Low-temperature correlation functions via forward–backward quantum dynamics

Jonathan Chen, Nancy Makri *

Department of Chemistry, University of Illinois, 601 S. Goodwin Avenue, Urbana, IL 61801, United States

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We present an extension of forward–backward quantum dynamics suitable for evaluating finite-temperature time correlation functions for one-dimensional systems at low temperatures. The procedure relies on the cooling action of the Boltzmann operator, which produces a state similar to the lowest energy eigenstate with the given symmetry. As we have shown earlier, the quantum trajectories of near-eigenstates can be integrated by a numerical procedure based on a generalization of Hamilton’s principle of stationary action. Evaluation of the trace may be performed in a generic basis set, obviating the need to calculate eigenstates. Numerical applications illustrate the method.

1. Introduction

Bohm’s hydrodynamic formulation of time-dependent quantum mechanics [1–4] has attracted considerable attention during the last decade [5–36]. Much of its appeal lies in the use of trajectories to propagate the density, although these differ dramatically from the familiar trajectories of classical mechanics. The quantum trajectories are subject to a nonclassical force that depends on spatial derivatives of the local wavefunction density [30]. This structure couples the quantum trajectories together, leading to nonlocal derivatives of the local wavefunction density. This structure continues to be challenging.

Forward–backward semiclassical methods [37–55] take advantage of the forward–backward pair of evolution operators in time correlation functions or expectation values to minimize phase cancellation, thereby alleviating the Monte Carlo sign problem. Forward–backward quantum dynamics (FBQD) [28] exploits the structure of correlation functions in two ways: (i) by obtaining a favorable initial wavefunction for the subsequent evolution of quantum trajectories; and (ii) by alleviating phase cancellation, as in the semiclassical case. Consider, for example, the position autocorrelation function

\[ C_{xx}(t) = \text{Tr} \left[ \rho_0 \hat{x} e^{i\hat{H}t/\hbar} \hat{x}^* e^{-i\hat{H}t/\hbar} \right] \tag{1.1} \]

where \( \rho_0 \) denotes the normalized density operator. In the limit of zero temperature, \( \rho_0 = |\psi_0\rangle \langle \psi_0 | \) and the correlation function becomes

\[ C_{xx}(t) = \langle \psi_0 | \hat{x} e^{i\hat{H}t/\hbar} \hat{x}^* e^{-i\hat{H}t/\hbar} | \psi_0 \rangle \tag{1.2} \]

where \(|\psi_0\rangle\) and \(E_0\) are the ground state and its energy, both presumed known. Operating from right to left, (1.2) entails a time evolution backwards to time \(-t\) starting from the “initial” state

\[ \hat{x}|\psi_0\rangle \tag{1.3} \]

applying the position operator to the result, and projecting on the ground state. For the harmonic oscillator, the initial state (1.3) is proportional to the first excited eigenstate of the Hamiltonian, and the quantum trajectories are simply stationary; thus, their integration becomes trivial in this case. In the general case of an anharmonic potential, the state \(\hat{x}|\psi_0\rangle\) will still resemble an eigenstate of \(\hat{H}\); as a result, the quantum trajectories are generally smooth and much better behaved compared to those emanating from arbitrary initial conditions [28]. Analogous arguments can be made for momentum correlation functions.

Recent work [36] described an approach based on Hamilton’s law of varying action (HLVA) [56,57], which has enabled direct, synthetic computation of FBQD trajectories for one-dimensional anharmonic systems at zero temperature, without independently obtaining the time-dependent quantum potential by conventional wavefunction or basis set methods. The stability of the zero-temperature HLVA method is governed by the similarity of the initial state \(\hat{x}|\psi_0\rangle\) to an eigenstate. Our approach led to accurate and stable computation of Eq. (1.2) for a purely quartic (and thus extremely anharmonic) oscillator, although some other potentials continue to be challenging.

The present paper describes a procedure for applying the FBQD idea to finite-temperature correlation functions, in which the density operator has the form

\[ \rho_0 = Z^{-1} e^{-\beta \hat{H}} \tag{1.4} \]

where \(\beta \equiv (k_B T)^{-1}\) and \(Z\) is the canonical partition function. Besides relaxing the assumption of zero temperature, the scheme described...
below provides a systematic and generic way of obtaining “nearly-stationary” states, thus facilitating integration of the quantum trajectories.

As is widely appreciated, the interdependence of quantum trajectories leads to scaling behavior similar to that of basis set or grid-based methods. Thus, just as in our previous work, we do not aim at formulating computational methods applicable to systems of many degrees of freedom. The practical utility that we envision for our work is in propagating the quantum trajectories in the subspace of one (or just a few) “quantum” degrees of freedom, while retaining a classical description for the heavier particles, in the context of a rigorous quantum-semiclassical approximation. In particular, the high stability and accuracy of the method for short times may prove ideal for constructing quantum-semiclassical propagators valid over large time steps, which could be used in iterative Monte Carlo path integral methods [58]. In this spirit, we assume that the Boltzmann part of the correlation function, which does not require any real-time propagation, is available by alternate methods.

In Section 2 we argue that the “cooling” action of the Boltzmann operator can be exploited to generate near-eigenstate initial conditions suitable for stable propagation. In Section 3 we present some numerical examples that illustrate the features of our method. Finally, some concluding remarks are given in Section 4.

2. Imaginary time cooling

Consider rotating the trace in (1.1) to obtain

\[ C_{xx}(t) = Z^{-1} \text{Tr} \left[ e^{iHt/\hbar} \hat{x} \ e^{-iHt/\hbar} \left( e^{-i\beta \hat{\chi}} \right) \right]. \]  

(2.1)

Evaluation of the trace in a generic basis of states \( |\phi_n\rangle \) gives

\[ C_{xx}(t) = Z^{-1} \sum_n \langle \phi_n | e^{iHt/\hbar} \hat{x} \ e^{-iHt/\hbar} \left( e^{-i\beta \hat{\chi}} \right) | \phi_n \rangle, \]  

(2.2)

and the initial state for the forward time evolution becomes

\[ e^{-i\beta \hat{\chi}} | \phi_n \rangle, \]  

(2.3)

which now includes the Boltzmann operator. Following the operations from right to left in (2.2), the system starts in a state \( |\phi_n\rangle \), gets “kicked” to the state \( \hat{x} |\phi_n\rangle \), and is then “thermalized” by the Boltzmann operator \( e^{-i\beta \hat{\chi}} \). Even in the special case where \( |\phi_n\rangle \) is the ground eigenstate of the Hamiltonian, the state \( \hat{x} |\phi_n\rangle \) may differ considerably from the first excited eigenstate if the potential is very strongly anharmonic. Further, if \( |\phi_n\rangle \) is an excited state, multiplication by \( \hat{x} \) will generate a highly non-stationary superposition of two (or more) eigenstates even in the harmonic case. Splitting the \( \hat{x} \) operator into raising and lowering operators by adding and subtracting \( \frac{1}{2} \beta \) will cure this problem only if the potential is mildly anharmonic. However, if the temperature is sufficiently low, the presence of the Boltzmann operator in Eq. (2.3) can improve the situation considerably, since its action will cool the state \( \hat{x} |\phi_n\rangle \). Namely, the state (2.3), which specifies the initial Bohmian density for the quantum trajectories, will approach the lowest energy eigenstate contributing to \( \hat{x} |\phi_n\rangle \), yielding a nearly stationary state that is ideally suited for propagation by our HLVA method. Unlike our previous zero-temperature work [36], this property of Eq. (2.2) does not rely on any special features of \( \hat{x} |\phi_n\rangle \) or on a particular choice of basis, as long as the temperature is sufficiently low (relative to the system’s eigenvalue spectrum) to achieve adequate quenching of excited state contributions.

For example, for a harmonic system \( V(x) = \frac{1}{2} \hbar \omega^2 x^2 \) and eigenstate basis, Eq. (2.2) yields

\[ C_{xx}(t) = \frac{\hbar [1 - e^{-i\beta \hbar \omega}]}{2m\omega} \left[ e^{-i\beta \hbar \omega} e^{-i\omega t} + (2 e^{-2i\beta \hbar \omega} e^{-i\omega t} + e^{i\omega t}) + \cdots \right]. \]  

(2.4)

where the terms in the square brackets originate from the ground and first excited state terms of (2.2), and only the latter survives in the limit of \( \beta \to \infty \). In general, even though the Boltzmann operator filters out high-energy states, since it does not operate directly on a basis state in Eq. (2.2), it does not guarantee that the ground state term will dominate in the limit of zero temperature. If the potential is symmetric (even), then the (odd) state \( \hat{x} |\phi_0\rangle \) will be orthogonal to the (even) ground state. So by symmetry, in the zero-temperature limit, the dominant term of (2.2) will be the ground state component of the (even) state \( \hat{x} |\phi_1\rangle \).

If the basis employed in the evaluation of the trace consists of system eigenstates, the second (backward) evolution operator amounts to a simple phase factor (operating to the left) and the backward propagation step is avoided. However, with the exception of the ground state, the system eigenstates are generally presumed unavailable. In that case, the backward propagation step will need to be carried out numerically. Since the state in Eq. (2.3) resembles an eigenstate of the Hamiltonian, it will remain similar to an eigenstate during the course of its evolution. Thus, the state

\[ e^{-i\beta \hat{\chi}} | \phi_n \rangle \]  

(2.5)

is still similar to an eigenstate of the Hamiltonian. Action with the position operator should again generate a near-eigenstate (or a sum of two near-eigenstates), which may be propagated backwards using our HLVA method as in our earlier work for zero temperature. Since there is no cooling operation immediately prior to the backward evolution step to quench any excited state components, this second propagation will prove more challenging.

Instead, we wish to exploit the cooling advantage of the Boltzmann operator in both (forward and backward) propagation steps. To achieve this, we resort to the symmetrized (or complex-time) form of the correlation function,

\[ G_{xx}(t) = Z^{-1} \text{Tr} \left[ e^{iHt/\hbar} \ e^{-i\beta /2} \ e^{-i\beta /2} \ e^{-i\beta /2} \ e^{-i\beta /2} \ e^{-iHt/\hbar} \right]. \]  

(2.6)

which is related to the standard real-time form (1.1) by the Fourier identity

\[ \tilde{C}_{xx}(\omega) = \frac{e^{i\beta \hbar \omega}}{\hbar} G_{xx}(\omega), \]  

(2.7)

where \( \tilde{f}(\omega) \equiv (2\pi)^{-1/2} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt \) denotes the Fourier transform of \( f(t) \). Eq. (2.6) involves a “cooling” operation before each real-time evolution. There are several ways to take advantage of this arrangement:

(i) Rotate the trace, use a basis set for the trace and the inner discretization, and operate with the exponential operators first. Eq. (2.6) takes the form

\[ G_{xx}(t) = \sum_{n=0}^{N} \sum_{j=0}^{N} \langle \phi_j | e^{i\beta \hbar \omega} | \phi_n \rangle \langle \phi_n | e^{-i\beta \hbar \omega} | \phi_j \rangle \langle \phi_j | e^{i\beta \hbar \omega} | \phi_j \rangle. \]  

(2.8)

Each basis function is cooled with the Boltzmann operator and propagated forward and also backward in real time. The resulting functions are multiplied by \( x \) and projected on the other basis functions.

(ii) Use a basis set for the trace and the inner discretization, and apply the cooling operation after operating with \( x \). This leads to the form

\[ G_{xx}(t) = \sum_{n=0}^{N} \sum_{j=0}^{N} \langle \phi_j | e^{i\beta \hbar \omega} | e^{-i\beta /2} \hat{x} | \phi_n \rangle \langle \phi_n | e^{-i\beta \hbar \omega} | e^{-i\beta /2} \hat{x} | \phi_j \rangle. \]  

(2.9)
In this expression, the cooling operation is applied to $\hat{x}(\varphi_\mu)$ in both matrix elements, and the result of real-time propagation is directly projected on the other basis functions.

(iii) Evaluate the trace in a discrete basis and insert a complete set of coordinate states between the forward and backward evolution operators:

$$G_{xx}(t) = \sum_{\mu=0}^{\infty} \int dx \langle \varphi_\mu | e^{-iHt/2} e^{-ib\hat{\mathcal{L}}/2} | \mathcal{X} \rangle dx | e^{iHt/2} e^{ib\hat{\mathcal{L}}/2} \rangle | \varphi_\mu \rangle. \quad (2.10)$$

Here the first and second matrix elements are evaluated as in methods (i) and (ii), respectively, using cooled basis functions as initial states, but avoiding the projection on basis functions. Since the wavefunction at the end of each propagation is available only at the instantaneous positions of the quantum trajectories, which in general are not identical for the forward and backward evolutions, interpolation is required to perform the integral over $x$. Moreover, the relative rate of cooling of (i) and (ii) has been observed to vary with system, with the most excited uncooled state cooling faster via (i) for some systems (e.g., the harmonic oscillator) and faster via (ii) for others (as in the examples presented in Section 3). The cooling effect achieved through Eq. (2.10) will be that of the less efficient of (i) and (ii).

We have found Eq. (2.9) to have a superior rate of cooling for the anharmonic oscillators studied, yielding stable results for higher temperatures, and results are given for this scheme only. The examples in the following section use the harmonic oscillator eigenstate basis, which is known analytically, to compute the symmetrized correlation function $G_{xx}(t)$.

**3. Numerical examples**

Evaluation of the symmetrized correlation function as written in Eq. (2.9) includes matrix elements of the type

$$\langle \varphi_\mu | e^{iHt/2} e^{-ib\hat{\mathcal{L}}/2} | \mathcal{X} \rangle.$$

Each term entails a propagation starting from the initial state $e^{-ib\hat{\mathcal{L}}/2} | \varphi_\mu \rangle$.

$$\exp\{iHt/2\} | \varphi_\mu \rangle,$$  

which, for sufficiently large $b$, will be “cooled” to a nearly stationary state as described in Section 2. This nearly stationary state then serves as an excellent starting point for obtaining real-time quantum trajectories. The CPU time required for obtaining the real-time trajectories and correlation function was very similar for the HLVA and the exact reference methods.

In principle, the cooling process can also be accomplished using imaginary-time quantum trajectories obtained with our HLVA procedure [36], with suitable modifications to avoid subtle issues that arise in imaginary time [29]. Alternatively, one may use truncated equation hierarchies [22,25], which lead to approximate, yet sufficiently accurate quantum trajectories in imaginary time [29]. Both of these procedures are stable and accurate for propagation to small or intermediate values of $\beta$ (high to intermediate temperature), but it seems more effort will be required to obtain accurate results at the low temperatures employed here. A third possibility is to use Gaussian representations of the Boltzmann operator [59,60]. In the examples below, the imaginary time dynamics was performed using the split-operator method [61].

As with our original zero-temperature implementation [36], we consider the quartic oscillator

$$V(x) = \frac{1}{4}x^4$$  

and the asymmetric oscillator

$$V(x) = \frac{1}{2}m\omega^2x^2 - 0.1x^3 + 0.1x^4.$$  

The mass is $m = 1$ and the harmonic frequency in the second model is $\omega = 1$. A basis of harmonic oscillator eigenstates with $\omega = 1$ was used in both cases. The symmetrized position autocorrelation functions and representative real-time trajectories for these systems are shown in Figs. 1 and 2 for temperatures corresponding to $\beta = 5$ and 10, respectively. As can be seen from the figures, the trajectories are stable and accurate at these temperatures, and the correlation functions are practically indistinguishable from the exact result. At higher temperatures there was insufficient cooling and the initial state (3.2) was highly non-stationary for certain values of $\nu$; the real-time trajectories were consequently unstable.

Interestingly, the less anharmonic but more asymmetric potential (3.4) again proved more challenging. Here, instead of problem-

![Fig. 1. Results for the quartic oscillator with $V(x) = \frac{1}{4}x^4$ with $\beta = 5$. (a) Symmetrized position correlation function $G_{xx}(t)$. The exact correlation function (solid line) was obtained from a separate basis set calculation; the approximate correlation function (points) was obtained from (2.9) with $0 \leq \mu \leq 4, 0 \leq \nu \leq 4$ using approximate Bohmian trajectories calculated as described previously [36]. (b) Approximate forward trajectories (dashed lines) starting from $e^{-ib\hat{\mathcal{L}}/2} | \varphi_\mu \rangle$. Exact trajectories (solid lines) were obtained by a separate split-operator calculation [61]. The backward trajectories for this initial state were very similar, and all other values of $\nu$ in (3.2) resulted in nearly-stationary trajectories (not shown).](image)
Fig. 2. Results for the asymmetric oscillator given in Eq. (3.4) with \( \beta = 10, 0 \leq \mu \leq 3, 0 \leq \nu \leq 3 \), and the harmonic frequency for the basis set in (2.9) was set to the harmonic frequency \( \omega = 1 \) at the well minimum, using the same methods as in Fig. 1. (a) Approximate and exact symmetrized position correlation function \( G_{xx}(t) \) (points and solid line, respectively). (b) Approximate and exact forward trajectories (points and solid lines, respectively) starting from an odd initial wavefunction (3.3), odd initial wavefunctions were cooled quickly and stably to a "metastable intermediate." In contrast, for the symmetric potential (3.1) resulted in nearly-stationary trajectories (not shown). This asymmetric oscillator proved less tractable, requiring a cooling time \( \hbar/2 \) twice as long as the symmetric but more anharmonic system illustrated in Fig. 1.

atic density fluctuations in real time as seen previously [36], when starting from an odd initial wavefunction (\( \psi(\cdot) = -\psi(\cdot) \)), the imaginary-time wavefunction was observed to linger near the first excited state (\( \phi_1 \)) before finally converging to the ground state; i.e., the cooling process in imaginary time was slowed down by a "metastable intermediate." In contrast, for the symmetric potential (3.3), odd initial wavefunctions were cooled quickly and stably to the first excited state, where they remained. Also, greater long-time trajectory accuracy was required to converge \( G_{xx}(t) \) in the asymmetric case. Specifically, although a time step of \( \Delta t = 2 \) sufficed for the more tractable symmetric potential, \( \Delta t = 1 \) was needed to converge results for the asymmetric oscillator, thus doubling the amount of computational effort (HLVA iterations) required. Note that in the zero-temperature case previously reported (with initial states \( X(\psi_0) \)), stable results with \( \Delta t = 1 \) could only be obtained up to \( t \sim 10 \) for both oscillators; the greater stability observed here is due to the higher degree of stationarity of the cooled initial states \( e^{-\beta H/2}X(\psi_0) \).

In summary, in the present work we have obtained results that are both more accurate and not restricted to zero temperature. For a given molecular potential and with a harmonic basis, the scheme is stable as long as the temperature is sufficiently low to quench excited state components. For highly anharmonic potentials, the temperature must be lower to satisfy the above requirement. As discussed earlier, symmetry features offer an advantage, increasing stability and facilitating convergence at higher temperatures.

4. Concluding remarks

In this paper we have shown that the FBQD approach can be extended to evaluate finite-temperature correlation functions. For sufficiently low temperatures, the presence of the Boltzmann operator is actually beneficial, as the cooling operation eliminates excited state components, producing a state that resembles the lowest eigenstate of the given symmetry and thus giving rise to stable quantum trajectories. Interestingly, the present method allows even more stable propagation than in the case of zero temperature (albeit for the symmetrized correlation function) as a result of pre-cooling the initial state used to propagate the quantum trajectories. Moreover, the cooling effect of the Boltzmann operator is universal (although the rate of cooling will vary between systems), providing a robust and general method of obtaining sufficiently stationary states for real-time propagation. An additional advantage of the present method is the option to work in an arbitrary basis set, eliminating the need for eigenstates.

As discussed in the introduction, perhaps the most practical utility for FBQD and similar methods will be in rigorous quantum-semiclassical simulations, which require a unified trajectory description for all degrees of freedom, and in which a few select degrees of freedom will be treated by full quantum mechanics through the inclusion of a quantum potential. Even though some progress has been made in this direction, the precise formulation for such calculations awaits further developments.

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