Matching-pursuit/split-operator-Fourier-transform computations of thermal correlation functions

Xin Chen, Yinghua Wu, and Victor S. Batista

Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

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A rigorous and practical methodology for evaluating thermal-equilibrium density matrices, finite-temperature time-dependent expectation values, and time-correlation functions is described. The method involves an extension of the matching-pursuit/split-operator-Fourier-transform method to the solution of the Bloch equation via imaginary-time propagation of the density matrix and the evaluation of Heisenberg time-evolution operators through real-time propagation in dynamically adaptive coherent-state representations. © 2005 American Institute of Physics.

I. INTRODUCTION

Rigorous and practical quantum-mechanical methods for computations of equilibrium and dynamical properties of complex systems (e.g., systems with many degrees of freedom) have yet to be established. This paper introduces one such method as an extension of the recently developed matching-pursuit/split-operator-Fourier-transform (MP/SOFT) method to calculations of thermal-equilibrium averages and finite-temperature time-dependent expectation values and time-correlation functions.

In recent years, there has been significant progress in the development of numerically exact methods for quantum dynamics propagation based on the SOFT approach, the Chebyshev expansion, or the short iterative Lanczos algorithms. These rigorous approaches, however, are limited to systems with very few degrees of freedom (e.g., molecular systems with less than three or four atoms) since they require storage space and computation effort that scale exponentially with the number of coupled degrees of freedom. Such an exponential scaling problem has limited studies of thermal correlation functions of complex systems to approximate methods built around semiclassical approximations, mixed quantum-classical treatments, centroid molecular dynamics, analytic-continuation of imaginary-time path-integral Monte Carlo data, or the self-consistent mode-coupling theory. However practical, these approximate 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. It is, therefore, essential to develop practical methods for rigorous computations of time-correlation functions of complex systems. Such methods would allow one to validate approximate approaches and provide new insights into the nature of quantum processes.

The MP/SOFT method has been recently introduced in an effort to develop a simple and rigorous time-dependent method for simulations of quantum processes in multidimensional systems. The MP/SOFT methodology is based on the recursive application of the time-evolution operator, as defined by the Trotter expansion to second-order accuracy, in nonorthogonal and dynamically adaptive coherent-state representations generated according to the matching-pursuit algorithm. 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 fast-Fourier-transform algorithm of usual grid-based implementations. When compared to other time-dependent methods based on coherent-state expansions, the MP/SOFT method has the advantage of avoiding the usual need of propagating expansion coefficients by solving a coupled system of differential equations. Further, the MP/SOFT method implements a successive orthogonal decomposition scheme that overcomes the usual numerical difficulties due to overcompleteness introduced by nonorthogonal basis functions. The main drawback of the MP/SOFT method is that it requires generating a new coherent-state expansion of the time evolving state for each propagation step, although the underlying computational task can be trivially parallelized.

The capabilities of the MP/SOFT method for simulations of quantum dynamics in multidimensional systems have already been demonstrated as applied to simulations of tunneling dynamics in model systems with up to 35 coupled degrees of freedom. There is, however, the nontrivial question as to whether such an approach can be efficiently implemented to provide accurate descriptions of thermal-equilibrium density matrices, finite-temperature time-dependent expectation values and time-correlation functions. This paper shows that the MP/SOFT methodology can indeed be effectively applied to computations of thermal correlation functions simply by combining the imaginary-time propagation of equilibrium density matrices with the evaluation of Heisenberg time-evolution operators via real-time propagation in dynamically adaptive coherent-state representations. While the paper is focused only on validating the MP/SOFT methodology by performing rigorous comparisons with benchmark calculations for reduced dimensional model systems, the results at least demonstrate the potentiality of...
the MP/SOFT method as applied to the description of thermal correlation functions of complex (i.e., nonintegrable) quantum systems.

The paper is organized as follows. Section II describes the generalization of the MP/SOFT method to calculations of finite-temperature equilibrium density matrices by imaginary-time integration of the Bloch equation and the calculation of thermal correlation functions through evaluation of Heisenberg time-evolution operators via real-time propagation. Section III describes the implementation of the MP/SOFT method, as generalized in Sec. II, to the description of finite-temperature time-dependent expectation values and thermal correlation functions for a model system that allows for rigorous comparisons with benchmark calculations. Section IV summarizes and concludes.

II. METHODS

Consider the problem of computing thermal correlation functions,

\[ C(t) = \langle A(0)B(t) \rangle = Z^{-1} \text{Tr}\left[ e^{-\beta \hat{H}_0} \hat{A} e^{i \hat{H}_1 t} \hat{B} e^{-i \hat{H}_1 t} \right], \]

where \( \langle \cdots \rangle \) indicates the Boltzmann ensemble average at temperature \( T=1/(k_B \beta) \), with \( k_B \) the Boltzmann constant; \( \hat{A} \) and \( \hat{B} \) are quantum-mechanical operators associated with measurements of observables at time 0 and \( t \), respectively; \( Z=\text{Tr}[e^{-\beta \hat{H}_0}] \) is the canonical partition function; and \( \hat{H}_1 = -\nabla_x^2/(2m) + V(x) \) is the Hamiltonian of the system of interest with \( N \) degrees of freedom interacting according to the potential \( V(x) \). An example is the correlation function \( C(t) \) for a system evolving on the excited state potential energy surface \( V(x) \), as would result from a photoexcitation process after the initial preparation at thermal equilibrium in the ground state potential energy surface \( V_0(x) \). 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 \( \hbar = 1 \).

Note that Eq. (1) provides an expression for computing not only time-dependent thermal correlation functions but also thermal-equilibrium ensemble averages \( \langle \hat{A} \rangle = Z^{-1} \text{Tr}[e^{-\beta \hat{H}_0} \hat{A}] \), when \( \beta = 1 \), and finite-temperature time-dependent ensemble averages,

\[ \langle B(t) \rangle = Z^{-1} \text{Tr}[e^{-\beta \hat{H}_0} e^{i \hat{H}_1 t} \hat{B} e^{-i \hat{H}_1 t}]. \]

when \( \hat{A} = 1 \).

Thermal correlation functions \( C(t) \) are obtained according to the following symmetric form of Eq. (1):

\[ C(t) = Z^{-1} \int dx \int dx' \int dx'' \langle x''|e^{-(\beta^2 t)|\hat{H}_0|}x'\rangle \hat{A}(x') \times \langle x'|e^{i \hat{H}_1 t} \hat{B} e^{-i \hat{H}_1 t} x''\rangle |e^{-(\beta^2 t)|\hat{H}_0|} x\rangle. \]

The computational task necessary to obtain \( C(t) \), according to Eq. (3), requires obtaining the matrix elements \( \hat{A}(x') \times \langle x'|e^{-(\beta^2 t)|\hat{H}_0|} x\rangle \) and \( \langle x''|e^{-(\beta^2 t)|\hat{H}_0|} x\rangle \) and the subsequent real-time propagation for time \( t \), according to \( \hat{H}_1 \). The matrix elements are computed, as described below by imaginary-time integration of the Bloch equation according to \( \hat{H}_0 \). The extension of the MP/SOFT method, introduced in this paper, involves the numerically exact treatment of both the real- and imaginary-time propagation steps as described below for the imaginary-time propagation. The real-time propagation is analogously performed by simply implementing the variable transformation \( \beta \rightarrow -i\tau/\hbar \) from imaginary to real time.

The Boltzmann-operator matrix elements are obtained by solving the Bloch equation,

\[ \left\{ \frac{\partial}{\partial \beta} - \frac{1}{2m} \nabla_x^2 + V_0(x) \right\} \rho(x,x';\beta) = 0, \]

for \( \rho(x,x';\beta) = \langle x|e^{-\beta \hat{H}_0}|x'\rangle \) subject to the initial condition given by the high-temperature approximation,

\[ \rho(x,x';\epsilon) = \left( \frac{m}{2\pi \epsilon} \right)^{1/2} e^{-\epsilon/2[V_0(x)+V_0(x')]}, \]

where \( \epsilon \) defines a sufficiently high temperature \( T=1/(k_B \epsilon) \). Equation (4) is formally integrated as follows:

\[ \rho(x,x';\beta) = \int dx''\rho(x,x'';\beta-\epsilon)\rho(x'',x';\epsilon), \]

where the propagator \( \rho(x,x'';\beta-\epsilon) = \langle x|e^{-(\beta-\epsilon)\hat{H}_0}|x''\rangle \) is imaginary time sliced by repeatedly inserting the resolution of identity,

\[ \mathbf{i} = \int dx_j|x_j \rangle \langle x_j|, \]

yielding

\[ \langle x|e^{-(\beta-\epsilon)\hat{H}_0}|x''\rangle = \int dx_{j-1} \ldots \int dx_1 \langle x|e^{-\hat{H}_0\tau}|x_{j-1}\rangle \times \ldots \langle x_i|e^{-\hat{H}_0\tau}|x''\rangle, \]

where \( \tau = -(\beta-\epsilon)/\epsilon \) is a sufficiently thin imaginary-time slice.

Each finite-time propagator, introduced by Eq. (8), is approximated for sufficiently small imaginary-time slices \( \tau \) by the Trotter expansion to second-order accuracy,

\[ e^{-\hat{H}_0\tau} = e^{-\hat{V}(\hat{\tilde{g}}(\tau))\tau^2} e^{-i(\hat{\tilde{g}}(\tau)/2m)\tau^2} e^{-i\hat{V}(\hat{\tilde{g}}(\tau))\tau^2}. \]

The MP/SOFT propagation of the initial condition, introduced by Eq. (5), according to the Trotter expansion introduced by Eq. (9) entails the following steps.

Step 1: Decompose

\[ \bar{\rho}(x,x';\epsilon) = \sum_{j=1}^{n} c_j \phi_j(x)\phi_j^*(x'), \]

where \( \phi_j(x) \) and \( \phi_j^*(x') \) are \( N \)-dimensional coherent states defined as follows:

\[ \phi_j(x) \equiv \prod_{k=1}^{N} A_{\phi}(k) e^{-\gamma_{\phi}(k)|x(k)-x_{\phi}(k)|^2/2} e^{ip_{\phi}(k)k} e^{i\eta_{\phi}(k)}, \]

with complex-valued coordinates \( x_{\phi}(k) \equiv r_{\phi}(k)+id_{\phi}(k) \), momenta \( p_{\phi}(k) \equiv g_{\phi}(k)+if_{\phi}(k) \) and scaling parameters.
The results reported in Sec. III were obtained by locally optimizing the Boltzmann-operator matrix elements and position-position thermal correlation functions for the asymmetric quartic oscillator described by the following Hamiltonian:

\[ H_1 = \frac{\hat{p}^2}{2m} + V_1(x), \]

where the product state \( \phi_1(x)[\phi'_1(x')]^* \). Therefore, the norm of the remaining residue \( \varepsilon_1(x,x') \) is smaller than the norm of the initial target state \( \tilde{\rho}(x,x';\varepsilon) \), i.e., \( \|\varepsilon_1\| < \|	ilde{\rho}\| \).

Step (1.2): Go to (1.1), replacing \( \tilde{\rho}(x,x';\varepsilon) \) by \( e_1(x,x') \), i.e., subdivide the residue by its projection along the direction of its locally optimum match as follows: 

\[ e_1(x,x') = c_2 \phi_2(x)[\phi'_2(x')]^* + \varepsilon_2(x,x'), \]

where

\[ c_2 = \int dx' dx \phi_2(x)e_1(x,x')(\phi'_2(x'))^* . \]
Therefore, the model is ideally suited for a rigorous analysis of the accuracy and efficiency of the MP/SOFT method as compared to classical, semiclassical, and benchmark quantum-mechanical calculations.

The model system, introduced by Eqs. (17)–(19), is particularly interesting since the highly anharmonic potential leads to ultrafast dephasing within a few oscillation periods as well as later rephasing of wave packet motion due to the effect of quantum coherences. The underlying dynamics can be described by rigorous quantum-mechanical approaches and has been investigated in terms of semiclassical approaches based on coherent-state representations.\cite{22,23,36} Therefore, the model is ideally suited for a rigorous analysis of the accuracy and efficiency of the MP/SOFT method as compared to classical, semiclassical, and benchmark quantum-mechanical calculations.

Figure 1 shows the time-dependent position ensemble averages \( \langle \mathbf{x}(t) \rangle \), obtained according to the MP/SOFT methodology (solid lines) and by the expansion introduced by Eq. (3), with \( A(x')=1 \) and \( \hat{B}=\hat{x} \). The MP/SOFT results are compared to the corresponding benchmark grid-based SOFT calculations (dots) and to the classical ensemble average predictions (thick-dashed lines) at two different temperatures, corresponding to \( \hbar \omega B = \sqrt{2} \) and \( \hbar \omega B = \sqrt{2}/2 \), in panels (a) and (b), respectively.

For reference, note that for a molecular vibration of \( \omega = 250 \text{ cm}^{-1} \) the two temperatures in panels (a) and (b) correspond to 254 K and 508 K, respectively.

The results shown in Fig. 1 indicate that during the early-time dynamics (i.e., within the first 20 a.u.) the relaxation of the system is dominated by classical dephasing due to the anharmonicity of the potential, a process that is faster at higher temperature. This early-time relaxation is therefore accurately described by classical mechanics, as indicated in Fig. 1 by the comparison between benchmark quantum-mechanical calculations (dots) and classical results (thick-dashed lines). Recurrences at later times, however, are due to quantum-mechanical coherences and therefore require an accurate description of coherent wave packet motion. Consequently, classical results fail to describe recurrences beyond \( t \approx 20 \text{ a.u.} \). In contrast, the MP/SOFT methodology provides a quantitative description of both the initial classical dephasing dynamics and the later quantum coherent recurrences as well as the effect of temperature on the classical and quantum relaxation time scales. The efficiency of the MP/SOFT method is demonstrated in terms of the moderate number of coherent states, required by the expansion introduced by Eq. (10), with \( n=100 \) for \( \hbar \omega B = \sqrt{2} \) and \( n=500 \) for \( \hbar \omega B = \sqrt{2}/2 \), respectively.

Figures 2 and 3 compare the real and imaginary parts of the position-position correlation functions computed according to Eq. (3), with \( A(x')=x' \) and \( \hat{B}=\hat{x} \). The MP/SOFT results (solid lines) are compared to benchmark grid-based quantum-mechanical calculations (dots) and classical Boltz-
match the quantum mechanical behavior. Note that the MP/SOFT approach provides an accurate description of both classical dephasing dynamics and quantum coherent recurrences as well as the effect of temperature on the classical and quantum relaxation time scales. While the study has been focused only on a reduced dimensional model system that allowed for rigorous comparisons with classical, semiclassical, and benchmark quantum calculations, the results reported in this paper at least demonstrate the potentiality of the MP/SOFT method as applied to the description of thermal correlation functions of complex (i.e., nonintegrable) quantum systems. Work in progress in our research group involves the application of the general computational approach introduced in this paper to studies of thermal correlation functions in multidimensional model systems.

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