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Efficient steady-state solver for hierarchical quantum master equations

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Steady states play pivotal roles in many equilibrium and non-equilibrium open system studies. Their accurate evaluations call for exact theories with rigorous treatment of system-bath interactions. Therein, the hierarchical equations-of-motion (HEOM) formalism is a nonperturbative and non-Markovian quantum dissipation theory, which can faithfully describe the dissipative dynamics and nonlinear response of open systems. Nevertheless, solving the steady states of open quantum systems via HEOM is often a challenging task, due to the vast number of dynamical quantities involved. In this work, we propose a self-consistent iteration approach that quickly solves the HEOM steady states. We demonstrate its high efficiency with accurate and fast evaluations of low-temperature thermal equilibrium of a model Fenna–Matthews–Olson pigment-protein complex. Numerically exact evaluation of thermal equilibrium Rényi entropies and stationary emission line shapes is presented with detailed discussion. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4995424]

The steady state of a system is a critical condition where all properties do not change over time. The thermal equilibrium of an open system is one representative example, with the total system-and-bath composite density operator of $\rho_T^{eq} \propto e^{-\beta H_e/(\hbar \omega_f)}$. In this case, there are no net fluxes of particles, energy, and information within the system or between the system and bath. Thermal equilibrium plays a fundamental role in many practical studies, such as quantum transfer and transport, quantum control, quantum phase spectroscopy, and condensed phase spectroscopy, and so on. Its significance is manifested in many quantum dissipation theories. However, the quest for accurate and entangled steady-state solutions to exact theories is often numerically extremely challenging. In an open quantum system, the fluctuating bath environment drives the system toward thermal equilibrium. Perturbative theories such as quantum master equations mainly deal with short-time dynamics. These approximate theories usually violate the total composite detailed-balance relation, leading to even unphysical long-time or steady-state reduced system distributions.

We shall focus on the steady-state solutions to the hierarchical equations-of-motion (HEOM) formalism. This is an exact and nonperturbative method, with extensive applications in various systems. However, there are a vast number of auxiliary density operators (ADOs), which are actually of explicit physical meanings. These auxiliary operators are defined also in the reduced system subspace and hierarchically coupled with the reduced system density operator. Thus, solving the exact HEOM steady states for a vast number of dynamical variables, via either the real-time propagation or the imaginary-time method is numerically extremely expensive. The situation gets worse as the temperature is lowered and/or the non-Markovian memories are increased, and it takes a very long time for the correlated system and environment to be fully relaxed to the thermal equilibrium. Furthermore, in strong system-bath coupling regimes, the hierarchy can be quite deep and a huge number of ADOs will participate, which is a considerable challenge to the computer memory resources.

In this work, we propose a self-consistent iteration (SCI) method that efficiently and accurately evaluates the steady states to HEOM. The advantage of the SCI scheme over existing methods will be elaborated in due course. The new method is based on a reformulated hierarchical set of linear equations for the steady states, which are solved in an iterative and recursive manner, without intermediate storage space. Moreover, each individual iteration step also goes by the efficient, on-the-fly numerical filtering algorithm with a preset accuracy control. This implementation feature remarkably reduces further the computer memory and processing unit consumption. The proposed SCI scheme will be a very promising HEOM steady-state solver for complex open systems. As numerical illustrations, we evaluate the stationary emission spectrum of a model Fenna–Matthews–Olson (FMO) pigment-protein complex. This requires an accurate preparation of the initial HEOM equilibrium states within the single-exciton manifold. We report the numerically exact results at low temperatures, in terms of the thermal equilibrium Rényi entropies and the steady-state emission spectrum, and discuss the appealing performance of the SCI scheme.

Let us start with the standard setup for quantum dissipation theories. Considered is an arbitrary system $H_s$ embedded in a harmonic bath $H_B$, with the system-bath coupling being expressed in a multiple-mode decomposition form,
\( H_{SB} = \hbar \sum_a Q_a F_a \). Here, \( Q_a \) is an arbitrary system operator, and \( F_a \) is a linearly collective bath operator. The environment influence is then completely characterized by the bath correlation functions,\(^{29}\) which are further expanded in optimized exponential series,\(^{30-33}\)

\[
\langle F_a(t) F_b(0) \rangle_B \approx \sum_{k=1}^{K} \eta_{abk} e^{-\gamma_k t} + 2\Delta_{ab} \delta(t).
\]

We can then perform the time-derivatives on the Feymann–Vernon influence functional path integral expression,\(^{29}\) resulting in the HEOM formalism,\(^{13–16}\)

\[
\rho^{(n)}_n = -\left(i L_S + \sum_{ak} n_{ak} \gamma_k + \delta R \right) \rho^{(n)}_n - i \sum_{ak} A_{ak} \rho^{(n+1)}_{nAk} - i \sum_{ak} n_{ak} C_{ak} \rho^{(n-1)}_{nAk},
\]

with \( L_S \equiv \hbar^{-1} [H_S, \dot{O}] \), and

\[
\delta R \dot{O} = \sum_{ab} \Delta_{ab} [Q_a, [Q_b, \dot{O}]], \quad A_{ak} \dot{O} \equiv [Q_a, \dot{O}], \quad C_{ak} \dot{O} \equiv \sum_{b} (\eta_{abk} \dot{Q}_b - \eta_{ak}^* \dot{Q}_a) \dot{Q}_b.
\]

Here, \( \rho^{(0)}_n(t) \equiv \rho_S(t) \), the reduced system density operator; \( \{\rho^{(n>0)}_n(t)\} \) are the ADOs that are physically related to the hybridization bath dynamics,\(^{23,24,34–38}\) with \( n = \{n_{ak}\} \) being the collective index and \( n = \sum_{ak} n_{ak} \) specifying the hierarchy tier level, respectively. Each \( \rho^{(n)}_n(t) \) couples to its neighboring tier ADOs, \( \rho^{(n+1)}_n(t) \) and \( \rho^{(n-1)}_n(t) \). The associate index \( n_{ak} \) differs from \( n \) by \( n_{ak} \pm 1 \) at the specified subindex.

Before presenting the new method, let us recall two conventional schemes of evaluating the HEOM steady states. One is called the time-propagation approach, referred to also as the Runge–Kutta integrator scheme, based on the consideration that the total system-and-bath composite undergoes irreversible processes toward the thermal equilibrium, usually regardless of the initial conditions. In the HEOM framework, this corresponds to the real-time propagation of Eq. (2) to \( t \rightarrow \infty \). The initial values, \( \{\rho^{(0)}_n(0)\} \) with \( \text{tr} \rho^{(0)}(0) = 1 \), can be rather arbitrary. Apparently, this asymptotic long-time approach is extremely expensive, especially for low-temperature and/or long-memory systems, where the relaxation processes are very slow. Meanwhile, the imaginary-time HEOM provides a convenient approach to calculate the thermal equilibrium and evaluate thermodynamical properties.\(^{26,27}\) In particular, its equations of motion contain only single-sided actions of operators, and the simulation of steady states involves a definite integral. Therefore, solving steady states via the imaginary-time HEOM propagation does save the processing unit time, despite the fact that it still involves huge amounts of auxiliaries.

Another approach is to directly solve the steady states, or the thermal equilibrium \( \{\rho^{(\text{eq})}_n\} \), by setting every \( \rho^{(n)}_n = 0 \) in Eq. (2). This leads to a set of sparse linear equations for \( \{\rho^{(\text{eq})}_n\} \) to be solved under the normalization constraint of \( \text{tr} \rho^{(\text{eq})}_n = 1 \). The standard choices for solving the high-dimension linear equations are the Krylov subspace methods, exploited in the biconjugate gradient and the quasi minimal residual techniques.\(^{39}\)

None of these existing schemes are sufficiently efficient. First of all, HEOM (2) involves the total \( (N_a K + L)!/(N_a K)! (L)! \) number of ADOs, where \( N_a, K, \) and \( L \) denote the numbers of dissipative modes, exponential terms in each mode, and hierarchy truncation level, respectively. Note also that each ADO is a matrix in the reduced system subspace. Therefore, the conventional approaches to the HEOM steady-state solutions could be very expensive, even for two-level systems. The complexity here arises from the strong and non-Markovian system-bath couplings at low temperatures. In this case, the relaxation to thermal equilibrium is dynamically slow; meanwhile, the converged values of \( K \) and \( L \) are large, resulting in a huge combinatory number of ADOs. Moreover, to implement those existing schemes, it requires multiple extra memory space to store the intermediate ADOs. For instance, the standard Runge–Kutta integrators and their analogue Taylor series methods\(^{30,41}\) involve at least twice the number of intermediate ADOs; the Krylov subspace methods in general require even more.

Proposed below is an efficient iterative approach to solve the steady states of HEOM (2), by setting every individual \( \rho^{(n)}_n = 0 \). Define \( D_n \equiv i L_S + \gamma_n \). We have

\[
0 = (D_n + \delta R) \rho^{(\text{eq})}_n + i \sum_{ak} (A_{ak} \rho^{(n+1)\text{eq}}_{nAk} + n_{ak} C_{ak} \rho^{(n-1)\text{eq}}_{nAk}),
\]

We then recast this equilibrium steady-state equation as

\[
\rho^{(n)\text{eq}}_n = (D_n + \epsilon)^{-1} \left[ (\epsilon + \delta R) \rho^{(n)\text{eq}}_n - i \sum_{ak} (A_{ak} \rho^{(n+1)\text{eq}}_{nAk} + n_{ak} C_{ak} \rho^{(n-1)\text{eq}}_{nAk}) \right] - 1.
\]

The relaxation parameter \( \epsilon > 0 \) will be specified later.

The SCI evaluation on the solutions to Eq. (5) is as follows. Apparently, Eq. (5) constitutes a blocked Jacobi iteration for the solutions to the steady-state ADOs, using the right-hand-side ADOs to update the left-hand-side one. The iteration also proceeds recursively with increasing \( n \) so that \( \rho^{(n-1)\text{eq}}_{nAk} \) in the right-hand-side of Eq. (5) had just been updated. The iteration will converge as long as the diagonal part of \( (D_n + \epsilon) \) dominates. This suggests the lower bound for the relaxation factor \( \epsilon > 0 \). Increasing \( \epsilon \) will increase the numerical stability but decrease the convergence speed. For a good balance between accuracy and efficiency, in weak system-bath coupling regimes, it is appropriate to have \( \epsilon \) as the value about the spectrum span of \( L_S \). However, in strong system-bath coupling regimes, \( \epsilon \) should be tuned up accordingly to guarantee the numerical stability, at the cost of convergence speed. Also note that Eq. (5) practically has no singularity as it is solved under the constraint \( \text{tr} \rho^{(0)}(0) = 1 \). During the SCI evaluation, one keeps updating the ADOs on the left-hand-side of the steady-state condition or Eq. (5), until the converged result is achieved.

The SCI scheme has several advantages over the Runge–Kutta long-time solver for Eq. (2) and the Krylov subspace solver for Eq. (4). The details are as follows.
First, the SCI solver for Eq. (5) directly works on the steady-state ADOs, requiring no additional memory for intermediate results, as they just update the old ones. In comparison, both the Runge–Kutta integrators and the Krylov subspace methods require several intermediate vectors of the size of full ADOs.

Second, unlike the Krylov subspace solvers, the SCI scheme works well with the on-the-fly filtering algorithm.\textsuperscript{28} Apparently, the amplitudes of ADOs decrease quickly as the hierarchy tier level goes up since the diagonal decay component $\gamma_n$ increases. The filtering algorithm goes by properly scaling parameters for individual ADOs to have the same error tolerance as the reduced density matrix.\textsuperscript{28} This also automatically truncates the hierarchy. By filtering out those ADOs with scaled amplitudes being negligibly small, the SCI scheme remarkably reduces both the active memory cost and the processing unit time consumption.

Third, SCI runs in a recursive manner, in which the updating of $\rho_n^A$ via Eq. (5) proceeds with the newest values of $\rho_{n-1}^A|\text{eq}$. This greedy strategy accelerates the convergence speed. In fact, the higher-tier ADOs converge faster, and the convergence check can be performed after each recursive step. In comparison, the Krylov subspace methods minimize the global space error, regardless of the individual ADO properties. Moreover, during the Krylov iterations, the residual error often oscillates violently (cf. the inset of Fig. 1), and one even confronts divergence and breakdown conditions.\textsuperscript{39} On the other hand, in the real-time propagation, despite the fact that the relaxation to equilibrium is a slow process, one still has to use a small time step to compromise with the fast dynamical events. This increases the numerical stability but results in very low convergence speed.

Evidently, as discussed above, the SCI scheme does outperform the Krylov subspace solvers and the time-propagation methods. Its implementation procedure is straightforward: (i) We start with an initial guess, say $\{\rho^{(0)}_n = e^{-\beta H_t}/\tr e^{-\beta H_t}, \rho_{n|\text{eq}}^{(0)} = 0\}$, that physically corresponds to the thermal equilibrium in the absence of system-bath correlation. (ii) In each recursive iteration, we update individual $\rho_{n}^{(n)}$ according to Eq. (5), with increasing $n$, so that the newest values of $\rho_{n|\text{eq}}^{(n-1)}$ are used. There are several schemes of implementing Eq. (5), such as solving linear equations characterized by the tensor $(D_n + 1)$ or evaluating this tensor inverse directly via the eigen equation of $L_S$. In the weak to intermediate system-bath coupling regimes, one can exploit the Dyson expansion, where the tensor inverse is only needed for the diagonal part of $(D_n + 1)^{-1}$, while its off-diagonal part is treated in expansion. As far as we have tested, the Dyson expansion converges with only several terms. (iii) After each iteration, we check the convergence by examining the numerical error. A measure on the global error over all ADOs is

$$\text{Error} = \frac{1}{\epsilon} \left[ \sum_{n,ij} |\rho_{n|\text{old}}^{(n)} - \rho_{n|\text{old}}^{(n)}| \right]^{1/2}. \quad (6)$$

Here, $\rho_{n|\text{old}}^{(n)}$ is evaluated via the left-hand-side of Eq. (2) at the local step. We choose the scaling factor $s_n = (\prod_k n_{ak}|\eta_{ak}|n_{ak})^{1/2}$ to let $s_n\rho_{n|\text{old}}^{(n)}$ be of dimensionless and uniform error tolerance.\textsuperscript{28} In fact the error of SCI on each ADO decays almost smoothly and monotonically, as we have tested. Therefore, a relative error measure, such as $\max\{|s_n|\rho_{n|\text{old}}^{(n)} - \rho_{n|\text{old}}^{(n)}|\}$, which can be conveniently obtained in each recursive step, is a proper a priori indicator for convergence. We repeat (ii) and (iii) until the preset error tolerance is achieved. The converged ADOs thus constitute the steady-state solutions to the HEOM.

In numerical demonstrations, we solve the steady states for the FMO pigment-protein complex by a seven-exciton model\textsuperscript{19} and simulate its steady-state entropy and emission lineshapes, at both numerically challenging cryogenic temperatures and room temperatures. The site energies and electronic couplings of the exciton Hamiltonian are adopted from a previous study.\textsuperscript{19} We adopt the on-site Drude dissipation with reorganization energy $\lambda = 35 \text{ cm}^{-1}$ and cutoff frequency $\gamma = 50 \text{ cm}^{-1}$. In all the simulations below, we use the filtering error tolerance $2 \times 10^{-5}$, and the hierarchy levels are all truncated automatically.

Figure 1 depicts the convergence behavior of the SCI in simulating the steady states of the model FMO complex at 77 and 298 K. We observe that the iterative error decays almost monotonically and the SCI converges within about 250 steps. Moreover, with the filtering algorithm, the numerical cost of the SCI is very low. In the 77 K simulation, where two optimized exponential terms [cf. Eq. (1)] are used for each mode and the truncation level is $L = 13$, the number of active ADOs in the converged result is only 781, compared to 20 058 300 without filtering. In the 298 K case, where one exponential term is used and the truncation level is $L = 7$, the SCI results in 136 out of 3432 active ADOs. In the inset, we make a comparison with the transpose-free quasi minimal residual (TFQMR), one of the well-known Krylov subspace methods,\textsuperscript{39} based on the 298 K simulation. Apparently, the SCI outperforms the TFQMR.

![Figure 1. Iterative error measured by Eq. (6) in the SCI calculations for the steady states of the FMO complex at 77 K (black) and 298 K (red). Inset shows the convergence behaviors of the SCI and the TFQMR, one of the well-known Krylov subspace methods,\textsuperscript{27} for the simulation at 298 K. To make a fair comparison, we involve all ADOs up to hierarchy level 7 and switch off the numerical filtering for the simulations in the inset. The relaxation factor $\epsilon$ is set to be 485 cm$^{-1}$.

\[\text{Error} = \frac{1}{\epsilon} \left[ \sum_{n,ij} |\rho_{n|\text{old}}^{(n)} - \rho_{n|\text{old}}^{(n)}| \right]^{1/2}. \quad (6)\]
The Renyi entropy has been gaining increasing attention since its iterative error decays much faster; see the caption for details.

To examine the SCI scheme, we simulate equilibrium Renyi entropies of the excitonic FMO system at temperatures from as low as 20 K to 320 K, as shown in Fig. 2. Recently, the Renyi entropy has been gaining increasing attention since it is found to be experimentally measurable for the entanglement in quantum many-body systems. The $\alpha$-order Renyi entropy is defined as $S_\alpha = \frac{1}{1-\alpha} \ln(\text{tr}(\rho^\alpha))$, with $\alpha \geq 0$ and $\alpha \neq 1$. The limiting case of $\alpha \to 1$ actually recovers the von Neumann entropy, $S_N = -\text{tr}(\rho \ln \rho)$. The latter validates physically meaningful density operators, which should always be positive-definite. We also demonstrate the second-order Renyi entropy, $S_{2\alpha} = -\text{tr}(\rho^2)$, which provides a lower bound for $S_N$ and converges to the linear entropy, $S_L = 1 - \text{tr}\rho^2$, when the system approaches a pure state. All the simulated entropies decrease as the temperature goes down, and their gradient with temperature becomes much smaller below 50 K. Moreover, these entropies will be finite values even at 0 K due to the nature of reduced description. The reduced equilibrium system is still not a pure but a mixture state. It is notable that the presented results are highly accurate. For the most challenging case in our simulations, where the system is still not a pure but a mixture state.

We further simulate the stationary emission (SE) and linear absorption (LA) lineshapes of the FMO complex at 77 and 298 K. For clearness, the emission signals have been scaled to have the same maximum as the absorption at the same temperature. The optical transition dipoles are extracted from the crystal structure of C. tepidum (PDB code: 3ENI).

FIG. 2. Equilibrium entropies of the model FMO complex at temperatures from 20 K to 320 K. The black, red, and blue curves show the results of the von Neumann entropy, $S_N = -\text{tr}(\rho \ln \rho)$, the second-order Renyi entropy, $S_{2\alpha} = -\ln(\text{tr}\rho^2)$, and the linear entropy, $S_L = 1 - \text{tr}\rho^2$, respectively.

FIG. 3. Stationary emission (SE) and linear absorption (LA) lineshapes of the model FMO complex at 77 and 298 K. For clearness, the emission signals have been scaled to have the same maximum as the absorption at the same temperature. The optical transition dipoles are extracted from the crystal structure of C. tepidum (PDB code: 3ENI).

In summary, we develop the SCI approach to an efficient and accurate evaluation on the steady states of open quantum systems in the HEOM framework. The new method works at a much lower numerical cost and faster convergence speed than the Krylov solver and the time-propagation method. Moreover, one can readily apply the SCI method to efficiently solve HEOM in the complex frequency domain on $\rho_n^\text{HEOM}(z) = \int_0^\infty dt e^{-iz\omega} \rho_n(\omega)$. The numerical inverse Laplace transformation can then be followed for the real time dynamics, the nonperturbative dissipative kernels, and the population transfer rate kernels, and so on. We conclude that SCI is a promising HEOM solver on both the steady states and the dynamics of large complex open systems.

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