Improving long time behavior of Poisson bracket mapping equation: A mapping variable scaling approach
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Citation: The Journal of Chemical Physics 141, 124107 (2014); doi: 10.1063/1.4895962
View online: https://doi.org/10.1063/1.4895962
View Table of Contents: http://aip.scitation.org/toc/jcp/141/12
Published by the American Institute of Physics

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I. INTRODUCTION

Nonadiabatic processes take place frequently in complex systems but their fundamental aspects are not fully understood yet. For example, photosynthesis, which has been extensively studied over many decades due to its scientific challenges and practical applicabilities, still remains as an elusive research topic in many respects. Indeed, it involves various nonadiabatic processes such as excitation energy, electron, and proton transfers, and that aspect adds a significant level of complication to already complex systems. Even the recently reported long lived coherences in photosynthetic systems have continuously been debated, likely due to the limitations in existing research tools from both theory and experiment. At the same time, such limitations have also been the driving forces behind the active developments in new experimental and theoretical methods.

Most theoretical means for explaining nonadiabatic behaviors in complex systems are constructed based on a partitioning scheme that divides the whole system into a quantum sub-system (often, just called a system) and its environment. They are commonly classified into two categories: quantum master equation formalisms and mixed quantum-classical approaches. Within the quantum master equation formalism, one can efficiently illustrate the system dynamics by taking the trace over the environmental information. In fact, it is possible to develop the formalism in many different flavors with various approximations in different model systems. A very well-known example will be the Redfield equation formalism, which includes the system-bath coupling in a perturbative manner to the second order with the Markovian approximation. This Redfield equation is often employed with the secular approximation as the conventional one does not guarantee correct equilibrium populations in the long time limit. However, the Redfield and its approximate equations are not capable of simulating system dynamics in all conditions. Thus, researchers have continuously reported improved quantum master equations with demonstrations toward reliable descriptions of the system dynamics.

In mixed quantum-classical approaches, the bath or the environmental degrees of freedom are explicitly treated, conventionally with classical representations. A few well-known examples of this class will be the Ehrenfest theory and the surface hopping method. Semiclassical propagator approaches, where the quantum degrees of freedom are represented and propagated by their classical analogs, are also available. A series of such approaches have been further developed depending on how the quantum degrees of freedom are formulated into classical representations. For instance, the mapping formalism describes the quantum degrees of freedom with continuous variables. Through this, electronic states can be assigned to fictitious harmonic oscillators with well-defined characters. Of course, our classification with the three types of mixed quantum-classical methods will be an oversimplification, as the distinction is actually obscure in many situations. In fact, an approximate variant of the semiclassical propagator approach was even shown to behave...
similarly to surface hopping algorithms.\textsuperscript{48,49} Furthermore, in certain conditions, a semiclassical propagator approach with the partial Wigner transform can be used to derive a surface hopping expression.\textsuperscript{50}

Until now, a number of different semiclassical propagator theories have been reported in combination with the mapping formalism. Representative examples are the linearized semiclassical initial value representation (L-IVR) method,\textsuperscript{51} the linearized approach to nonadiabatic dynamics based on mapping (LAND-map) formalism,\textsuperscript{45} the iterative linearized density matrix (ILDM) approach,\textsuperscript{18} and the Poisson bracket mapping equation (PBME) dynamics.\textsuperscript{46} In fact, these methods have been usefully adopted in revealing important aspects of various nonadiabatic events including the coherent dynamics in photosynthetic systems.\textsuperscript{15,20,52-54} Despite the usefulness, they often do not reproduce equilibrium populations in the long time limit even after adopting a large number of simulations.\textsuperscript{15,55} For example, L-IVR and PBME are not free from negative population issues depending on simulation conditions.\textsuperscript{15,56} Indeed, such unphysical populations can become a serious limitation in practical applications. One of its causes is the aspect that the zero-point energy is improperly described in semiclassical approaches,\textsuperscript{57} in conjunction with the fact that the energy flows between the quantum and the classical degrees of freedom are not correctly balanced. To overcome this difficulty, utilization of the coherent basis representations was suggested with the partially linearized density matrix (PLDM) approach\textsuperscript{17,47} and with the forward-backward trajectory solution (FBTS) of the quantum-classical Liouville equation (QCLE).\textsuperscript{19,58} Recently, combinations of the mapping approaches with the ring polymer molecular dynamics\textsuperscript{59-61} have also been proposed to adequately handle the zero-point energy effect.\textsuperscript{62}

In this paper, we present a pragmatic approach for correcting the zero-point energy leak issue in the PBME semiclassical dynamics. As the zero-point energy leak is symptomatically manifested by inappropriate distributions of the mapping variables, our correction is achieved by gradually adjusting the distributions in the mapping phase space. The idea can be described in comparison to a recent derivation of a non-Hamiltonian variant of PBME with improved long time behaviors, which we designate as PBME-nH to distinguish it from the original PBME formalism.\textsuperscript{63} In a sense, based on the apparent Hamiltonian modification, PBME-nH can be thought of as an analogue of the Nosé-Hoover type extension\textsuperscript{64,65} in the conventional classical mechanics. As we know that there are different approaches that fulfill the same purpose as the Nosé-Hoover scheme in classical dynamics, we can imagine applying a different approach in PBME that fulfills the same purpose as PBME-nH, again in an analogous manner to classical simulations. Among several available algorithms\textsuperscript{64,66-68} that satisfy the same purpose as the Nosé-Hoover approach, simple scaling-based approaches often perform reasonably well.\textsuperscript{69} Berendsen’s thermostat\textsuperscript{57} and Bussi and co-workers’ velocity-rescaling thermostat\textsuperscript{68} will likely be the most widely applied methods in that category. Based on this intuition, we propose a similar scaling-based population correction method for dynamically correcting the mapping variable distributions along with PBME simulations.

Of course, the simple scaling is intuitively formulated and is not as rigorous as other alternatives such as iterative approaches based on the PLDM,\textsuperscript{47} whose results have been shown to be similar or even equivalent to the QCLE results.\textsuperscript{47} Instead, we aim to design our approach for performing large scale simulations, preferably with atomistic details with realistic interaction potentials. As the detailed role of the bath is becoming important,\textsuperscript{6,20,21,70-72} a scheme that is capable of describing the necessary details will surely be important in future studies.

The organization of this paper is as follows. In Sec. II, we describe our mapping variable scaling approach together with brief reviews on PBME and the secular-Redfield equation. We then present simulation details and procedures for employing our scaled PBME variant. In Sec. III, we test our approach by simulating energy transfers both in simple systems and in a more extended photosynthetic model system, and observe that the equilibrium population is achieved in the long time limit. By analyzing the errors in a range of parameters, we suggest conditions where our correction method can be reliable. In addition, we test how the initial bath energy distribution changes in time by adopting different schemes for sampling the initial bath modes, and then try to see its effect on the system dynamics. Finally, in Sec. IV, we summarize our results and provide practical remarks on employing this population correction scheme toward all-atom mixed quantum-classical simulations.

II. THEORIES AND SIMULATION DETAILS

A. Hamiltonian and non-Hamiltonian PBME

Let us first begin by reviewing the Poisson bracket mapping equation (PBME) and its non-Hamiltonian variant. PBME is a mixed quantum-classical approach that can be derived from quantum-classical Liouville equation (QCLE),\textsuperscript{46} and its equations of motion describe the propagations of both the quantum and the classical degrees of freedom as in the seminal development by Meyer and Miller.\textsuperscript{40,41} In QCLE, partial Wigner transformation is performed over the bath degrees of freedom in the quantum Liouville equation\textsuperscript{48} and then the bath derivative terms are truncated to the first order. The partially Wigner transformed Hamiltonian can be explicitly written as

\[ \hat{H}_W = \frac{p^2}{2M} + V_b(R) + \hat{h}_s(\hat{p}, \hat{q}) + \hat{V}_r(\hat{q}, R), \]  

where \( P, R, \) and \( M \) are momentum, position, and mass of the bath, respectively. \( V_b \) is the bath potential, and \( \hat{h}_s(\hat{p}, \hat{q}) \) is the system Hamiltonian operator which depends on the system momentum and position, \( \hat{p} \) and \( \hat{q} \). The system-bath coupling is denoted as \( \hat{V}_r(\hat{q}, R) \).

In fact, this Hamiltonian is based on operators of quantum degrees of freedom. Mathematical handling becomes naturally easier by recasting the operator equation with a certain basis set.\textsuperscript{48,73,74} For this purpose, PBME adopts the mapping formalism. In the mapping formalism,\textsuperscript{42,44} nuclear electronic states are assigned to as many fictitious harmonic oscillators. Specifically, the \( \alpha \)th electronic state is matched to a state with the \( \alpha \)th harmonic oscillator in its first excited
The density in the mapping space, \( \rho_m(t) \), is given as
\[
\frac{\partial}{\partial t} \rho_m(t) = -\frac{1}{\hbar} \sum_{\lambda,\kappa} h_{\lambda,\kappa}(R) \left( p_{\lambda} \frac{\partial}{\partial p_{\kappa}} - r_{\lambda} \frac{\partial}{\partial r_{\kappa}} \right) \rho_m(t)
\]
\[
- \left( \frac{P}{M} \frac{\partial}{\partial R} - \frac{\partial H_m}{\partial R} \right) \frac{\partial}{\partial P} \rho_m(t).
\]
This leads to Hamilton’s equations of motion for phase space variables:
\[
\frac{dr_{\lambda}}{dt} = \frac{\partial H_m}{\partial p_{\lambda}} = \frac{1}{\hbar} \sum_{\kappa} h_{\lambda,\kappa} p_{\kappa},
\]
\[
\frac{dp_{\lambda}}{dt} = -\frac{\partial H_m}{\partial r_{\lambda}} = -\frac{1}{\hbar} \sum_{\kappa} h_{\lambda,\kappa} r_{\kappa},
\]
\[
\frac{dR}{dt} = \frac{\partial H_m}{\partial P} = \frac{P}{M},
\]
\[
\frac{dP}{dt} = -\frac{\partial H_m}{\partial R} = -\frac{\partial V_b}{\partial R} - \frac{1}{2\hbar} \sum_{\lambda,\kappa} \frac{\partial h_{\lambda,\kappa}}{\partial R} \left( r_{\lambda} r_{\kappa} + p_{\lambda} p_{\kappa} - \hbar \delta_{\lambda,\kappa} \right).
\]
With these, we can track the time evolution of any physical observable through its expectation value written as
\[
B(t) = \int dX dx B_m(x, X, t) \rho_m(x, X).
\]
with Tr(h) denoting the trace of h. For consistency with Ref. 63, this non-Hamiltonian PBME will be referred to as PBME-nH.

B. Scaling-based dynamical population correction for PBME

Even though the non-Hamiltonian variant PBME-nH outperforms its Hamiltonian analogue in many respects, it still does not completely resolve the zero-point energy leak issue and subsequently suffers from negative population in extreme cases.63 At the very least, the populations in the long time limit deviate from a proper equilibrium distribution. This implies that (r, p) values corresponding to the electronic states are not properly distributed. To correct this, one may consider adopting a scaling scheme as alluded in Sec. I.

For this purpose, we suggest introducing an imaginary heat bath that exchanges energies with the fictitious harmonic oscillators that map the electronic degrees of freedom. In fact, an imaginary heat bath is often applied to controlling temperature in classical molecular dynamics simulations. For example, in the Berendsen thermostat, the temperature is adjusted by a relation \( dt/dt = (T_{\text{ref}} - T)/\tau_T \), where \( T \) and \( T_{\text{ref}} \) are, respectively, the system and the reference temperatures and \( \tau_T \) dictates the time constant for coupling the system and the imaginary bath. With this, we can envision that an imaginary heat bath can play a reasonable role of distributing the kinetic energy of the system. This aspect motivates us to adopt an imaginary heat bath in modulating the energies of the fictitious mapping oscillators, as their energies are related to populations through Eq. (10). Similarly to the Berendsen thermostat, the form of the equation for correcting the population of the state \( \lambda \) can be constructed as

\[
\frac{d}{dt} \rho_{\lambda\lambda}(t) = \frac{Q_{\lambda} - \rho_{\lambda\lambda}(t)}{\tau},
\]

where \( Q_{\lambda} \) represents the reference population and \( \tau \) determines the rate of correcting \( \rho_{\lambda\lambda}(t) \) toward \( Q_{\lambda} \). To connect with the phase space variables \( r \) and \( p \), we define \( s_\lambda(t) \) with squares of \( r \) and \( p \) from all individual trajectories:

\[
s_\lambda(t) = \sum_i \frac{1}{2\hbar} \left\{ \left( r_i(t) \right)^2 + \left( p_i(t) \right)^2 \right\} w_i. \tag{15}
\]

Here, the index \( i \) runs over individual trajectories as already given in Eq. (10). Because this leads to \( \rho_{\lambda\lambda}(t) = s_\lambda(t) - \sum_i w_i (x_i, X)/2 \), Eq. (14) transforms to

\[
\frac{d}{dt} s_\lambda(t) = \frac{Q_{\lambda} - s_\lambda(t) + \frac{1}{2} \sum_i w_i}{\tau}. \tag{16}
\]

Assuming that \( \tau \) is much longer than the trajectory integration time step (\( \Delta t \)), the scaling can be performed separately from PBME integration in an alternating manner. The simple first order integration in this case can be

\[
s_\lambda(t + \Delta t) = s_\lambda(t) \left( 1 + \frac{\Delta t}{\tau} y_\lambda(t) \right), \tag{17}
\]

with \( y_\lambda(t) = (Q_{\lambda} + \sum_i w_i)/2/s_\lambda(t) - 1 \). This also implies that we can uniformly scale \( r \) and \( p \) by a factor \( \kappa \) to correct the population, namely \( r_\lambda \leftarrow \kappa_r r_\lambda \) and \( p_\lambda \leftarrow \kappa_p p_\lambda \), after recalling that \( s_\lambda(t) \) is proportional to the sum of the squares of \( r \) and \( p \) (Eq. (15)). This scaling factor is given as

\[
\kappa_\lambda(t) = \sqrt{1 + \frac{\Delta t}{\tau} y_\lambda(t)}. \tag{18}
\]

From the above equations, one can easily notice that information from all trajectories at any given time is needed in computing \( \kappa \) with \( Q_{\lambda} \). Therefore, all trajectories should be propagated in a parallel manner. Namely, at each time step, all phase space variables evolve in time on all trajectories and then the system variables are scaled by the factor \( \kappa \) after combining the trajectory information. In practice, this is not a critical issue as parallelism is widely adopted in modern computations. An additional care that should be taken is the fact that \( \kappa \) is real only when \( \tau > |y_\lambda(t)\Delta t| \) is satisfied. This condition can be met by construction as we assume that \( \tau \) is much longer than \( \Delta t \). In experience, we observe that \( \kappa \) remains real when \( \tau \) is longer than \( \sim 100\Delta t \).

Having defined the scaling equation, we now need the time constant (\( \tau \)) and the reference population (\( Q_{\lambda} \)). In this study, we set \( \tau \) as the bath relaxation time (\( \tau_r \)) as it is related directly to the thermal system-bath relaxation and thus indirectly to the system relaxation. In addition, it is observed that the system equilibrates more slowly than this bath relaxation time,13, 77 so it will be a lower bound of the system equilibration time. Also, in this manner, the corrections are made solely based on the system characteristics, but not by an arbitrarily selected parameter. Choosing \( Q_{\lambda} \) is not as simple, as we are interested in non-equilibrium situations. Namely, if the equilibrium populations computed from the system characteristics are used as \( Q_{\lambda} \), non-equilibrium simulations will experience excessive bias toward equilibration in the short time limit and the early dynamics will deviate significantly from correct behaviors. Thus, it will be desirable to adopt time-dependent \( Q_{\lambda} \) that starts from the initial conditions of PBME simulations and gradually changes to the final equilibrium. Here, we achieve this by employing the Redfield equation with the secular approximation.1, 32 The Redfield equation treats the system dynamics through perturbation with the Markovian approximation1, 32 and is widely employed for explaining various phenomena in the condensed phase.2,78–80 It is usually written in the eigenstate basis \((|a, b, \ldots \rangle)\) of the system Hamiltonian \( h_s \):1, 27

\[
\frac{\partial}{\partial t} \rho_{ab}(t) = -i \omega_{ab} \rho_{ab}(t) + \sum_{c,d} R_{ab,cd}(t) \rho_{cd}(t), \tag{19}
\]

where \( \hbar \omega_{ab} = \varepsilon_a - \varepsilon_b \) is the energy difference between two excitonic states with \( U^{-1} h U = \varepsilon \). The Redfield tensor \( R \) determines the relaxation dynamics and can be obtained from a damping matrix,27 which can be constructed from the site-to-excitonic basis transform matrix \( U \) and the site energy time correlation.23, 81 The Redfield equation in this general form does not guarantee correct equilibrium populations in the long time limit33, 34 and sometimes shows negative or diverging populations.11 As these problems can be avoided in its secular approximation (often called as a Bloch model), where rapidly oscillating terms are neglected in the interaction
picture, we have adopted the secular-Redfield equation given as:

$$\frac{\partial}{\partial t} \rho_{ab}(t) = -i\omega_{ab}\rho_{ab}(t) + (1 - \delta_{ab})R_{ab,ab}\rho_{ab}(t) + \delta_{ab} \sum_{c} R_{ac,cc}\rho_{cc}(t).$$

As it stems from the Redfield equation, it is a good approximation as long as the system-bath coupling is small and the Markovian approximation is valid. With a basis transformation, the time-dependent reference can be obtained as

$$Q_{j}(t) = \sum_{a,b} U_{ja}\rho_{ab}(t)U_{jb}.$$  

This version of the Redfield equation surely shows deviating behaviors from the correct dynamics in the short time limit, but we are adopting it mainly toward correcting the long time behaviors in PBME.

### C. Models and simulation details

In our simulations, we have adopted Hamiltonians with the popular Frenkel exciton model:

$$H = h_{s} + h_{b} + V_{c},$$

where $h_{s} = \sum_{j} h_{s}^{j}\ket{\lambda}_{j}\bra{\lambda}$ is the system part and $h_{b} = \sum_{j,k} (P_{jk}^{2} + \omega_{k}^{2}R_{jk}^{2})/2$ is the bath part with harmonic oscillators. Of course, the frequency of the $k$th bath mode is $\omega_{k}$. For the system-bath coupling, we have utilized a bilinear form,

$$V_{c} = -\sum_{j,k} c_{jk}R_{jk}\ket{\lambda}_{j}\bra{\lambda},$$

with the coupling strength $c$. The mapping Hamiltonian in Eq. (4) is straightforwardly constructed and is subsequently used for PBME simulations.

We have first adopted a series of rather simple models to investigate how our scaling scheme performs. As a more realistic system, we have also employed the model of a representative photosynthetic system, the Fenna-Matthews-Olson (FMO) complex. Its system Hamiltonian elements were extracted from earlier studies on this complex. Following the widely adopted concept in photosynthetic model simulations, we have assumed that site energies are affected by independent harmonic baths. It is noted that this independent bath model is a special case of a common bath model, when the common bath is divided into $N$ non-overlapping segments. As noted previously, testing with a general common bath may give a straightforward interpretation on atomistic simulations beyond the harmonic bath description. In this study, however, we will focus on the computationally simpler independent bath case.

We have performed PBME simulations with scaled mapping variables with the following procedures:

1. Set necessary parameters such as the system Hamiltonian.
2. Solve the secular-Redfield equation into an analytic expression at any arbitrary time.

### III. RESULTS AND DISCUSSION

Let us begin our discussion with a two-state case. Figure 1 displays the time progresses of the density matrix elements when the system Hamiltonian is given with $h_{11} - h_{22}$ and $h_{21} = 100$ cm$^{-1}$.

![Figure 1](image)

**FIG. 1.** Site populations and concurrences in two-state model simulations. PBME-nH-S (solid line) is compared with PBME-nH (dashed) and HEOM (dotted) at different reorganization energies ($\lambda$). The other simulation parameters are $h_{11} - h_{22} = 100$ cm$^{-1}$, $h_{12} = h_{21} = 100$ cm$^{-1}$, $\tau_{c} = 100$ fs, and $T = 300$ K.
In this figure, we present coherent to incoherent transitions in the vertical direction by adopting reorganization energies in an increasing order. In general, both PBME-nH-S and PBME-nH are reproducing the coherent features well to a level comparable to the hierarchical equation of motion (HEOM),\textsuperscript{13} a numerically more accurate method than PBME. When the reorganization energy is excessively large ($\lambda = 500$ cm$^{-1}$), the PBME-nH-S does not give a correct population transfer pattern in the short time regime while PBME-nH displays a good agreement with HEOM in the same regime. This is rather expected as the Redfield approach will not be reliable in the Förster limit with large reorganization energies.\textsuperscript{27} At least, PBME-nH-S converges to a better population in the long time limit. The off-diagonal density elements from both PBME-nH-S and PBME-nH, depicted with the concurrence $C_{12} = 2|\rho_{12}|$, are also in reasonable agreements with the HEOM results.

To gain more comprehensive views, we have further tested two-state models with different settings of various parameters. Figure 2 shows the error levels of PBME-nH-S with these various simulation conditions, obtained by scanning the bath relaxation time ($\tau_c$), the temperature ($T$), the excitonic energy difference ($\varepsilon_1 - \varepsilon_2$), and the reorganization energy ($\lambda$). Ideally, our hope is to have PBME-nH-S behave as reliably as PBME-nH in the short time limit and converge to the secular-Redfield results in the long time limit. To facilitate quantitative analysis, we have defined a metric that measures the root-mean-squared error of the site 1 population:

$$\sigma^2_{\text{site1}} = \sum_i (\rho_{W,\text{HEOM}}(t_i) - \rho_{W,\text{PBME-nH-S}}(t_i))^2 / L.$$ 

Of course, in measuring the errors of secular-Redfield results, we used the Redfield density from Eq. (20) in the place of $\rho_W$. For the $t_c$-sum, we consider two windows: the initial 1 ps (0–1 ps) and the last 1 ps (4–5 ps) periods, to represent the short time and the long time limits, respectively. Time intervals of 1 fs were adopted for the sums with $L = 1000$. Not surprisingly, for most cases, $\sigma^2_{\text{site1}}$ from PBME-nH-S is in between the secular-Redfield and PBME-nH results as can be observed in Fig. 2. In the case of $\tau_c$ and $T$ with Figs. 2(a) and 2(b), PBME-nH-S provides semi-quantitative agreements with HEOM with $\sigma_{\text{site1}} \sim 0.03$. Meanwhile, the secular-Redfield equation gives satisfactory results for the tested $T$ range but relatively large errors with $\tau_c > 200$ fs. This indicates that PBME-nH-S can yield more reliable dynamics with a wider range of $\tau_c$. With PBME-nH, although the long time errors become larger at lower $T$, these errors are still in an acceptable regime for quantitative assessments. In the case of $\varepsilon_1 - \varepsilon_2$ and $\lambda$ with Figs. 2(c) and 2(d), however, we observe deterioration in the short time dynamics especially with $\varepsilon_1 - \varepsilon_2 > 350$ cm$^{-1}$ and $\lambda > 200$ cm$^{-1}$ with PBME-nH-S and the secular-Redfield equation. This deterioration in the short time limit is likely originating from the secular-Redfield equation, with its base on the Markovian approximation and the perturbative treatment. Because a large excitonic energy difference will increase the characteristic frequency in the system dynamics, namely $(\varepsilon_1 - \varepsilon_2)/\hbar$, it will drive the system to change rapidly in time. In such situations, the bath motions will become slow in a comparative sense, consequently breaking the ground for the Markovian approximation. On the other hand, the deterioration with large reorganization energies can be explained by excessive system-bath interactions that will render the perturbative treatment invalid.

In a sense, PBME-nH is already performing very well for the two-state system,\textsuperscript{63} and the gain from using PBME-nH-S is only marginal up to this stage. As it aims to correct the long time dynamics, its benefit will be more apparent at low temperatures. In addition, with the above error analyses, we expect that PBME-nH-S will perform reasonably well in the case of small $\lambda$ and small eigenstate energy differences. In order to confirm this proposition, in Fig. 3, we additionally present population dynamics in higher dimensional model systems with $N = 3–6$. In these cases, we consistently observe that PBME-nH-S achieves correct equilibrium populations with insignificant amounts of negative populations, while PBME-nH displays negative populations even at 1 ps. In all test cases, we also notice that oscillation patterns in
FIG. 3. Population dynamics in model systems with dimensions of $N = 3 - 6$. Short and long time populations are, respectively, shown in the left and the right panels. In these models, the $i$th site is coupled to the $(i - 1)$th and the $(i + 1)$th sites with the coupling constant of 100 cm$^{-1}$. Of course, the boundary sites (sites 1 and $N$) are only coupled to their direct neighbors (sites 2 and $N - 1$). Site energies are assigned in decreasing order with the energy step of 100 cm$^{-1}$. For example, the site energies of the 4-state model are 150, 50, −50, and −150 cm$^{-1}$. The other parameters were set to $\lambda = 50$ cm$^{-1}$, $\tau_c$ = 50 fs, and $T = 77$ K in all cases.

FIG. 4. Site populations of the FMO complex at 77 K, obtained with (a) PBME-nH-S and (b) PBME-nH up to 1 ps (left panels) and up to 10 ps (right panels). For sites 1−4, HEOM results are also displayed with dotted lines in the left panels.

short time regimes are similar in both PBME-nH and PBME-nH-S results. This aspect is encouraging as it suggests that PBME-nH-S will not distort the PBME-nH results to any significant extent in the short time limit. It was reported that the PBME-nH dynamics can become unreliable when the energy dispersion of the system is larger than $\sim 3 k_BT$.63 Thus, in the low temperature condition where the PBME-nH dynamics is expected to fail, one can adopt PBME-nH-S as a remedy.

As we have seen that PBME-nH-S can be reliably adopted in simple systems, let us move on to test it with a more realistic system. For this, we have adopted the FMO complex model at 77 K condition with the reorganization energy of 35 cm$^{-1}$.77 In fact, these parameters are in the regime where PBME-nH-S can outperform PBME-nH at $t > 1$ ps as we have demonstrated with simple model systems. In Fig. 4, we have displayed its population dynamics in comparison with the HEOM results with the bath relaxation time of 50 fs. We can clearly see that the short time behavior is in good accord with the patterns obtained from HEOM.77 On average, up to 1 ps, the site 1 population differs from the HEOM population by only $\sim 0.05$. The oscillating pattern is accurately reproduced with slight discrepancies in its amplitude and oscillation period. In addition, PBME-nH-S populations overlay favorably with the HEOM populations at $\sim 1$ ps and continues to converge to correct equilibrium values in the long time limit within an error level of $\sim 0.02$ at all sites. The population of the site 6 is slightly negative but is still within this error range. Indeed, in the long time regime, the improvement of PBME-nH-S over the uncorrected PBME-nH is obviously seen. Especially, when we attempted simulations in a wide range of temperatures, we always obtained reliable long time populations with less than 5% errors in all cases as shown in Fig. 5.

Even with this improvement in the long time limit, PBME-nH-S still does not guarantee proper system-bath interactions. For example, when the 77 K FMO model simulations were inspected in more detail, we could observe that the total mapping Hamiltonian ($H_m$) kept increasing by $\sim 0.001$ a.u. over the 10 ps time window. Even though the increased amount is rather insignificant compared to the total value ($H_m > 16$ a.u.), this is definitely in contrast to a good conserving behavior from PBME-nH.63 As the system energy is well-maintained through the scaling algorithm, we can deduce that the pure bath energy mainly contributes to the increase in $H_m$. This also evidences that scaling system variables induces the energy flow from the system to the bath, which induces a heating effect on the bath. In a sense, this is in a somewhat analogous situation with the “hot solvent-cold solute” case.
faced during classical MD simulations when a heat bath is coupled to different types of degrees of freedom. In addition, because a single scaling factor is employed to all system variables in all trajectories, how the scaling affects the energy flow in each individual trajectory is rather unclear. This aspect may require a further investigation with a focus on the system variable distributions in individual trajectories.

Another aspect that we have to consider with PBME-nH-S as a practical simulation tool will be its efficiency. This is especially important as we aim to use it for investigating dynamics with all-atom details. Basically, PBME-nH-S requires parallel computation to collect the density matrix information from multiple trajectories (Eq. (10)). However, the data size that needs to be transferred is rather small (\(\sim N^2\)) and the cost of data transfers for the global sum in Eq. (10) grows only logarithmically with respect to the number of trajectories. Thus, the overall cost will not be significantly higher than the case with PBME-nH. Indeed, when we tested with the FMO model, the increase in the computation time for the scaling operations was only \(\sim 5\%\). Moreover, when all-atom style simulations are attempted with numerous evaluations of interatomic/intermolecular interactions, the overhead for performing the present scaling approach will become even less significant. Thus, we believe that the PBME-nH-S costs will be comparable to the PBME-nH costs in large scale simulations.

As a last issue, let us discuss the effect that the initial bath distribution can have on the dynamics. Up to this point, we have always sampled the bath variables from the Wigner distribution with an assumption that it is a proper representation for the statistical distribution of harmonic oscillators. However, in mixed quantum-classical simulations, the bath does not strictly follow quantum mechanical rules and its distribution will eventually equilibrate to a classical Boltzmann distribution unless the bath modes are completely independent from each other. In addition, in large scale simulations with realistic bath environments, attaining Wigner distribution may not be even straightforward. Therefore, it will be informative if we can see how the bath energy distribution among different modes changes in time and how the change affects the system dynamics depending on the initial bath energy distribution.

Because the harmonic bath model that we adopted does not possess direct bath-bath coupling, the bath energy redistribution will be very slow. Thus, for clear inspection, we have performed rather long simulations over 500 ps with the FMO complex model. In addition, we have included only 20 bath modes to each electronic state, as the energy change per bath mode is more visible with a smaller number of modes. The average energy at each bath frequency computed with both PBME-nH-S and PBME-nH simulations with Wigner baths is displayed in Fig. 6. As noted in the above, the relaxation within the bath is quite slow. However, one can clearly see that the distributions migrate toward horizontally flat shapes (equipartition), a representative classical nature. Because the system-bath coupling which indirectly drives the bath energy redistribution vanishes in low and high frequency limits due to the spectral density shape, the bath mode energies are not changing in these limits. In addition, the PBME-nH-S (Fig. 6(a)) exhibits higher bath energies than the PBME-nH (Fig. 6(b)). This is because the zero-point energy leak, namely the unbalanced energy flow from the system to the bath, is compensated by the scaling operations on the system variables. It is also interesting to see that this compensation in PBME-nH-S also maintains the zero-point energies of the bath modes in the cases we tested. We should also note that the size of the energy flow between the system and the bath should be independent of the bath size as we are using a fixed value of the reorganization energy. Namely, when the bath is large enough, the energy change per bath mode becomes negligible. Thus, the collapse of the Wigner bath will not likely be an issue as long as the bath-bath coupling does not exist.
and as long as the simulation is performed for a finite amount of time.

Although the bath equilibration takes much longer time than the system relaxation, different patterns of system-bath energy flows may still affect the population dynamics. With this regard, in Fig. 7, we compare the population progresses of the FMO complex model obtained with the Wigner and the Boltzmann bath distributions. At lower temperature, where the difference between the distributions becomes more meaningful, the population dynamics appears indeed differently. The classical Boltzmann sampling leads to somewhat better agreements with the HEOM profiles at 77 K. Namely, with the Boltzmann sampled bath, oscillation amplitudes of the populations become higher and the population transfer from the site 1 to the site 2 becomes slower. In a sense, this is in agreement with a previous study, reporting that classical Boltzmann sampling at the trajectory initiation displayed a somewhat better behavior at a low temperature, implying that the classical distribution might be a good or even better option for semiclassical simulations with a large extent of classical natures involved. Of course, more in-depth studies are still required to verify this issue in a careful manner. At least, it will be interesting to investigate how the system dynamics is affected by the bath when the bath modes themselves are coupled to each other in a direct manner. In a sense, the observation that the Boltzmann sampling improved the system dynamics is in line with a recent report on a better representation from the classical formulation toward spectral density. In that case, the formulation based on the classical Boltzmann distribution led to the best agreement with experimental data with an appropriate temperature dependence, when it was applied to obtaining the spectral density from classical molecular dynamics trajectories. This type of an aspect should be considered carefully for employing mixed quantum-classical approaches in the future.

In principle, our mapping variable scaling approach can be adopted for revealing the role of the bath degrees of freedom in nonadiabatic phenomena at the atomic resolutions, similarly to the case where an Ehrenfest-style PBME was employed for simulating the FMO complex with atomic details. Once a proper modelling strategy is adopted, a large scale simulation should become possible with PBME-nH-S.
Operationally, to solve the secular-Redfield equation, a model Hamiltonian and the time correlation functions of system Hamiltonian elements are additionally required. These can be straightforwardly obtained with all-atom simulations. With the solution of the secular-Redfield equation, PBME-nH-S simulations can be performed by propagating all phase space variables with the scaling scheme. The added computational cost for performing scaling was only marginal with simple model based simulations, and will likely contribute even less in the relative sense with the large scale all-atom simulations toward complex systems.

We believe that the scaling method described here can be generally hybridized with other existing theories with the mapping formalism. That way, a new hybrid approach with complementary features from the mixed quantum-classical approaches and the quantum mater equation formalisms may be devised, as we have shown with the combination of PBME-nH and the secular-Redfield equation. With the recently accelerated theoretical developments, we expect that the utilizations of semiclassical simulations will continuously expand toward understanding more complex systems in longer time scales.

ACKNOWLEDGMENTS

This work was supported by the Institute for Basic Science (IBS) in Korea. The supercomputer time from Korea Institute of Science and Technology Information (KISTI) is also gratefully acknowledged.

22 Of course, a more detailed division scheme with core and reservoir distinctions of the bath have also been adopted. For example, see Ref. 16.