Iterative Monte Carlo formulation of real-time correlation functions

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We present an iterative Monte Carlo path integral methodology for evaluating thermally averaged real-time correlation functions. Standard path integral Monte Carlo methods are used to sample paths along the imaginary time contour. Propagation of the density matrix is performed iteratively on a grid composed of the end points of the sampled paths. Minimally oscillatory propagators are constructed using energy filtering techniques. A single propagation yields the values of the correlation function at all intermediate time points. Model calculations suggest that the method yields accurate results over several oscillation periods and the statistical error grows slowly with increasing propagation time. © 2010 American Institute of Physics. [doi:10.1063/1.3488106]

I. INTRODUCTION

The calculation of time-dependent properties in polyatomic systems by numerically exact quantum mechanical methods poses an extremely difficult problem. Because the demands of such calculations grow exponentially with the number of particles, simulating the dynamical response of large clusters or condensed phase systems is currently practical only by using simplifying approximations. The development of first-principles fully, quantum mechanical methods applicable to systems of many atoms continues to be the central focus of our research.

To this end, our group has recently introduced the iterative Monte Carlo (IMC) path integral formulation of complex-time correlation functions. In this, the path integral expression for the correlation function of interest is evaluated incrementally, incrementing the complex time in a stepwise fashion in a manner similar to matrix-vector multiplication schemes employed in wave function propagation. At the same time, IMC takes full advantage of the favorable scaling of the Metropolis Monte Carlo method, evaluating the integrals on grids selected by a Monte Carlo random walk. Because the severity of phase cancellation encountered in the real (or complex) time path integral grows exponentially with the number of time steps, the stepwise evaluation of IMC amounts to a dramatic improvement in convergence, while the Monte Carlo nature of the algorithm offers the possibility of favorable scaling with the number of particles.

In this paper, we extend the IMC methodology to the calculation of real-time correlation functions. Even though the real-time form is related to its complex-time counterpart in frequency space, the required Fourier transformation of the complex-time correlation function can be unstable in the presence of statistical noise. The obvious difficulty in the direct evaluation of real-time correlation functions via Monte Carlo based methods is the absence of localization of the propagator and its very rapidly oscillatory character. In the present work, we deal with this difficulty by using energy filters, which eliminate the rapid oscillations and restrict the spatial extent of the real-time propagator.

The methodology is described in Sec. II. Following an imaginary time (equilibrium) path integral Monte Carlo procedure that generates the IMC grid, the density matrix is propagated iteratively by individual forward-backward time steps. We show that the time correlation function can be obtained at each step in a single IMC propagation and that the procedure can be extended to long times. These features are illustrated in the model calculations presented in Sec. III. We conclude in Sec. IV with a summary and outlook.

II. ITERATIVE MONTE CARLO FORMULATION OF REAL-TIME CORRELATION FUNCTIONS

Our focus is on finite-temperature correlation functions, which have the general form

$$C(t) = Z^{-1} \text{Tr}(e^{-\beta \hat{A} i\hat{H} t / \hbar} e^{-i\hat{H} t / \hbar}),$$

(2.1)

where $\beta = 1/k_B T$ and $Z$ is the canonical partition function. By choosing $\hat{A}$ and $\hat{B}$ as the momentum operator of a particle in solution, one can calculate its diffusion coefficient while setting the operators equal to the force function gives the absorption spectrum. Defining the functions

$$R_k(x_k^+, x_k^-) = \langle x_k^+ | e^{-i\hat{H}(\Delta t) / \hbar} e^{-\beta \hat{A} i\hat{H} t / \hbar} | x_k^- \rangle$$

(2.2)

and

$$P_k(x_k^+, x_k^-) = \langle x_k^+ | e^{-i\hat{H}(\Delta t) / \hbar} e^{-\beta \hat{B} i\hat{H} t / \hbar} | x_k^- \rangle = \langle x_k^+ | e^{-\beta \hat{B} t / \hbar} | x_k^- \rangle,$$

(2.3)

where $k$ is an integer, it is straightforward to show that

$$C\left(\left(k + \frac{1}{2}\right) \Delta t \right) = Z^{-1} \int dx_k^+ R_k(x_k^+, x_k^-) \times \langle x_k^- | e^{i\hat{H} \Delta t / 2 \hbar} e^{-i\hat{D} \Delta t / 2 \hbar} | x_k^+ \rangle,$$

(2.4)

where $\int dx_k^+ = \int dx_k^- \int dx_k^-$. Setting $\hat{A} = \hat{B} = 1$. 

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A. Thermal loop

We wish to generate pairs of points with coordinates \((x_0^+, x_0^-)\) with (un-normalized) probability distribution given by Eq. (2.8). Choosing an imaginary time step \(\Delta \beta = \beta/(2M+1)\) where \(M\) is an integer, the discretized path integral representation of the Boltzmann matrix element becomes

\[
\langle x_0^+ | e^{-\beta H} | x_0^- \rangle = \int dx_1^+ \cdots \int dx_M^+ \int dx_M^- \cdots \int dx_1^- \times \langle x_0^+ | e^{-\Delta \beta H} | x_1^+ \rangle \cdots \langle x_M^+ | e^{-\Delta \beta H} | x_M^+ \rangle
\]

\[
\times \langle x_M^- | e^{-\Delta \beta H} | x_1^- \rangle \cdots \langle x_1^- | e^{-\Delta \beta H} | x_0^- \rangle.
\]  

(2.10)

As will become clear later, our choice of notation is motivated by the nature of the algorithm, which involves a step-wise propagation of pairs of beads along the forward and backward branches of the real-time contour (see the schematic representation in Fig. 1). The short imaginary time propagators can be obtained using a suitable approximation. In this work, we use the Trotter splitting with respect to a suitable reference Hamiltonian.

We perform a Metropolis random walk in the space of the variables \(x_1^+ \ldots, x_M^+\) using the sampling function

\[
\rho_1(x_1^+, \ldots, x_M^+) = \langle x_1^+ | e^{-\Delta \beta H} | x_1^+ \rangle \cdots \langle x_{M-1}^- | e^{-\Delta \beta H} | x_{M-1}^+ \rangle
\]

\[
\times \langle x_M^- | e^{-\Delta \beta H} | x_1^- \rangle \cdots \langle x_1^- | e^{-\Delta \beta H} | x_0^- \rangle.
\]  

(2.11)

The coordinates of all beads are moved simultaneously. For each selected configuration, the coordinates of the pair \(x_1^\pm\) are stored, forming a two-dimensional grid. Rejected moves in the random walk are accounted for by increasing the multiplicity of the grid point. The grid pairs \(x_1^\pm\) generated from this random walk are distributed as the integral of the sampling function with respect to all other variables

\[
P_1(x_1^+, x_1^-) = \int dx_2^+ \cdots \int dx_M^+ \rho_1(x_1^+, \ldots, x_M^+)
\]

\[
= \langle x_1^+ | e^{-(2M-1) \Delta \beta H} | x_1^- \rangle.
\]  

(2.12)

Next, we perform a second random walk in the space of the variables \(x_0^\pm, x_1^\pm, \ldots, x_M^\pm\) using the sampling function

\[
\rho_0(x_0^+, \ldots, x_M^+) = \langle x_0^+ | e^{-\Delta \beta H} | x_1^+ \rangle \cdots \langle x_{M-1}^+ | e^{-\Delta \beta H} | x_M^+ \rangle
\]

\[
\times \langle x_M^- | e^{-\Delta \beta H} | x_1^- \rangle \cdots \langle x_1^- | e^{-\Delta \beta H} | x_0^- \rangle.
\]  

(2.13)

Again, the end point coordinates \(x_0^\pm\) of the discretized paths are stored (with multiplicities arising from rejected moves.) Each coordinate pair \(x_0^\pm\) is distributed as
Using this form and eliminating the resolution of identity, the filtering out the oscillations is possible because of the finite context where the initial condition is the Boltzmann density, densities. Thus, it would be necessary to bin the selected grid points for convergence. Finally, we use the obtained numerical values of \( P_0 \) to also calculate

\[
R_0(x_0, x_0) = \left( x_0^1 | e^{-\Delta \hat{H}} | x_0^1 \right) A(x_0),
\]

the initial condition in Eq. (2.6).

**B. Smooth real-time propagator**

In principle, the short real-time propagators can be obtained using any approximation, e.g., the Trotter factorization. However, the latter (as well as any approximation based on the exact free particle propagator) is a very rapidly oscillatory function of its variables. The use of such approximations would require a very large number of grid points for convergence.

As argued in earlier works, it is possible to eliminate the rapid oscillations of the propagator without loss of accuracy by using an energy (or momentum) filter. In the present context where the initial condition is the Boltzmann density, filtering out the oscillations is possible because of the finite spectral span of the density matrix. Specifically, consider the spectral expansion of the propagator in terms of the eigenstates \( \Phi_n \) and eigenvalues \( E_n \) of the Hamiltonian

\[
\langle x_0^1 | e^{-i \Delta \hat{H} / \hbar} | x_0^n \rangle = \sum_{n=0}^{\infty} \Phi_n(x_0^1) e^{-i E_n \Delta \hbar / \hbar} \Phi_n^*(x_0^n). \tag{2.18}
\]

Using this form and eliminating the resolution of identity, the first step in the propagation becomes

\[
R_1(x_1^1, x_1^1) = \int dx_0^1 \left( x_1^1 | e^{-i \Delta \hat{H} / \hbar} | x_0^1 \right) R_0(x_0^1, x_0^1) \left( x_1^1 | e^{-i \Delta \hat{H} / \hbar} | x_0^1 \right)
\]

\[
= \int dx_0^1 \sum_{n=0}^{\infty} \Phi_n(x_1^1) e^{-i E_n \Delta \hbar / \hbar} \Phi_n^*(x_0^1) \times \left( x_0^1 | e^{i \Delta \hat{H} / \hbar} | x_1^1 \right).
\]

Equivalently, it is sufficient to truncate the propagator Eq. (2.18). Thus, we evaluate the latter from the expression

\[
\langle x_1^n | e^{-i \Delta \hat{H} / \hbar} | x_0^n \rangle = \sum_{n=0}^{\infty} \Phi_n(x_1^n) e^{-i E_n \Delta \hbar / \hbar} \Phi_n^*(x_0^n). \tag{2.21}
\]

Unlike Eq. (2.20), which holds for any \( \epsilon \), the difference between Eq. (2.21) and the exact propagator of Eq. (2.18) is much larger than \( \epsilon \). Specifically, Eq. (2.21) is a much smoother function which (as long as \( \hat{H} \) has a bound potential) decays exponentially to zero beyond a certain coordinate range (see Fig. 2). While filtering out the undesirable high frequency oscillations changes the propagator very significantly, the accuracy of the propagated density matrix Eq. (2.20) is affected only by \( \epsilon \), an error allowance that can be made as small as desired. The smoothness and finite extent of the effective propagator given by Eq. (2.21) are benefits of the energy filter, i.e., the use of the projector

\[
\sum_{n=0}^{\infty} | \Phi_n \rangle \langle \Phi_n | \tag{2.22}
\]

in place of the identity operator.
(which may include separable potentials) and a (many-particle, anharmonic, and coordinate-dependent) potential term $V$

$$\hat{H} = \hat{H}_0 + \hat{V},$$  \hspace{1cm} (2.23)

$$\langle x | e^{-i\hat{H}\Delta t/h} | x' \rangle = e^{-i(V(x)\Delta t/2h)}\langle x | e^{-i\hat{H}_0\Delta t/h} | x' \rangle e^{-i(V(x')\Delta t/2h)}.$$  \hspace{1cm} (2.24)

If the zero of energy is placed at the potential minimum, $\hat{V}$ consists of anharmonic potential terms, and [as required for the validity of Eq. (2.24)] the time step is small, the potential factors will be only mildly oscillatory. Thus only the reference propagator is highly oscillatory. Since the eigenstates and eigenvalues of the reference Hamiltonian $\hat{H}_0$ are presumed available (analytically or numerically), it is straightforward to use the energy filtering procedure described above to obtain a smooth and spatially localized propagator. Thus, the effective propagator has the form

$$\langle x | e^{-i\hat{V}\Delta t/h} | x' \rangle = e^{-i(V(x)\Delta t/2h)}\langle x | e^{-i\hat{H}_0\Delta t/h} | x' \rangle e^{-i(V(x')\Delta t/2h)}$$

$$\times e^{-iV(x')\Delta t/2h}.$$  \hspace{1cm} (2.25)

Clearly, it is advantageous to choose $n_{\text{max}}$ as small as allowed by the given temperature in order to arrive at a propagator that is as free of oscillations as possible.

In addition to the effective short time propagator, we note here that a similar procedure can be used to calculate the Heisenberg operator for $\hat{B}$ [the last factor in Eq. (2.4)] for a time step $\Delta t/2$, which is required in the final step of the procedure. Splitting the half-step evolution operators, we obtain

$$\langle x | e^{i\hat{H}\Delta t/2h} e^{-i\hat{H}_{\Delta t/2h}} | x' \rangle = e^{i(V(x)\Delta t/2h)}\langle x | e^{-i\hat{H}_0\Delta t/h} | x' \rangle e^{{-i(V(x')\Delta t/2h)}}$$

$$\times e^{-i\hat{H}_{\Delta t/2h}} e^{i\hat{H}_{\Delta t/2h}}.$$  \hspace{1cm} (2.26)

Similarly, the matrix element in the termination step of the partition function, whose exact value is a delta function, is obtained by the filtering procedure

$$\langle x | e^{i\hat{V}\Delta t/2h} e^{-i\hat{V}_{\Delta t/2h}} | x' \rangle = e^{i(V(x)\Delta t/2h)}\langle x | \sum_{n=0}^{n_{\text{max}} \Delta t/2h} \Phi_n(x) \Phi_n^*(x') \rangle.$$  \hspace{1cm} (2.27)

### C. Real-time propagation of the density matrix

Our goal is to propagate the functions $R_0$ and $P_0$ by individual forward-backward steps, as suggested by Eqs. (2.6) and (2.7). We use the grid selected above for all real-time propagation steps. Proceeding as in the case of the complex-time correlation function, the forward-backward step is achieved by evaluating the integral

$$R_1(x_1^+, x_1^-) = \int d\phi(x_1^-) e^{-i\hat{H}_{\Delta t/h}} R_0(x_1^+, x_0) e^{i\hat{H}_{\Delta t/h}} | x_1^- \rangle.$$  \hspace{1cm} (2.28)

Since the coordinates of the integration variables are distributed according to Eq. (2.8), the Monte Carlo approximation to this integral is

$$R_1(x_1^+, x_1^-) = \sigma_0 \sum_{x_0} \langle x_1^+ | e^{-i\hat{H}_{\Delta t/h}} | x_0 \rangle \langle x_0 | e^{i\hat{H}_{\Delta t/h}} | x_1^- \rangle.$$  \hspace{1cm} (2.29)

where $\sigma_0$ is the normalization integral of the probability distribution $P_0$ (i.e., the partition function). Since the latter is not readily available, we actually calculate the function

$$\tilde{P}_1(x_1^+, x_1^-) = \sum_{x_0} \langle x_1^+ | e^{-i\hat{H}_{\Delta t/h}} | x_0 \rangle \langle x_0 | e^{i\hat{H}_{\Delta t/h}} | x_1^- \rangle.$$.  \hspace{1cm} (2.30)

Similarly, the IMC propagation of the density matrix can be propagated by a forward-backward step

$$P_1(x_1^+, x_1^-) = \int d\phi(x_1^-) e^{-i\hat{H}_{\Delta t/h}} P_0(x_1^+, x_0) e^{i\hat{H}_{\Delta t/h}} | x_1^- \rangle.$$  \hspace{1cm} (2.31)

Again, we compute the proportional function

$$\tilde{P}_1(x_1^+, x_1^-) = \sum_{x_0} \langle x_1^+ | e^{-i\hat{H}_{\Delta t/h}} | x_0 \rangle \langle x_0 | e^{i\hat{H}_{\Delta t/h}} | x_1^- \rangle.$$  \hspace{1cm} (2.32)

Note that since the equilibrium density is stationary, the function obtained through Eq. (2.32) is proportional to $P_0$. As will become clear in Sec. II D, the purpose of evaluating this function numerically is to cancel the unknown normalization factors. Following the first iteration, IMC propagation in real-time proceeds iteratively in a fashion similar to Eq. (2.28)

$$R_{k+1}(x_{k+1}^+, x_{k+1}^-) = \int d\phi(x_{k+1}^-) e^{-i\hat{H}_{\Delta t/h}} R_k(x_{k+1}^+, x_k) e^{i\hat{H}_{\Delta t/h}} | x_{k+1}^- \rangle.$$  \hspace{1cm} (2.33)

Motivated by the time invariance of the propagated Boltzmann density [see Eq. (2.3)], we use the same grid for all the real-time iterations. Thus the IMC estimate of Eq. (2.33) is given by the relation

$$R_{k+1}(x_{k+1}^+, x_{k+1}^-) = \sigma_0 \sum_{x_k} \langle x_{k+1}^+ | e^{-i\hat{H}_{\Delta t/h}} | x_k \rangle R_k(x_{k+1}^+, x_k) e^{i\hat{H}_{\Delta t/h}} | x_k \rangle.$$  \hspace{1cm} (2.34)

Again, the actual sum performed omits the normalization factor and thus the calculated function
\[
\begin{align*}
\tilde{R}_{k+1}(x_{k+1}^+, x_{k+1}^-) &= \sum_{x_k^+} \langle x_k^+ | e^{-iH\Delta t/2h} | x_k^+ \rangle R_k(x_k^+, x_k^-) P_0(x_k^+, x_k^-) \\
&\times \langle x_k^- | e^{iH\Delta t/2h} | x_{k+1}^- \rangle 
\end{align*}
\]  
(2.35)

differs from Eq. (2.34) by a factor of \(\sigma_r^N\). The same is done for the density matrix, yielding the function

\[
\begin{align*}
\tilde{P}_{k+1}(x_{k+1}^+, x_{k+1}^-) &= \sum_{x_k^+} \langle x_k^+ | e^{-iH\Delta t/2h} | x_k^+ \rangle R_k(x_k^+, x_k^-) P_0(x_k^+, x_k^-) \\
&\times \langle x_k^- | e^{iH\Delta t/2h} | x_{k+1}^- \rangle.
\end{align*}
\]  
(2.36)

As discussed in Sec. II A, the functions \(\tilde{R}_k\) and \(\tilde{P}_k\) obtained in each step of the IMC iteration are used in two ways: to produce the value of the correlation function at the time \((k + \frac{1}{2})\Delta t\), as described in Sec. II D, and as input in the next iteration that generates \(\tilde{R}_{k+1}\) and \(\tilde{P}_{k+1}\).

### D. Termination to obtain the correlation function

We wish to use the functions \(\tilde{R}_k\) and \(\tilde{P}_k\) generated in the \(k\)th IMC iteration in order to obtain the value of the correlation function. From Eqs. (2.4) and (2.5),

\[
C\left(\left(k + \frac{1}{2}\right)\Delta t\right) = \frac{\int dx_k^+ \tilde{R}_k(x_k^+ x_k^-) \langle x_k^- | e^{iH\Delta t/2h} B e^{-iH\Delta t/2h} | x_k^+ \rangle}{\int dx_k^+ \tilde{P}_k(x_k^+ x_k^-) \langle x_k^- | e^{iH\Delta t/2h} B e^{-iH\Delta t/2h} | x_k^+ \rangle},
\]  
(2.37)

and since the calculated functions \(\tilde{R}_k\) and \(\tilde{P}_k\) differ from \(R_k\) and \(P_k\) by the same proportionality constant \(\sigma_r^N\), it follows that

\[
C\left(\left(k + \frac{1}{2}\right)\Delta t\right) = \frac{\int dx_k^+ \tilde{R}_k(x_k^+ x_k^-) \langle x_k^- | e^{iH\Delta t/2h} B e^{-iH\Delta t/2h} | x_k^+ \rangle}{\int dx_k^+ \tilde{P}_k(x_k^+ x_k^-) \langle x_k^- | e^{iH\Delta t/2h} B e^{-iH\Delta t/2h} | x_k^+ \rangle}.
\]  
(2.38)

The half-forward-backward matrix elements in this expression are available form the procedure described in Sec. II B. Converting again the integrals into IMC sums, we obtain

\[
C\left(\left(k + \frac{1}{2}\right)\Delta t\right) = \sum_{x_k^+} \langle x_k^- | e^{iH\Delta t/2h} B e^{-iH\Delta t/2h} | x_k^+ \rangle.
\]  
(2.39)

Equation (2.39) is the IMC estimate of the time correlation function at the time \((k + \frac{1}{2})\Delta t\).

To summarize, the IMC formulation of real-time correlation functions involves sampling with the Boltzmann density and a series of IMC steps in real-time. In order to keep the statistical error small, we use effective propagators in which the high energy components responsible for rapidly oscillatory behavior have been removed. Besides producing the real-time version of a correlation function directly, the present methodology is in some regards more convenient than its complex-time form. First, a single propagation in real-time directly gives rise to the correlation function over the entire time interval of interest, unlike the complex-time formulation which requires a separate calculation with a different complex-time step for each time point. Second, the present methodology is more stable and efficient for long time calculations. The reason for this is that the temperature, thus the spread of the sampled distribution, remains constant throughout the calculation. This is in contrast to the iterative calculation of a complex-time correlation function, where in order the need to maintain a small complex-time step \(\Delta t = \left(t - i \beta/2\right)/N\) leads when \(t \gg \beta\) to a very small imaginary time step \(\Delta t/2N\), thus a broad grid point distribution over which the integrand may oscillate considerably.

### III. APPLICATION TO SIMPLE MODELS

In this section, we illustrate the real-time IMC methodology by calculating the position autocorrelation function in a one-dimensional anharmonic oscillator described by the Hamiltonian

\[
H = \frac{p^2}{2m} + \frac{\alpha}{2} x^2 + \frac{\beta}{4} x^4.
\]  

![Fig. 3. Position autocorrelation function for the anharmonic oscillator of Eq. (3.1) for \(h\omega\beta=2\). The solid lines shows converged basis set results. The markers show IMC results. Left: real part. Right: imaginary part.](http://jcp.aip.org/jcp/copyright.jsp)
We calculate the position autocorrelation function, setting $\hat{A}=\hat{x}$.

Calculations were performed at two temperatures corresponding to $\hbar\omega\beta=2$ and 6. The real and imaginary time steps were set equal to $\omega\Delta t=\hbar\omega\Delta\beta=0.4$. The energy filter for the real-time propagators was set to $n_{\text{max}}=3$. IMC calculations were performed with a grid of 20,000 points. We performed ten separate runs in each case in order to estimate statistical error bars.

Figures 3 and 4 show the averaged results for the position autocorrelation function at these two temperatures. The correlation function at these two temperatures. The IMC results are accurate over more than three oscillation periods. For the higher of these temperatures, the propagation time corresponds to $t/\hbar\beta=7.3$. The statistical error is very small during the first oscillation period and even though it grows somewhat with repeated iteration, it remains reasonably small during the entire propagation interval. We note that because the calculations for all time points in each run are performed using the same grid, the statistical errors of different time points are correlated, leading to the smooth results.

IV. CONCLUDING REMARKS

We have shown that the IMC path integral formulation of quantum dynamics can be extended to real-time correlation functions. The numerical implementation of the real-time IMC formulation is rather simple and straightforward, consisting of a single Monte Carlo sampling of the Boltzmann part of the loop, followed by iterative propagation along the forward and backward real-time directions with an effective propagator. All steps in the real-time propagation utilize the same grid and the use of energy filters to eliminate rapidly oscillatory components in the effective real-time propagator leads to minimal phase cancellation. The specific filtering procedure used in the present paper was based on a simple (harmonic) reference Hamiltonian. Momentum filters (which are based on the Cartesian form of the kinetic energy) may offer a better choice for application to clusters, liquids, or biomolecules.

In addition to the direct calculation of the (often desirable) real-time correlation function, the present formulation allows evaluation of the correlation function at all time points from a single run, in contrast to complex-time formulations, in which propagation proceeds with a fixed complex-time step, thus separate calculations are required to obtain values at different times. Further, our numerical examples indicate that the scheme can yield stable results over long propagation periods. Thus, it should be possible to Fourier transform the real-time IMC results in order to obtain symmetrized complex-time or Kubo correlation functions, should this be desirable.

Based on these features, we believe the real-time IMC methodology shows promise for the simulation of polyatomic systems. Clearly, the efficiency of a scheme is critical for such applications and we are considering various possibilities toward that goal, including the construction of more compact grids and the use of semiclassical-based filters. Work along these lines is in progress in our group.

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