\rangle$ by its projection along the direction of its locally optimum match $|2\rangle$ as follows: $|\epsilon_1\rangle = c_2|2\rangle + |\epsilon_2\rangle$, where $c_2 \equiv \langle 2|\epsilon_1\rangle$. Note that $|\epsilon_2| \leqslant |\epsilon_1|$, since $|\epsilon_2\rangle$ is orthogonal to $|2\rangle$.

Step 1.2 is repeated each time on the following residue. After n successive projections, the norm of the residual vector $|\epsilon_n\rangle$ is smaller than a desired precision ϵ—i.e., $|\epsilon_n| = (1 - \Sigma_{j=1}^{n} |c_j|^2)^{1/2} < \epsilon$, and the resulting expansion is given by Eq. (2). Note that norm conservation is maintained within a desired precision, just as in a linear orthogonal decomposition, although the coherent states in the expansion are nonorthogonal basis functions. Also, note that $|c_j| \leqslant 1$ although the basis functions are nonorthogonal.

It is important to mention that the computational bottleneck of the MP/SOFT method involves the calculation of overlap matrix elements $\langle j|e^{-i\hat{V}(\mathbf{x})\tau/2}|\tilde{k}\rangle$ and $\langle j|e^{-i\hat{V}(\mathbf{x})\tau/2}|k\rangle$, where $|k\rangle$ and $|\tilde{k}\rangle$ are localized Gaussians introduced by Eqs. (3) and (5), respectively. The underlying computational task

is however trivially parallelized according to a portable single-program-multiple-data streams code that runs under the message-passing-interface environment.

The overlap integrals are most efficiently computed in applications to reaction surface Hamiltonians where a large number of harmonic modes can be *arbitrarily* coupled to a few reaction (tunneling) coordinates (see, e.g., models I and II in this paper and reaction surface Hamiltonians in Refs. 34–36). For such systems, the Gaussian integrals over harmonic coordinates can be analytically computed and the remaining integrals over reaction coordinates are efficiently obtained according to numerical quadrature techniques. For more general Hamiltonians, the overlap matrix elements can be approximated by analytic Gaussian integrals when the choice of width parameters $\gamma_j(k)$ allows for a local expansion of $V(\hat{\mathbf{x}})$ to second order accuracy. Otherwise, the quadratic approximation is useful for numerically computing the corresponding full-dimensional integrals according to variance-reduction Monte Carlo techniques.

III. RESULTS

The capabilities of the generalized MP/SOFT approach introduced in Sec. II are demonstrated in simulations of deep-tunneling quantum dynamics associated with two multidimensional model systems (models I and II, for future reference). Both model systems mimic a quantum particle, coupled to a quantum bath, tunneling through a high energy barrier. The main difference between the two models is that the effective tunneling barrier in model I is independent of the number of coupled degrees of freedom in the system, while the effective barrier in model II linearly increases with the number of degrees of freedom in the system.

The system is initially prepared in a metastable state $\langle \mathbf{x}|\Psi_0\rangle$, localized near the bottom of the well on one side of the potential energy barrier. Due to the light mass of the particle and the high energy barrier, the subsequent relaxation dynamics is highly quantum mechanical in the deep quantum tunneling regime. Tunneling is quantitatively described in terms of the correlation function $C_R(t) = \langle \Psi_R|\Psi_t\rangle$ that measures the overlap between the time-dependent wave function $|\Psi_t\rangle$ and the "mirror image" of the initial state $\langle \mathbf{x}|\Psi_0\rangle$ reflected through the center of the barrier, $\langle \mathbf{x}|\Psi_R\rangle$.

Model I is described by the following Hamiltonian:

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + V_1(\hat{x}_1) + \sum_{j=2}^{N} \left(\frac{\hat{p}_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \hat{x}_j^2 + c_j \hat{x}_j \hat{x}_{j-1} \right), \tag{6}$$

where $m_j = 1.0$ a.u., $\omega_j = 1.0$ a.u., and $c_j = 0.2$ a.u. for $j = 1-N$ and

$$V_1(\hat{x}_1) = \frac{1}{16\eta} \hat{x}_1^4 - \frac{1}{2} \hat{x}_1^2, \tag{7}$$

with $\eta = 1.3544$.

The initial wave function $\langle \mathbf{x}|\Psi_0\rangle$ is defined by the multidimensional harmonic state

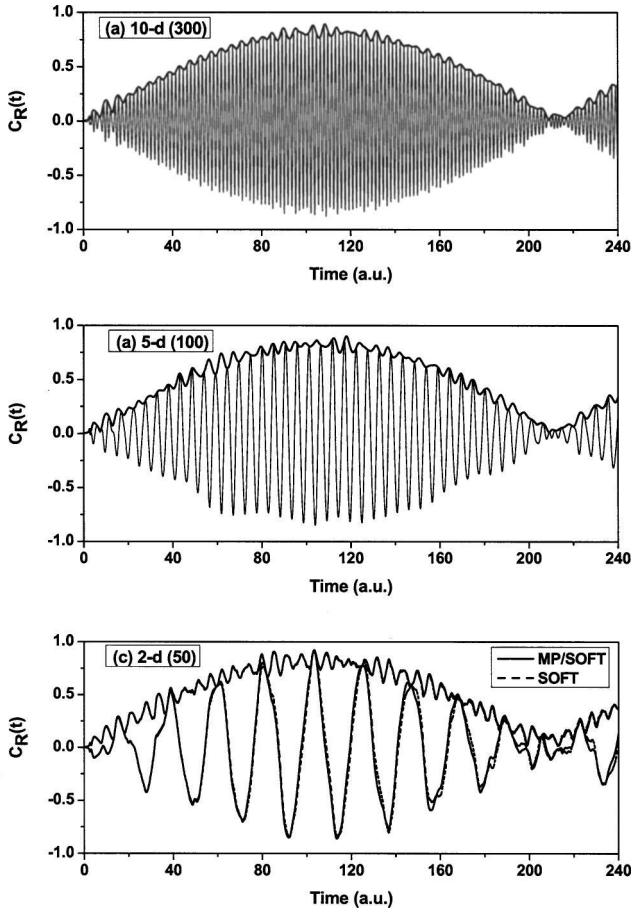

FIG. 1. Comparison of $\mathrm{Re}[C_R(t)]$ and $|C_R(t)|$ for model I with $N = 10$, 5, and 2 degrees of freedom, in panels (a), (b), and (c), respectively. Panel (c) compares the MP/SOFT results (solid lines) for $N = 2$ with benchmark grid-based SOFT calculations (dashes). The inserted labels indicate the dimensionality of the system and the number of basis elements in the MP/SOFT coherent-state expansions.

$$\langle \mathbf{x}|\Psi_0\rangle = \pi^{-N/4} \prod_{j=1}^{N} \exp[-\tfrac{1}{2}(x_j - \bar{x}_j)^2], \tag{8}$$

where $\bar{x}_1 = -2.5$ a.u., and $\bar{x}_j = 0$ for $j = 2-N$.

Figure 1 compares $C_R(t)$ for model I with $N = 10$, 5, and 2, in panels (a), (b), and (c), respectively. Panel (a) illustrates the efficiency of the MP/SOFT methodology in terms of the small number of basis functions ($n = 300$) required for the description of deep quantum tunneling in a model system with 10 coupled degrees of freedom. In contrast, analogous calculations based on the standard grid-based SOFT method would be severely hindered by the exponential scaling problem. Panels (b) and (c) show the corresponding results after reducing the dimensionality of the system to 5 and 2 degrees of freedom, respectively. These results are consistent with the form of the Hamiltonian introduced by Eq. (6). As expected, tunneling occurs along the x_1 direction, a coordinate that is coupled directly to x_2 but only indirectly to the additional degrees of freedom in the system. Therefore, decreasing the dimensionality of the system from 10 to 2, decreases the frequency of $C_R(t)$ but does not significantly affect the rate, or amount of quantum tunneling. Finally, note that panel (c) compares the MP/SOFT results for $N = 2$ (solid lines)

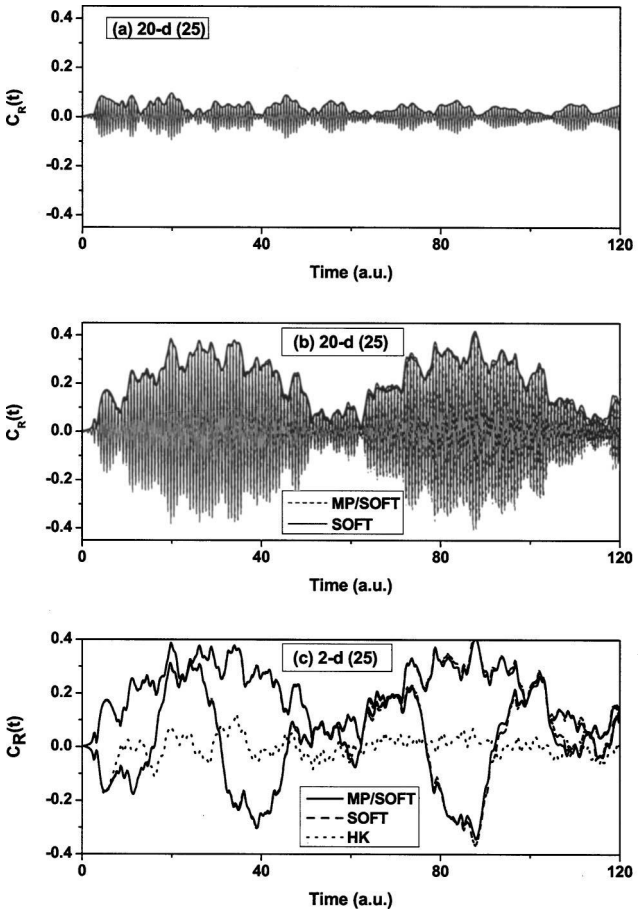

FIG. 2. Calculations of $C_R(t)$ for model II described in the text. Panel (a): 20-dimensional model system ($N=20$). Panel (b): $N=20$ and $c_j=0$. Panel (c): MP/SOFT results (solid lines) are compared to benchmark (dashes) and semiclassical (dots) calculations for $N=2$. The inserted labels indicate the dimensionality of the system and the number of basis elements in the MP/SOFT coherent-state expansions.

with benchmark SOFT calculations (dashes). The comparison shows that there is quantitative agreement with benchmark results for both the real part and modulus of $C_R(t)$ throughout the whole simulation time. The final propagation time represents 1200 propagation time slices ($\tau=0.2$ a.u.), about 60 oscillation periods at the bottom of the well where $|\Psi_0\rangle$ is initially localized.

Model II is defined by the following Hamiltonian:

$$\hat{H}=\frac{\hat{p}_1^2}{2m_1}+V_1(\hat{x}_1)+\sum_{j=2}^{N}\left(\frac{\hat{p}_j^2}{2m_j}+\frac{1}{2}m_j\omega_j^2\hat{x}_j^2+\frac{1}{2}c_j\hat{x}_1\hat{x}_j^2\right), \tag{9}$$

where V_1 is defined according to Eq. (7), $c_j=0.1$ a.u. and $m_j=1.0$ a.u. for $j=1-N$, with $N=1-20$.

Figure 2, panel (a), shows $C_R(t)$ for the 20-dimensional model II ($N=20$) computed according to the MP/SOFT method introduced in this paper. Remarkably, these efficient calculations require rather compact matching-pursuit coherent-state expansions with only 25 basis elements ($n=25$). The efficiency of these dynamically adaptive coherent-state representations is probably due to the underlying simplicity of the model Hamiltonian, where the quantum bath is defined according to a manifold of harmonic oscillators that are directly coupled only to the tunneling coordinate. The accuracy of the methodology is verified in Fig. 2, panel (b), where $C_R(t)$ for model II with $N=20$ and $c_j=0$ (solid lines) is compared with benchmark calculations (dashes). Note that the solid and dashed curves are almost completely superimposed throughout the whole simulation time, demonstrating quantitative agreement between the MP/SOFT results and benchmark calculations. In addition, note that the net effect of decoupling the harmonic bath from the reaction surface is to reduce the effective tunneling barrier, as expected. Therefore, decoupling the bath from the tunneling coordinate increases the amount of quantum tunneling without significantly affecting the frequency of the correlation function. Furthermore, Fig. 2, panel (c) compares the MP/SOFT calculations (solid lines) of $C_R(t)$ for model II with $N=2$ with benchmark calculations (dashes) and semiclassical Herman-Kluk (Ref. 37) results (dots). Note that quantitative agreement with benchmark calculations is shown not only for the phase and amplitude of $C_R(t)$ but also for all the detailed temporal structure of $C_R(t)$. Furthermore, note that the MP/SOFT calculations required matching-pursuit coherent-state expansions with only 25 basis elements. In contrast, semiclassical results obtained according to the most popular semiclassical initial value representation method[37] (dots) employed more than 2×10^4 coherent states and became increasingly difficult to converge even beyond rather short propagation times (5 a.u.), probably due to the highly quantum-mechanical nature of the deep-tunneling dynamics.

IV. CONCLUDING REMARKS

We have shown how to generalize the MP/SOFT method to complex-valued coherent-state representations. The method propagates time-dependent wave functions in terms of coherent-state expansions generated according to a successive decomposition scheme that combines the matching-pursuit algorithm with a gradient-based optimization method. The efficiency of the approach relies on the fact that, contrary to the original formulation of the MP/SOFT, the method avoids the need of generating overcomplete basis sets for each propagation time slice. In addition, the method generates more flexible (complex-valued) representations that still allow for an analytic implementation of the time-evolution operator as defined by the Trotter expansion to second order accuracy.

We have demonstrated the efficiency of the generalized MP/SOFT approach for simulations of deep-tunneling quantum dynamics in model systems with up to 20 coupled degrees of freedom. These results at least demonstrate the potentiality of a rigorous methodology for simulations of quantum processes in systems that are beyond the capabilities of the state-of-the-art in numerically exact time-dependent methods. Work in progress in our research group includes the implementation of this approach to simulations of intramolecular proton transfer dynamics[38] and calculations of equilibrium properties of quantum systems by imaginary-time propagation of the density matrix.[39]

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