

## ARTICLES

## Matching-pursuit for simulations of quantum processes

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(Received 17 December 2002; accepted 24 January 2003)

The matching-pursuit algorithm is implemented to develop an extension of the split-operator Fourier transform method to a nonorthogonal, nonuniform and dynamically adaptive coherent-state representation. The accuracy and efficiency of the computational approach are demonstrated in simulations of deep tunneling and long time dynamics by comparing our simulation results with the corresponding benchmark calculations. © 2003 American Institute of Physics.

[DOI: 10.1063/1.1560636]

## I. INTRODUCTION

Quantum dynamics simulation methods are extremely useful computational tools to study a broad range of atomic and molecular processes. Direct methods for numerically solving the time-dependent Schrödinger equation have become quite powerful due to recent advances in both methodology and computer technology.<sup>1</sup> These methods usually combine spatial-grid representations (e.g., the discrete variable representation (DVR)/pseudospectral representation<sup>2,3</sup>) with propagation schemes such as the split operator,<sup>4</sup> Chebychev,<sup>5</sup> or short iterative Lanczos<sup>6</sup> approaches. Unfortunately, these techniques require storage space and computational effort that scale *exponentially* with the number of coupled degrees of freedom. These requirements limit the applicability of rigorous approaches to systems with very few degrees of freedom (e.g., molecular systems with up to 3 or 4 atoms).<sup>7</sup> Developing rigorous quantum dynamics simulation methods that are not limited by the exponential scaling problem is, therefore, one of the important challenges in modern computational chemistry. In this paper we introduce one such method by combining the split-operator Fourier-transform (SOFT) technique<sup>4,8</sup> with a coherent-state representation generated according to the matching-pursuit (MP) algorithm.<sup>9</sup> One may think of this approach (called MP/SOFT throughout this paper) as an exact quantum mechanical version of the time-sliced coherent-state propagation method, recently developed<sup>10</sup> and implemented<sup>11</sup> according to the Herman–Kluk semiclassical initial value representation (HK/SC-IVR).<sup>12</sup>

Several authors, inspired primarily by Heller,<sup>13–15</sup> have considered overcoming the exponential scaling problem by developing propagation methods based on coherent-state representations. Work by Coalson and Karplus,<sup>16</sup> Metiu and Jackson<sup>17</sup> and Kay<sup>18</sup> is the earliest of this kind. More recently Ben-Nun and Martinez,<sup>19</sup> as well as Shalashilin and Jackson,<sup>20</sup> Andersson<sup>21</sup> and Shalashilin and Child<sup>22,23</sup> have developed approaches based on coherent-state expansions. These are rigorous collocation schemes where the expansion coefficients are propagated by solving a coupled system

of differential equations (i.e., the coupled system of differential equations obtained by substituting the coherent-state expansion into the time-dependent Schrödinger equation). Solving the system of differential equations is, however, a computational task that becomes increasingly difficult as the number of coupled degrees of freedom in the system increases. In addition, these primitive collocation methods have the drawback of over-completeness in the representation which usually leads to numerical difficulties.<sup>24</sup> In contrast, the MP/SOFT method developed in this paper bypasses the need for solving a coupled system of differential equations and implements a compact coherent-state expansion where the over-completeness is reduced by successive orthogonal projections. The main drawback of the MP/SOFT approach is, however, that it requires generating a coherent-state expansion of the time-evolved wave function for each propagation time step.

The paper is organized as follows: Section II describes the MP/SOFT method as a generalization of the SOFT method to a coherent-state representation. Section III describes the implementation of the MP algorithm to generate rapidly convergent coherent-state expansions. Section IV demonstrates the accuracy and efficiency of the MP/SOFT method by comparing our simulation results for the description of deep tunneling and long time dynamics with the corresponding benchmark calculations. Section V summarizes and concludes.

## II. MP/SOFT METHOD

The essence of the SOFT method is to time-slice matrix elements of the quantum mechanical propagator

$$K(\mathbf{x}_n, t_n | \mathbf{x}_0, t_0) = \langle \mathbf{x}_n | e^{-i\hat{H}(t_n - t_0)/\hbar} | \mathbf{x}_0 \rangle, \quad (1)$$

by repeatedly inserting the resolution of identity

$$\hat{1} = \int d\mathbf{x} |\mathbf{x}\rangle \langle \mathbf{x}|, \quad (2)$$

yielding

$$\begin{aligned} \langle \mathbf{x}_n | e^{-i\hat{H}(t_n-t_0)/\hbar} | \mathbf{x}_0 \rangle &= \int d\mathbf{x}_{n-1} \dots \int d\mathbf{x}_1 \\ &\times \langle \mathbf{x}_n | e^{-(i/\hbar)\hat{H}(t_n-t_{n-1})} | \mathbf{x}_{n-1} \rangle \dots \\ &\times \langle \mathbf{x}_1 | e^{-(i/\hbar)\hat{H}(t_1-t_0)} | \mathbf{x}_0 \rangle, \end{aligned} \quad (3)$$

where  $t_0 < t_1 < \dots < t_{n-1} < t_n$ . For sufficiently thin time slices (i.e., when  $\tau = t_k - t_{k-1}$  is sufficiently small) each finite-time propagator introduced by Eq. (3) can be approximated to second-order accuracy by the Trotter expansion

$$\begin{aligned} \langle \mathbf{x}_1 | e^{-(i/\hbar)\hat{H}\tau} | \mathbf{x}_0 \rangle &\approx \langle \mathbf{x}_1 | e^{-(i/\hbar)\hat{V}\tau/2} \text{FT}^{-1} \\ &\times e^{-(i/\hbar)\frac{\mathbf{p}^2}{2m}\tau} \text{FT} e^{-(i/\hbar)\hat{V}\tau/2} | \mathbf{x}_0 \rangle, \end{aligned} \quad (4)$$

where  $\hat{H} = (\mathbf{p}^2/2m) + \hat{V}(\mathbf{x})$ . Here, FT indicates the action of the Fourier transform,

$$\text{FT}[f] \equiv (2\pi\hbar)^{-N/2} \int_{-\infty}^{\infty} d\mathbf{x}' e^{i\mathbf{p}\cdot\mathbf{x}'} f(\mathbf{x}'), \quad (5)$$

for an  $N$ -dimensional problem and  $\text{FT}^{-1}$  indicates the action of the inverse Fourier transform, analogously. To keep the notation as simple as possible we write all expressions in mass-weighted coordinates, so that all degrees of freedom have the same mass  $m$ .

The SOFT method implements the Trotter expansion, introduced by Eq. (4), according to a lattice approach. The wave function  $\langle \mathbf{x} | \Psi_t \rangle$  is usually represented in an equidistant spatial-grid and the Fourier transform is implemented according to the fast Fourier transform (FFT) algorithm.<sup>25</sup> The propagation of  $\langle \mathbf{x} | \Psi_t \rangle$  for a time-slice  $\tau$  entails the following steps:

- Step (1): Multiplication of the wave function  $\langle \mathbf{x} | \Psi_t \rangle$  by the potential energy part of the Trotter expansion:  
 $\langle \mathbf{x} | \tilde{\Psi}_t \rangle \equiv \langle \mathbf{x} | e^{-i/\hbar \hat{V}(\mathbf{x}) \tau/2} | \Psi_t \rangle.$
- Step (2): Fourier transform to the momentum representation:  
 $\langle \mathbf{p} | \tilde{\Psi}_t \rangle \equiv \text{FT}[\langle \mathbf{x} | \tilde{\Psi}_t \rangle].$
- Step (3): Multiplication of  $\langle \mathbf{p} | \tilde{\Psi}_t \rangle$  by the kinetic energy part of the Trotter expansion:  
 $\langle \mathbf{p} | \tilde{\tilde{\Psi}}_t \rangle \equiv \langle \mathbf{p} | e^{-i/\hbar \mathbf{p}^2/2m \tau} | \tilde{\Psi}_t \rangle.$
- Step (4): Inverse Fourier transform to the coordinate representation:  
 $\langle \mathbf{x} | \tilde{\tilde{\Psi}}_t \rangle \equiv \text{FT}^{-1}[\langle \mathbf{p} | \tilde{\tilde{\Psi}}_t \rangle].$
- Step (5): Multiplication by the potential energy part of the Trotter expansion:  
 $\langle \mathbf{x} | \Psi_{t+\tau} \rangle \equiv \langle \mathbf{x} | e^{-i/\hbar \hat{V}(\mathbf{x}) \tau/2} | \tilde{\tilde{\Psi}}_t \rangle.$

This step is, however, merged with step (1) of the next propagation time slice for all but the last propagation time increment.

It is important to note that a problem requiring an order  $O(l)$  grid points (i.e., basis functions) for an accurate solution of a one-dimensional problem requires an order  $O(l^N)$

grid points for the solution of a similar problem in  $N$  dimensions. Spatial mapping techniques have been developed<sup>26</sup> to overcome this problem. However, in general, the applicability of the SOFT method is still limited to systems with very few degrees of freedom since both the storage and the FFT of multidimensional grids is prohibitive for other than very small values of  $l$  and  $N$ .

The MP/SOFT method is developed by substituting the lattice representation of  $\langle \mathbf{x} | \tilde{\Psi}_t \rangle$  by a coherent-state expansion,

$$\langle \mathbf{x} | \tilde{\Psi} \rangle = \sum_{j=1}^n a_j \langle \mathbf{x} | j \rangle, \quad (6)$$

where  $a_j$  are expansion coefficients,  $n$  is the number of terms in the expansion and  $\langle \mathbf{x} | j \rangle$  are  $N$ -dimensional coherent-states defined as follows,

$$\begin{aligned} \langle \mathbf{x} | j \rangle &\equiv \prod_{k=1}^N \left( \frac{\gamma(k)}{\pi} \right)^{1/4} e^{-\gamma(k)/2(x(k)-x_j(k))^2} \\ &\times e^{(i/\hbar)p_j(k)(x(k)-x_j(k))}, \end{aligned} \quad (7)$$

where  $x_j(k)$ ,  $p_j(k)$  and  $\gamma(k)$  are the translation, frequency modulation and scaling parameters, respectively. The main advantage of expanding  $\langle \mathbf{x} | \tilde{\Psi}_t \rangle$ , instead of expanding  $\langle \mathbf{x} | \Psi_t \rangle$ , is that such expansion allows one to compute the propagation steps (2)–(4) *analytically* even for multidimensional problems. We, thus, obtain

$$\langle \mathbf{x} | \tilde{\tilde{\Psi}} \rangle = \sum_{j=1}^n a_j \langle \mathbf{x} | \tilde{j} \rangle, \quad (8)$$

where

$$\begin{aligned} \langle \mathbf{x} | \tilde{j} \rangle &\equiv \prod_{k=1}^N \left( \frac{\gamma(k)}{\pi} \right)^{1/4} \sqrt{\frac{m}{m + i\tau\hbar\gamma(k)}} \\ &\times \exp \left( \frac{\left( \frac{p_j(k)}{\hbar\gamma(k)} - i(x(k)-x_j(k)) \right)^2}{\left( \frac{2}{\gamma_j} + \frac{i2\tau\hbar}{m} \right)} \right. \\ &\left. - \frac{p_j(k)^2}{2\gamma(k)\hbar^2} \right). \end{aligned} \quad (9)$$

Note that the MP/SOFT approach overcomes the exponential scaling problem associated with both the storage and the FFT of multidimensional wave functions. The Fourier transforms are analytically computed and, therefore, the computational task is reduced to generate a coherent-state expansion of  $\langle \mathbf{x} | \tilde{\Psi}_t \rangle$  for each propagation time-slice.

### III. MATCHING-PURSUIT EXPANSION

A popular approach to expand an  $N$ -dimensional target state  $\langle \mathbf{x} | \tilde{\Psi} \rangle$  as a linear combination of coherent-states is the importance sampling Monte Carlo (MC) technique, an approach usually implemented in conjunction with the

HK/SC-IVR.<sup>12</sup> Coherent-state parameters  $x_j(k)$  and  $p_j(k)$  are sampled from an infinitely dense set (labeled herein by  $D$ ) according to sampling functions defined in terms of the coherent-state transform  $\langle j|\tilde{\Psi}\rangle$ . The expansion coefficients are defined as  $a_j \equiv \langle j|\tilde{\Psi}\rangle$  and, therefore, the contribution of each coherent-state to the expansion is proportional to its partial overlap with the target state. Such approach is usually inefficient—i.e., it requires a large number of coherent-states (e.g.,  $n > 10^4$ ) for expanding even the simplest possible target state (e.g., a Gaussian wave function). The inefficiency is due to the *infinite redundancy* introduced by the continuous representation of nonorthogonal coherent-states. Note that even when a target state could be represented by a single basis function, it is infinitely “diluted” across the continuous coherent-state representation by virtue of the definition of the expansion coefficients  $a_j$ . This problem poses a serious computational obstacle in the re-expansion procedure required by a time-sliced propagation method. In recent work,<sup>10,11</sup> we have implemented a discretization method in an effort to improve the efficiency of the re-expansion procedure as implemented in low-dimensional problems. In this section we introduce the MP algorithm, a more general approach that drastically improves the efficiency of the re-expansion procedure.

The MP algorithm can rapidly decompose the state  $|\tilde{\Psi}\rangle$  by successive approximations through orthogonal projections on elements of  $D$ . Its implementation is described as follows:

- Step (1): Generate a slightly over-complete set  $\mathcal{F}$  of coherent-states (i.e., a subset of  $D$ ) by importance sampling MC. The sampling functions can be defined in terms of the coherent-state transform  $\langle j|\tilde{\Psi}\rangle$ .
- Step (2): Select from  $\mathcal{F}$  the coherent-state  $|1\rangle$  that has maximum overlap with  $|\tilde{\Psi}\rangle$  (i.e., the best match) and project out such component as follows,

$$|\tilde{\Psi}\rangle = c_1|1\rangle + |\varepsilon_1\rangle, \quad (10)$$

where  $c_1 \equiv \langle 1|\tilde{\Psi}\rangle$ . Note that the residual vector  $|\varepsilon_1\rangle$  is orthogonal to  $|1\rangle$ , due to the definition of  $c_1$ .

- Step (3): Go to (2), replacing  $|\tilde{\Psi}\rangle$  by  $|\varepsilon_1\rangle$ —i.e., sub-decompose  $|\varepsilon_1\rangle$  by its projection along the direction of its best match  $|2\rangle$ ,
- $$|\varepsilon_1\rangle = c_2|2\rangle + |\varepsilon_2\rangle, \quad (11)$$
- where  $c_2 \equiv \langle 2|\varepsilon_1\rangle$ . Note that, since  $|\varepsilon_2\rangle$  is orthogonal to  $|2\rangle$ ,  $|\varepsilon_2| \leq |\varepsilon_1|$ .

Step (3) is repeated each time on the following residue. After  $n$  successive orthogonal projections, the norm of the residual vector  $|\varepsilon_n\rangle$  is smaller than a desired precision  $\epsilon$ ,

$$|\varepsilon_n| = \sqrt{1 - \sum_{j=1}^n |c_j|^2} < \epsilon, \quad (12)$$

and the resulting expansion is

$$\langle \mathbf{x}|\tilde{\Psi}\rangle \approx \sum_{j=1}^n \langle j|\varepsilon_{j-1}\rangle \langle \mathbf{x}|j\rangle, \quad (13)$$

where

$$\langle j|\varepsilon_{j-1}\rangle = \langle j|\tilde{\Psi}\rangle - \sum_{k=0}^{j-1} \langle j|k\rangle \langle k|\varepsilon_{k-1}\rangle, \quad (14)$$

with  $|\varepsilon_0\rangle = |\tilde{\Psi}\rangle$ . Note that although coherent-states are non-orthogonal basis functions, norm conservation is maintained within a desired precision just as in a linear orthogonal decomposition. In addition, coherent-states could be orthogonalized relative to the previously selected coherent-states by implementing the Gram–Schmidt algorithm.<sup>27</sup> The results reported in Sec. IV, however, do not include such orthogonalization procedure.

The implementation of the MP algorithm, as described in this section, requires the computation of matrix elements  $\langle j|e^{-i/\hbar\hat{V}(\mathbf{x})\tau/2}|\bar{k}\rangle$  and  $\langle j|e^{-i/\hbar\hat{V}(\mathbf{x})\tau/2}|k\rangle$ , where states  $|\bar{k}\rangle$  and  $|k\rangle$  are the Gaussian functions introduced by Eqs. (7) and (9), respectively. In low dimensional problems these matrix elements can be efficiently computed by numerical quadrature (e.g., as implemented by Light and co-workers).<sup>28</sup> More generally, these matrix elements can be approximated by analytic Gaussian integrals when the choice of width parameters  $\gamma$  allows for an expansion of  $\hat{V}(\mathbf{x})$  to second order around  $\bar{x} \equiv (x_j + x_k)/2$ . Otherwise, the quadratic approximation is useful for numerically computing the corresponding integrals according to a variance-reduction MC technique (e.g., control-variates).<sup>29</sup>

Independently of the approach chosen to evaluate the matrix elements  $\langle j|e^{-i/\hbar\hat{V}(\mathbf{x})\tau/2}|\bar{k}\rangle$  and  $\langle j|e^{-i/\hbar\hat{V}(\mathbf{x})\tau/2}|k\rangle$ , the rate of convergence of the coherent-state expansion depends *only* on the quality of  $\mathcal{F}$  (i.e., the number of iterations required by the MP algorithm depends *only* on whether  $\mathcal{F}$  includes basis functions that overlap sufficiently well with the target state structures). The rate of convergence of the MP coherent-state expansion is, therefore, *independent* of the dimensionality of the problem. In order to illustrate this important aspect of the method consider the problem of expanding a multidimensional target state that overlaps very well with one of the elements of  $\mathcal{F}$ , so well that the norm of the residual vector generated by projecting out such element of  $\mathcal{F}$  is smaller than a desired precision. Independently of the dimensionality of the problem, the MP coherent-state expansion will immediately converge after projecting out such element of  $\mathcal{F}$  since the truncation condition will be satisfied. In contrast, the rate of convergence of a MP expansion will be very slow (even when expanding a *1-dimensional* target state) whenever the quality of  $\mathcal{F}$  is poor (i.e., whenever the basis functions in  $\mathcal{F}$  have little overlap with the target state).

## IV. RESULTS

This section tests the accuracy and efficiency of the MP/SOFT method, introduced by Secs. II and III, as applied to the simulation of electron tunneling between disjoint classically allowed regions (i.e., “deep tunneling”) in the one-dimensional double-well model system described by the following Hamiltonian:

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{16\eta}x^4 - \frac{1}{2}x^2, \quad (15)$$

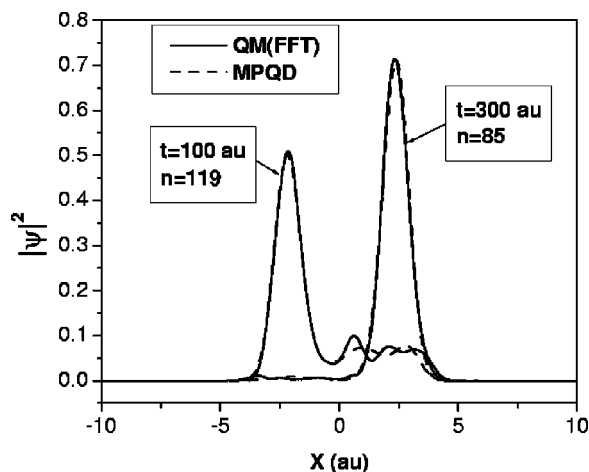


FIG. 1. Comparison of the time evolved wave function at 100 and 300 a.u., respectively, vs benchmark grid-based calculations.

where  $m = 1$  a.u. and  $\eta = 1.3544$  a.u. The model introduced by Eq. (15) is particularly interesting since it has so far defied the capabilities of *all* SC-IVR methods, except when implemented according to a time-sliced approach.<sup>10</sup>

We examine the dynamics of the system by propagating a wave packet  $\langle x | \psi_t \rangle$ , initially centered at  $x_0 = -2.5$  a.u.,

$$\langle x | \psi_0 \rangle = \pi^{-1/4} \exp(-\frac{1}{2}[x - x_0]^2). \quad (16)$$

The algorithm is implemented in terms of coherent-state basis functions with uniform widths  $\gamma = 1.0$  a.u. The overcomplete basis set  $\mathcal{F}$  is regenerated after each propagation time-slice by implementing an importance sampling MC method. Sampling functions are defined in terms of the coherent-states involved in the previous propagation time-slice. Simulations results are obtained by truncating the coherent-state expansion according to a cutoff parameter  $\epsilon = 10^{-4}$  for the norm of the residual vector. Benchmark calculations are performed according to the standard grid-based SOFT method, using an extended grid with 256 points. The time-slice interval for both the SOFT and the MP/SOFT method is  $\tau = 1.0$  a.u.

Figure 1 compares the time evolved wave function obtained according to the MP/SOFT propagation method (dashed lines) to the corresponding benchmark calculations (solid lines). Both the efficiency and accuracy of the methodology are illustrated in Fig. 1 in terms of both the small number of basis functions required for convergence ( $n = 119$  at  $t = 100$  a.u. and  $n = 85$  at  $t = 300$  a.u., respectively) and the quantitative agreement with benchmark calculations. The small deviations in the probability amplitude could be removed by further decreasing the value of the cutoff parameter  $\epsilon$ . Note that the number of basis functions required by the MP/SOFT method ( $n = 80 - 120$ ) favorably compares to the number of grid points (i.e., 256 grid points) required by benchmark quantum mechanical calculations.

In order to analyze the accuracy of the method throughout the whole simulation time, we report calculations of the time-dependent electron tunneling probability  $P(t)$ , defined as the probability of finding the electron on the right of  $x = 0$ ,

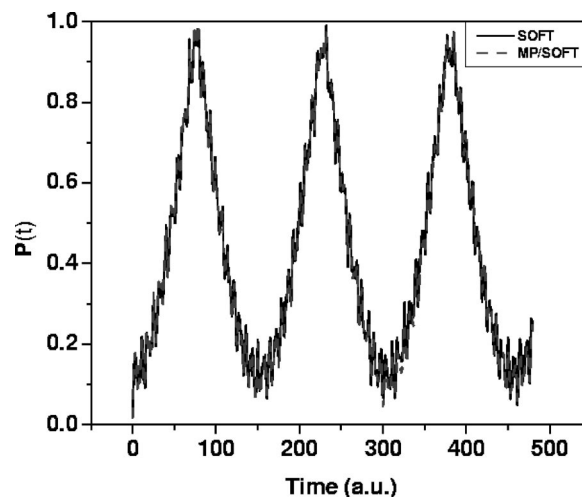


FIG. 2. Comparison of the time-dependent electron tunneling probability computed with MP/SOFT method (dashed line) vs benchmark calculations (solid line).

$$P(t) = \langle \psi_t | h | \psi_t \rangle, \quad (17)$$

where the step function  $h(x) = 1$  for  $x > 0$ , and 0 otherwise.

Figure 2 shows the evolution of  $P(t)$  as a function of time. The final time ( $t = 480$  a.u.) represents about 120 vibrational periods for a state that oscillates in the bottom of one of the wells. The comparison presented in Fig. 2 shows that the results obtained according to MP/SOFT propagation method quantitatively agree with benchmark calculations throughout the whole propagation time, even after several tunneling events (i.e., barrier recrossing events).

Having validated the MP/SOFT method in terms of its capability to produce accurate results, the remaining of this section analyzes its efficiency. Note that such analysis includes only expansions constructed with coherent-states of

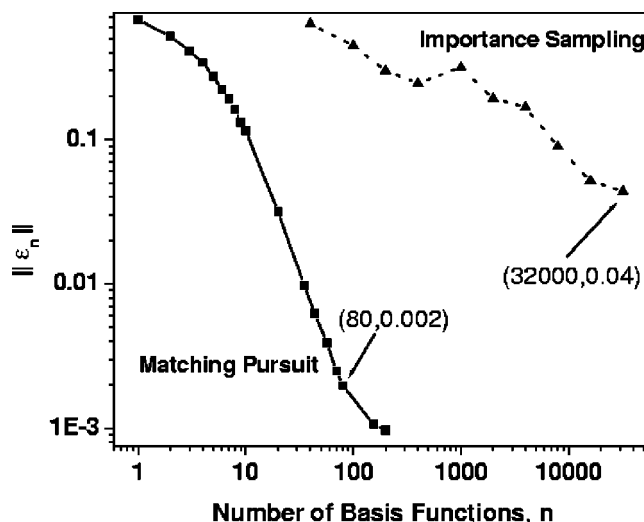


FIG. 3. Comparison of convergence rates for coherent-state expansions of a representative time evolved wave function, obtained according to the MP algorithm (solid line) and the standard importance sampling MC approach (dashed line).

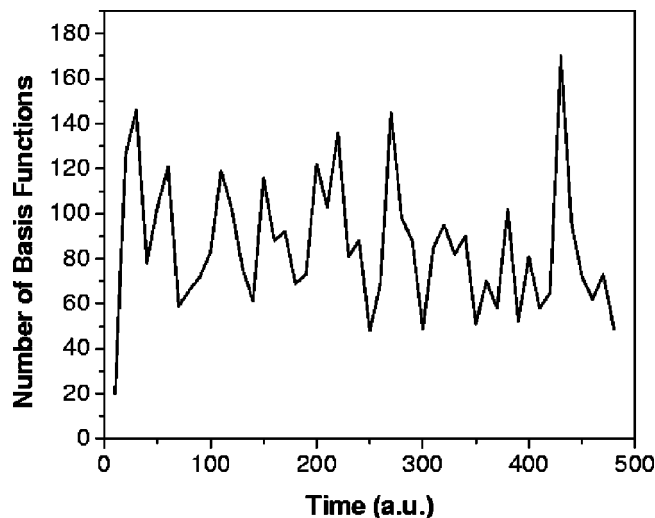


FIG. 4. Number of coherent-states necessary to represent the time evolved wave function according to the MP algorithm along the electron tunneling dynamics.

uniform widths—i.e., further optimization could still be possible by generating over-complete basis sets of coherent-states with nonuniform widths.

Figure 3 compares the efficiency of the MP algorithm versus the standard importance sampling MC technique for expanding a representative target state (e.g., the time-evolved wave function of a tunneling electron at  $t=200.0$  a.u.) in a coherent-state representation. Convergence rates are compared in terms of the norm of the residual vector,  $|\varepsilon_n|$ , as a function of the number  $n$  of coherent-states in the expansion. Figure 3 shows that the MP algorithm is able to generate a rapidly convergent coherent-state expansion. In contrast, the standard importance sampling MC technique is highly inefficient.

Figure 4 shows the number of coherent-states necessary to represent the time evolved wave function as a function of time according to the MP/SOFT propagation method. These results illustrate the efficiency of the propagation method in the description of the electron tunneling dynamics. It is important to note that the size of the basis set fluctuates in time but its mean value remains approximately constant.

## V. CONCLUDING REMARKS

We have shown in this paper how the MP/SOFT method can be implemented to simulate exact quantum dynamics according to a nonorthogonal, nonuniform and dynamically adaptive representation. The method bypasses the need for solving the coupled system of differential equations necessary to propagate expansion coefficients. Furthermore, the method overcomes the exponential scaling problem natural of grid-based methods by analytically computing the Fourier Transforms required by the SOFT approach. We have demonstrated that the MP/SOFT method accurately describes electron tunneling dynamics in a one-dimensional model system for propagation times that correspond to more than 120

oscillation periods at the bottom of one of the wells. Quantitative agreement with benchmark calculations was achieved in the description of both the time-evolved wave function and the time-dependent probability of electron tunneling. Furthermore, we have demonstrated the efficiency of the MP/SOFT algorithm in terms of the small number of coherent-states necessary to propagate the time-dependent electron wave function even after several recrossing tunneling events. We have shown that the efficiency of the MP coherent-state representation depends only on the quality of the over-complete basis set and is, therefore, independent of the dimensionality of the system. In future applications, we will implement the MP/SOFT method on higher dimensional problems.

## ACKNOWLEDGMENTS

One of the authors (V.S.B.) acknowledges a generous allocation of supercomputer time from the National Energy Research Scientific Computing Center and financial support from Research Corporation under the Research Innovation Award, from the American Chemical Society under the Petroleum Research Fund Award (type G), from the F. Warren Hellman Family under a junior faculty award, and from the Provost's office at Yale University under the start-up package funds.

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