

Communication: Importance sampling including path correlation in semiclassical initial value representation calculations for time correlation functions

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Full semiclassical (SC) initial value representation (IVR) for time correlation functions involves a double phase space average over a set of two phase points, each of which evolves along a classical path. Conventionally, the two initial phase points are sampled independently for all degrees of freedom (DOF) in the Monte Carlo procedure. Here, we present an efficient importance sampling scheme by including the path correlation between the two initial phase points for the bath DOF, which greatly improves the performance of the SC-IVR calculations for large molecular systems. Satisfactory convergence in the study of quantum coherence in vibrational relaxation has been achieved for a benchmark system-bath model with up to 21 DOF. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4794191>]

Quantum effects play a key role in materials science and energy applications, such as energy relaxation on surfaces,¹ charge transfer in electronic nanowires,² and electronic excitation energy transfer in photosynthesis.³ To describe quantum effects in realistic molecular systems is beyond the capability of the popular classical molecular dynamics (MD) simulations. A well-defined way for adding the quantum effects to classical MD simulations of such large molecular systems is the semiclassical (SC) theory via initial value representation (IVR).^{4–10} Extensive research work has demonstrated the usefulness of the SC-IVR methodology; however, there are some problems preventing the SC method from the practical applications on large molecular systems. Two major problems are: (1) the sign problem, i.e., the integrand of the SC phase space average contains an oscillatory phase factor; and (2) the prefactor problem, i.e., the SC calculations require the evaluation of the second derivatives of phase points with respect to their initial values (monodromy matrix elements) in a cumbersome prefactor. Some further approximations are made to simplify the SC expressions, such as the linearized SC-IVR (LSC-IVR),^{11–13} and the forward-backward IVR (FB-IVR),^{14–16} but the cost is the deterioration of accuracy in describing quantum effects. An alternative way to improve the efficiency of the SC calculations without loss of accuracy is to perform importance sampling for initial phase points. Conventionally, the sampling function of initial conditions is time independent, and once an initial phase point is picked up by the Monte Carlo procedure, the following classical path is governed by Hamiltonian dynamics. In the full SC-IVR calculations, no correlation between the paths generated by the initial phase points is considered. Recently, a time-dependent (TD) importance sampling method¹⁷ for the SC-IVR calculations (TD-SC-IVR) was proposed to include the time-evolved phase points in the

importance sampling. By doing this, the path correlation at time t is effectively introduced into the sampling function, which greatly reduces the number of configurations (by statistically disregarding those uncorrelated paths) used in the SC calculations of time correlation functions to satisfy certain convergence criteria. In this work, we will show that the inclusion of the path correlation in the importance sampling function for the initial phase points may also greatly improve the efficiency of the SC calculations. A benchmark example that considers the vibrational quantum coherence of an anharmonic oscillator coupled with thermal bath is used to illustrate the application of the new importance sampling method.

The quantum mechanical time correlation function that describes the dynamics of complex molecular systems can be expressed in the form¹⁸

$$C_{\text{QM}}(t) = \text{tr}[\hat{A}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}], \quad (1)$$

here \hat{A} and \hat{B} are operators for general quantities of interest. The SC-IVR theory approximates the time evolution operators by a phase space average over the initial phase points of classical path (trajectories); e.g., the coherent state IVR due to Herman and Kluk^{19,20} is

$$e^{-i\hat{H}t/\hbar} = (2\pi\hbar)^{-F} \int d\mathbf{q}_0 \int d\mathbf{p}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{p}_t, \mathbf{q}_t\rangle \langle \mathbf{p}_0, \mathbf{q}_0|, \quad (2)$$

where $|\mathbf{p}_0, \mathbf{q}_0\rangle$ and $|\mathbf{p}_t, \mathbf{q}_t\rangle$ are the coherent states with $(\mathbf{p}_0, \mathbf{q}_0)$ and $(\mathbf{p}_t, \mathbf{q}_t)$ the initial and time-evolved classical phase points, respectively, $S_t(\mathbf{p}_0, \mathbf{q}_0)$ is the classical action (the time integral of the Lagrangian) along the classical path, and $C_t(\mathbf{p}_0, \mathbf{q}_0)$ a pre-exponential factor involving the monodromy matrix elements. Substitute Eq. (2) for the two time evolution operators in Eq. (1) gives the SC-IVR correlation function as the

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following *double* phase average:

$$C_{SC}(t) = (2\pi\hbar)^{-2F} \int d\mathbf{q}_0 d\mathbf{p}_0 \int d\mathbf{q}'_0 d\mathbf{p}'_0 C_t(\mathbf{p}_0, \mathbf{q}_0) C_t(\mathbf{p}'_0, \mathbf{q}'_0)^* \times e^{i[S_t(\mathbf{p}_0, \mathbf{q}_0) - S_t(\mathbf{p}'_0, \mathbf{q}'_0)]/\hbar} \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}'_0 \mathbf{q}'_0 \rangle \langle \mathbf{p}'_0 \mathbf{q}'_0 | \hat{B} | \mathbf{p}_t \mathbf{q}_t \rangle \quad (3)$$

over the initial phase points of two paths. In the classical limit, both Eqs. (1) and (3) reduce to the corresponding classical correlation function that is given by a phase space average over initial conditions of classical paths

$$C_{CL}(t) = (2\pi\hbar)^{-F} \int d\mathbf{q}_0 d\mathbf{p}_0 A_{CL}(\mathbf{p}_0, \mathbf{q}_0) B_{CL}(\mathbf{p}_t, \mathbf{q}_t), \quad (4)$$

where A_{CL} and B_{CL} are the classical functions corresponding to operators \hat{A} and \hat{B} ; and F is the degrees of freedom of the system.

The evaluation of Eq. (3) involves the Monte Carlo (MC) importance sampling of a set of initial phase points $(\mathbf{p}_0, \mathbf{q}_0, \mathbf{p}'_0, \mathbf{q}'_0)$ for a pair of classical paths with the time-independent sampling function $|\langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}'_0 \mathbf{q}'_0 \rangle|$. However, the exact form of the matrix elements $|\langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}'_0 \mathbf{q}'_0 \rangle|$ is nontrivial except for simple (normally 1D) systems and traditionally the corresponding Husimi function is used as the sampling function for both $(\mathbf{p}_0, \mathbf{q}_0)$ and $(\mathbf{p}'_0, \mathbf{q}'_0)$, i.e.,

$$\rho_{MC}(\mathbf{p}_0, \mathbf{q}_0, \mathbf{p}'_0, \mathbf{q}'_0) \propto |\langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}_0 \mathbf{q}_0 \rangle \langle \mathbf{p}'_0 \mathbf{q}'_0 | \hat{A} | \mathbf{p}'_0 \mathbf{q}'_0 \rangle|. \quad (5)$$

The efficiency of this conventional MC sampling is poor because the two time-evolved phase points are sampled independently and will often be far apart, and the matrix element of operator \hat{A} (and presumably for \hat{B} too) is thus negligibly small. These uncorrelated paths normally contribute very little to the integrand therefore their sampling is simply a waste of computational time.

The importance of the inclusion of path correlation in the sampling function was underappreciated. In the LSC-IVR approximation, the pair of paths is assumed to be coupled with each other on the first order of the difference of the two phase points. In the FB-IVR approximation, two final phase points are correlated by the operator \hat{B} (going beyond the linearized approximation since two paths may be distinct from each other); by selecting those “very important” forward-backward paths, the calculation of FB correlation functions can be simplified significantly.^{21,22} For the TD-SC-IVR approach, the correlation of the paths via two final phase points is explicitly included in the sampling function,¹⁷ which results in a very efficient Monte Carlo sampling. The improvement in the efficiency of the above approximations and methods lies in the importance sampling of those very important path (VIP) pairs (normally correlated with each other) while leaving out the very large amount of uncorrelated paths. Similar in spirit to the above ideas, here we demonstrate that the efficiency of the full SC-IVR could be improved significantly by properly including the correlation between two initial phase points in the sampling function, and one simple form of such correlated

sampling functions reads

$$\rho_{MC}(\mathbf{p}_0, \mathbf{q}_0, \mathbf{p}'_0, \mathbf{q}'_0) \propto |\langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}_0 \mathbf{q}_0 \rangle f(\mathbf{p}_0, \mathbf{q}_0, \mathbf{p}'_0, \mathbf{q}'_0)|, \quad (6a)$$

here, $f(\mathbf{p}_0, \mathbf{q}_0, \mathbf{p}'_0, \mathbf{q}'_0)$ is a correlated function of two initial phase points to be determined by specific operators of interest, e.g., $f(\mathbf{p}_0, \mathbf{q}_0, \mathbf{p}'_0, \mathbf{q}'_0) = \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}'_0 \mathbf{q}'_0 \rangle / \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}_0 \mathbf{q}_0 \rangle$ if $\langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}'_0 \mathbf{q}'_0 \rangle$ can be evaluated straightforwardly. An even simpler and more practical correlated sampling function takes the form

$$\rho_{MC}(\mathbf{p}_0, \mathbf{q}_0, \mathbf{p}'_0, \mathbf{q}'_0) \propto |\langle \bar{\mathbf{p}}_0 \bar{\mathbf{q}}_0 | \hat{A} | \bar{\mathbf{p}}_0 \bar{\mathbf{q}}_0 \rangle \langle \mathbf{p}_0, \mathbf{q}_0 | \mathbf{p}'_0, \mathbf{q}'_0 \rangle|, \quad (6b)$$

where $\bar{\mathbf{p}}_0 = (\mathbf{p}_0 + \mathbf{p}'_0)/2$, $\bar{\mathbf{q}}_0 = (\mathbf{q}_0 + \mathbf{q}'_0)/2$. This symmetric and separable correlated sampling function is simply the product of the diagonal matrix element of operator \hat{A} and the overlap of the two initial coherent states.

As a benchmark test, we study the vibrational quantum coherence of an anharmonic oscillator coupled with a harmonic heat bath,¹⁶ for which the Hamiltonian is

$$H = H_0(p, s) + \sum_{j=1}^{N_b} \left[\frac{1}{2} P_j^2 + \frac{1}{2} \omega_j^2 \left(Q_j + \frac{c_j}{\omega_j^2} (s - s_e) \right)^2 \right], \quad (7a)$$

and

$$H_0(p, s) = \frac{1}{2\mu} p^2 + V(s), \quad (7b)$$

where s and p are the vibrational coordinate and momentum of the system and (Q_j, P_j) are the mass-scaled coordinates and momenta of the j th bath modes. The frequencies ω_j and coupling constants c_j of the bath modes are determined by discretization of the continuous spectral density of an Ohmic bath. The characteristic frequency of the bath $\omega_c = 20 \text{ cm}^{-1}$, and the maximum frequency $\omega_m = 100 \text{ cm}^{-1}$. The vibrational degree of freedom is that of a Morse potential,

$$V(s) = D_e (e^{-2\alpha(s-s_e)} - 2e^{-\alpha(s-s_e)}), \quad (8)$$

where $D_e = 12547 \text{ cm}^{-1}$, $s_e = 2.6663 \text{ \AA}$, $\alpha = 1.8576 \text{ \AA}^{-1}$ and we take the reduced mass $\mu = 63.452 \text{ amu}$ to model the ground state I_2 molecule. The specific quantity we consider is the time-dependent probability distribution function (PDF) of the vibrational coordinate $P_t(r)$, which is a correlation function of the form in Eq. (3) with $\hat{A} = e^{-\beta \hat{H}_B} |\Phi_0\rangle \langle \Phi_0|$ and $\hat{B} = \delta(r - s)$. The initial state of the system is the coherence state of the s -degree of freedom $|\Phi_0\rangle = |p_i q_i\rangle$ with $p_i = 0$ and $q_i = 2.4 \text{ \AA}$. And the initial phase points are sampled from a sampling function including path correlation given by Eqs. (6a) or (6b), i.e.,

$$\rho_{MC}(\mathbf{p}_0, \mathbf{q}_0, \mathbf{p}'_0, \mathbf{q}'_0) \propto |\langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}'_0 \mathbf{q}'_0 \rangle| = \left| \langle p_0 s_0 | \Phi_0 \rangle \langle \Phi_0 | p'_0 s'_0 \rangle \times \prod_{j=1}^{N_b} \langle P_{j0} Q_{j0} | e^{-\beta \hat{H}_{Bj}} | P'_{j0} Q'_{j0} \rangle \right|, \quad (9a)$$

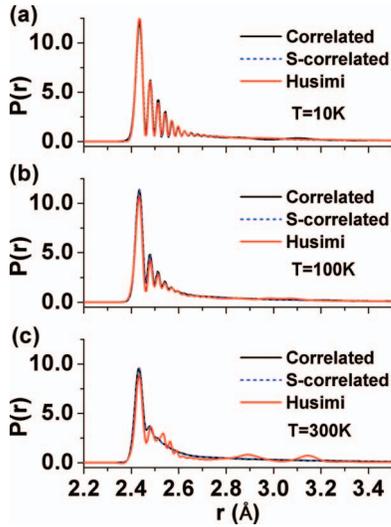


FIG. 1. The time-dependent probability distribution function (PDF) for an anharmonic oscillator coupled with 5 harmonic bath modes. The results are the full semiclassical (SC-IVR) correlation function of Eq. (3), calculated by using the correlated sampling (Eq. (9a), Correlated), the symmetric-correlated sampling (Eq. (9b), S-correlated), and by using the conventional Husimi sampling (Eq. (10), Husimi) approaches. The system-bath coupling strength $\eta/\mu\omega_s = 0.15$, $t = 190$ fs, and (a) $T = 10$ K, (b) $T = 100$ K, (c) $T = 300$ K.

and

$$\begin{aligned} \rho_{MC}(\mathbf{p}_0, \mathbf{q}_0, \mathbf{p}'_0, \mathbf{q}'_0) &\propto |\langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}'_0 \mathbf{q}'_0 \rangle| \\ &= \left| \langle p_0 s_0 | \Phi_0 \rangle \langle \Phi_0 | p'_0 s'_0 \rangle \right. \\ &\quad \left. \times \prod_{j=1}^{N_b} \langle \bar{P}_{j0} \bar{Q}_{j0} | e^{-\beta \hat{H}_{Bj}} | \bar{P}_{j0} \bar{Q}_{j0} \rangle \langle P_{j0} Q_{j0} | P'_{j0} Q'_{j0} \rangle \right|. \end{aligned} \quad (9b)$$

In comparison, the conventional Husimi function of the Boltzmann operator is also used in the sampling function, i.e.,

$$\begin{aligned} \rho_{MC}(\mathbf{p}_0, \mathbf{q}_0, \mathbf{p}'_0, \mathbf{q}'_0) &\propto \left| \langle p_0 s_0 | \Phi_0 \rangle \langle \Phi_0 | p'_0 s'_0 \rangle \times \prod_{j=1}^{N_b} \langle P_{j0} Q_{j0} | e^{-\beta \hat{H}_{Bj}} | P_{j0} Q_{j0} \rangle \right. \\ &\quad \left. \times \prod_{j=1}^{N_b} \langle P'_{j0} Q'_{j0} | e^{-\beta \hat{H}_{Bj}} | P'_{j0} Q'_{j0} \rangle \right|. \end{aligned} \quad (10)$$

We present in Figure 1 the full SC-IVR results of the PDF of the vibrational coordinate coupled with 5 harmonic bath modes by using the correlated sampling function Eq. (9a), the symmetric-correlated (s-correlated) sampling function Eq. (9b) and the Husimi sampling function Eq. (10). The numbers of initial configurations in the SC-IVR calculations are given in Table I. Clearly, the correlated (s-correlated) importance sampling scheme significantly reduces the number of initial configurations used to obtain converged results in comparison with the conventional Husimi sampling scheme. Figure 1 also shows the temperature effect on the vibrational coher-

TABLE I. Number of initial configurations used in different importance sampling schemes for the SC-IVR calculations of the probability distribution function of an anharmonic oscillator coupled with thermal bath.

| Temperature (K) | 10 | 100 | 300 |
|-----------------|-------------|---------------|---------------|
| Husimi | 500 000 000 | 5 000 000 000 | 5 000 000 000 |
| Correlated | 5 000 000 | 5 000 000 | 5 000 000 |
| S-correlated | 5 000 000 | 5 000 000 | 5 000 000 |

ence/decoherence. Noticeably, the Husimi sampling scheme requires more configurations to converge at higher temperature. To examine the temperature dependence of the convergence, we calculate the variance of the PDF $\sigma_r(r)$ for all sampling schemes (see Figure 2). In contrast to the Husimi sampling, the correlated sampling converges better at higher temperature. This temperature dependence may be due to the following fact. We note that

$$\begin{aligned} &|\langle P_{j0} Q_{j0} | e^{-\beta \hat{H}_{Bj}} | P'_{j0} Q'_{j0} \rangle| \\ &\rightarrow \begin{cases} C e^{-\frac{\gamma_j}{4} (Q_{j0}^2 + Q'_{j0}{}^2) - \frac{1}{4\gamma_j} (P_{j0}^2 + P'_{j0}{}^2)} & (T \rightarrow 0) \\ C e^{-\frac{\gamma_j}{4} (Q_{j0} - Q'_{j0})^2 - \frac{1}{4\gamma_j} (P_{j0} - P'_{j0})^2} & (T \rightarrow \infty) \end{cases}, \end{aligned} \quad (11a)$$

$$\begin{aligned} &|\langle \bar{P}_{j0} \bar{Q}_{j0} | e^{-\beta \hat{H}_{Bj}} | \bar{P}_{j0} \bar{Q}_{j0} \rangle \langle P_{j0} Q_{j0} | P'_{j0} Q'_{j0} \rangle| \\ &\rightarrow \begin{cases} C e^{-\frac{\gamma_j}{2} \bar{Q}_{j0}^2 - \frac{1}{2\gamma_j} \bar{P}_{j0}^2} e^{-\frac{\gamma_j}{8} (Q_{j0} - Q'_{j0})^2 - \frac{1}{8\gamma_j} (P_{j0} - P'_{j0})^2} & (T \rightarrow 0) \\ C e^{-\frac{\gamma_j}{4} (Q_{j0} - Q'_{j0})^2 - \frac{1}{4\gamma_j} (P_{j0} - P'_{j0})^2} & (T \rightarrow \infty) \end{cases}, \end{aligned} \quad (11b)$$

and

$$\begin{aligned} &|\langle P_{j0} Q_{j0} | e^{-\beta \hat{H}_{Bj}} | P_{j0} Q_{j0} \rangle \times \langle P'_{j0} Q'_{j0} | e^{-\beta \hat{H}_{Bj}} | P'_{j0} Q'_{j0} \rangle| \\ &\rightarrow \begin{cases} C e^{-\frac{\gamma_j}{2} (Q_{j0}^2 + Q'_{j0}{}^2) - \frac{1}{2\gamma_j} (P_{j0}^2 + P'_{j0}{}^2)} & (T \rightarrow 0) \\ C & (T \rightarrow \infty) \end{cases}, \end{aligned} \quad (11c)$$

here, C is a proper constant. In the low temperature limit, the two initial phase points are sampled from independent

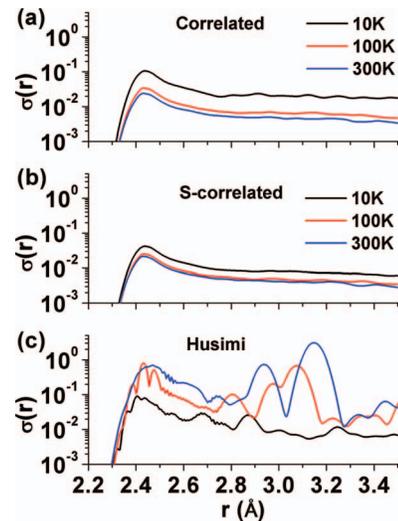


FIG. 2. Same system as in Figure 1, but comparing the result of the variance of the PDF in the full SC-IVR calculations. The numbers of initial configurations used are 5 000 000 for (a) the correlated sampling, 5 000 000 for (b) the s-correlated, and 500 000 000 for (c) the Husimi sampling.

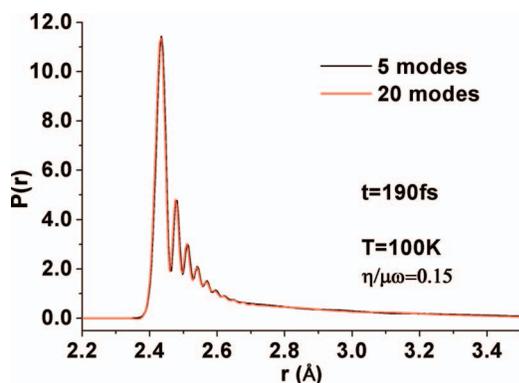


FIG. 3. The PDF for an anharmonic oscillator coupled with harmonic heat bath, comparing the results given by the full SC-IVR using the *s*-correlated sampling scheme for 5 modes (5 000 000 configurations) and 20 modes (500 000 000 configurations).

Gaussians and the corresponding paths are uncorrelated for the correlated sampling and the Husimi sampling. In the high temperature classical limit, the two paths tends to be strongly correlated as shown in Eq. (11a), while the Husimi sampling Eq. (11c) gives no information on path correlation. The *s*-correlated sampling Eq. (11b) has the same mathematical limits as the correlated one. However, when sampling for the transformed variables \bar{P}_{j0} , \bar{Q}_{j0} and $\Delta Q_{j0} = Q_{j0} - Q'_{j0}$, $\Delta P_{j0} = P_{j0} - P'_{j0}$; effectively, it includes path correlation in both high and low temperature limits. Therefore, the correlated and *s*-correlated sampling schemes result in a similar convergence at high temperatures while the latter converges better at low temperatures. So, the proper inclusion of path correlation in the sampling function is the key to assure a good statistical efficiency, as shown in Figs. 1 and 2.

It is worth comparing the new importance sampling method with the TD importance sampling approach in Ref. 17. With the same number of trajectories used, both provide almost identical results for the same calculation of PDFs (not shown). However, in general the TD sampling method requires a separate calculation for each time in which one is interested (in the current application for each distance *r*) and the normalization factor is also time-dependent.¹⁷ The advantage of the new method over the TD sampling is that there is no need to do such a separate calculation since only initial conditions are included in the sampling function Eq. (6).

The highly efficient importance sampling scheme including path correlation makes the full SC-IVR calculations for large molecular systems possible. Figure 3 demonstrates the SC-IVR result of the PDF of the vibrational coordinates cou-

pled with 20 harmonic bath modes by using the *s*-correlated sampling function. In comparison with the 5-modes system, the bath effect is negligible for this case.

This work has shown that the importance sampling including path correlation for the initial phase points provides an accurate way for carrying out semiclassical calculations of correlation functions without further approximation beyond the SC approximation itself. It provides identical results to the traditional sampling approach (for initial conditions only) but is much more efficient (i.e., requires many fewer trajectories to converge the phase space averages). Tests of this new correlated sampling approach showed it to be very efficient for the PDF of an anharmonic oscillator coupled with thermal bath (as many as 20 bath modes). The solvent effect is studied over a wide range of temperatures. Further investigations are needed to test this new approach on other systems, e.g., anharmonic bath.

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