Note: A simple improved termination scheme for the hierarchical equations of motion

Thomas P. Fay\textsuperscript{a)

Department of Chemistry, University of California, Berkeley, CA 94720, USA

The study of open system quantum dynamics has been transformed by the hierarchical equations of motion (HEOM) method, which gives the exact dynamics for a system coupled to a harmonic bath at arbitrary temperature and system-bath coupling strength. However, in its standard form the method is only consistent with the the weak-coupling master equation at all temperatures when many auxiliary density operators are included in the hierarchy, even when low temperature corrections are included. In this Note we propose a new correction scheme for the termination of the hierarchy which alleviates this problem, and restores consistency with the weak-coupling master equation with a minimal hierarchy. The new scheme is found to improve convergence of the HEOM even beyond the weak-coupling limit and is very straightforward to implement in existing HEOM codes.

The hierarchical equations of motion (HEOM) method is a powerful tool for studying the dynamics of open quantum systems.\textsuperscript{1,2} As we will describe, in these equations a low temperature correction is often included to correct for truncation of the series expansion of bath correlation functions, and in this Note we propose an improved version of this correction.

In short, the HEOM method gives the exact system dynamics for a system coupled to a harmonic bath, $\hat{H} = \hat{H}_s + \hat{H}_b + \hat{V} \hat{B}$, in terms of a hierarchy of auxiliary system density operators (ADOs), which can be obtained by differentiating the exact path-integral expression for the system density operator.\textsuperscript{1} The ADOs are denoted $\hat{\rho}_n(t)$, indexed by $n = (n_0, n_1, \ldots)$, and the system dynamics are obtained as the zeroth element, i.e. $\hat{\rho}(t) = \text{Tr}_b[\hat{\rho}_0(t)] = \hat{\rho}_0(t)$, of this hierarchy.\textsuperscript{2} The ADOs obey the following equation of motion,

$$\frac{d}{dt} \hat{\rho}_n(t) = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}_n(t)] - \sum_k n_k \nu_k \hat{\rho}_n(t) + \sum_k \left( \sqrt{n_k + 1} \mathcal{L}_k \cdot \hat{\rho}_n(t) + \sqrt{n_k} \mathcal{L}_k^+ \hat{\rho}_n(t) \right)$$  \hspace{1cm} (1)

where $n_k^\pm = (n_0, \ldots, n_k \pm 1, \ldots)$, $\mathcal{L}_k^- = -\sqrt{n_k} [\hat{V}, \cdot]$, and $\mathcal{L}_k^+ = (a_k \hat{V} - a_k^\dagger \hat{\mathcal{V}})/\sqrt{n_k}$, $a_k$, $a_k^\dagger$ and $\nu_k$ are obtained from the decomposition of the bath correlation function as $C(t) = \sum_{k=0}^\infty a_k e^{-\nu_k t}$ and $C(t)^* = \sum_{k=0}^\infty \bar{a}_k^\dagger e^{-\nu_k t}$. Note we assume $\nu_k$ are indexed in ascending order by their real part, and we have written the HEOM in their scaled form.\textsuperscript{3}

Although this hierarchy is formally infinite, the set of auxiliary density operators can be truncated to some finite set by only including some set of modes up to $k = M = k_c - 1$, and by truncating this infinite set of ADOs to some finite set. The dynamics can be converged to arbitrary precision by increasing the number of modes included and the number of ADOs included. A standard approach to correct for the truncated terms in the series expansion of $C(t)$ is to approximate the exponential with a one-sided delta function, $e^{-\nu_k t} \approx (1/\nu_k) \delta_\nu(t)$, for $k \geq k_c$.\textsuperscript{5,4} This gives the following low-temperature correction, which is added to the right-hand side of Eq. (1),

$$\Xi_0 \hat{\rho}_n(t) = \sum_{k=k_c}^{\infty} \nu_k^{-1} \mathcal{L}_k \cdot \mathcal{L}_k^+ \hat{\rho}_n(t)$$ \hspace{1cm} (2)

For this approximation to be valid, we require that the approximated terms decay much faster than the characteristic system frequencies. In other words $\nu_k \gg \omega_s$ should be satisfied for $k \geq k_c$. For problems with large system energy scales this approximation can break down, leading to slow convergence of the HEOM dynamics with respect to $k_c$, even though such systems can be well approximated with simple perturbative theories. This is because the $k_c = 0$ limit of $\Xi_0$ is not consistent with weak-coupling perturbative theories. Examples of this slow convergence of the HEOM is shown in the left hand panels of Figs. 1 and 2 for a spin boson model (details of which are given below).

An alternative modified low temperature correction term can be derived by taking an alternative perspective on the truncation. First we note that we can write down the hierarchy of ADOs as

$$|\rho(t)\rangle = \sum_{n=0}^{\infty} |\rho_n(t)\rangle \otimes |n\rangle$$ \hspace{1cm} (3)

where $|n\rangle$ is a basis vector corresponding to auxiliary density operator $n$, and $|\rho_n(t)\rangle$ is the Liouville space vector of

---

\textsuperscript{a)Electronic mail: tom.patrick.fay@gmail.com
FIG. 2. Convergence of the HEOM dynamics for the spin boson model with $\beta\varepsilon = 15, \beta\Delta = 5, \beta\hbar\omega_D = 5, \beta\lambda_D = 2.5$. The $\Gamma_c = 6\omega_D$ results contain explicit modes up to $M = 5$, and for $\Gamma_c = 12\omega_D$ up to $M = 6$. Converged results use $\Gamma_c = 20\omega_D$.

This ADO. We can write down the equation of motion more compactly as

$$\frac{d}{dt}\langle \rho(t) \rangle = \mathcal{L}\langle \rho(t) \rangle = (\mathcal{L}_s \otimes \mathcal{I}_{\text{ado}} - \mathcal{I}_s \otimes \Gamma + \mathcal{V})\langle \rho(t) \rangle$$ (4)

where $\mathcal{L}_s = -(i/\hbar)[\hat{H}_s, \cdot]$ is the system Liouvillian, $\mathcal{I}_s$ and $\mathcal{I}_{\text{ado}}$ are identity operators on the system Liouville space and the set of ADOs respectively, $\Gamma$ is diagonal matrix of decay rates for each ADO, and $\mathcal{V}$ is the term that couples different ADOs within the hierarchy.

We can obtain an equation for the hierarchy of ADOs where the number of modes is truncated at $k = M$, by projecting this equation with the projection operator $\mathcal{P} = \sum_{n \in \mathcal{N}_M} \mathcal{P}_n = \sum_{n \in \mathcal{N}_M} \mathcal{I}_s \otimes [n]|n\rangle\langle n|$ where $\mathcal{N}_M$ is the set of all ADO indices where $n_k = 0$ for $k > M$. We can combine use this projection operator in the second order Markovian Nakajima-Zwanzig equation $^5$ to obtain a correction for the truncation of the number of modes. This perturbative correction is

$$\mathcal{K} = \int_0^\infty dt \mathcal{P}\mathcal{V}e^{\mathcal{L}_0 t}\mathcal{V}\mathcal{P} = \sum_{n \in \mathcal{N}_M} \Xi_n \mathcal{P}_n.$$ (5)

where $\mathcal{L}_0 = \mathcal{L}_s \otimes \mathcal{I}_{\text{ado}} - \mathcal{I}_s \otimes \Gamma$. The new low temperature correction term $\Xi_n$ for each ADO is given by

$$\Xi_n = \sum_{k = M + 1}^{\infty} \mathcal{L}_k \Pi_k (\nu_k + \gamma_n - \Lambda_k)^{-1}\Pi^{-1}_{k-1} \mathcal{L}_{k-1}$$ (6)

where $\Pi_k$, $\Lambda_k$, and $\gamma_n$ are the matrix of eigenvectors, and eigenvalues of $\mathcal{L}_s$, i.e. $\mathcal{L}_s = \Pi_k \Lambda_k \Pi^{-1}_k$, and $\gamma_n = \sum_{k = M + 1}^{\infty} n_k \nu_k$. This gives an alternative low-temperature correction which accounts for the finite system frequencies. Clearly it is very closely related to the original form in Eq. (2), to which it reduces if $|\nu_n - \Lambda_k| \ll \nu_k$.

This new low temperature correction reduces the HEOM to the perturbative Markovian Nakajima-Zwanzig equation in the limit where only $\rho_0(t)$ is included in the hierarchy, which in the weak-coupling limit is exact and obeys detailed balance. In this limit the original low-temperature corrected HEOM reduces to a high temperature master equation $^4$ which does not satisfy detailed balance at all temperatures, and for this reason it is reasonable to expect that the new low temperature corrected HEOM should converge faster in the low temperature limit.

We can also extend this projection operator treatment of the HEOM truncation to obtain a correction term for the termination of the hierarchy to some truncated set of $n \in \mathcal{N}_{\text{trunc}}$. If we only include the diagonal contributions in the hierarchy, i.e. terms that only couple $|\rho_n(t)\rangle$ to itself, then the correction term for ADO $n$ arising from hierarchy truncation is

$$\Xi^{\text{trunc}}_n = \sum_{k \in \mathcal{M}_{\text{trunc}}^n} (n_k + 1) \mathcal{L}_k \Pi_k (\nu_k + \gamma_n - \Lambda_k)^{-1}\Pi^{-1}_{k-1} \mathcal{L}_{k-1}$$ (7)

where $\mathcal{M}_{\text{trunc}}^n$ is the set of mode indices at which ADO $n$ terminates. Including this correction term adds no additional dense blocks to the effective generator for the truncated hierarchical equations of motion, meaning it can be added with negligible extra computational cost. This truncation term can be viewed as modification of the Yanimura et al.’s fast modulation scheme $^9$ and unlike other proposed schemes $^{10}$ does not produce a time-dependent generator in the equations of motion, which adds complexity to the time propagation.

In order to test the convergence properties of the HEOM with the new low-temperature corrections, calculations were performed on the spin boson model with the two correction schemes. In this model $\hat{H}_c = (\epsilon/2)\sigma_z + \Delta\sigma_x$, and $\hat{V} = \hat{\sigma}_x$, where $\sigma_\alpha$ are the Pauli operators, and the spectral density for the bath is taken to be a Debye spectral density $\mathcal{J}(\omega) = (\lambda_D/2)\omega\delta\omega/(\omega^2 + \omega_D^2)$. The standard Matsubara decomposition of the bath correlation function was used, and the hierarchy was truncated using a frequency cut-off criterion where only ADOs with $\gamma_n \leq \Gamma_c$ were included. The initial condition was set to $\hat{\rho}_c(0) = |1\rangle\langle 1| = (1 + \hat{\sigma}_z)/2$ and other parameters are given in the figure captions.

In Fig. 1 we see that even for a case with relatively weak system-bath coupling, where the reorganisation energy $\beta\lambda_D = 0.1$ is small compared to the system energy scales, the original low temperature corrected HEOM converges very slowly with respect to the cut-off parameter $\Gamma_c$, with contributions from Matsubara terms up to $M = 3$ (when $\Gamma_c = 6\pi/\beta$) still not being sufficient to converge the results. Conversely the new low-temperature correction scheme gives essentially converged results for a hierarchy consisting of one ADO. The same trend is seen in a more challenging case in Fig. 2, in which $\beta\lambda_D = 5$ and $\beta\omega_D = 5$, where small hierarchies give converged results with the new correction scheme, whereas the original scheme is unstable and gives unphysical populations for the same sizes of hierarchy.

The improved convergence of the new low temperature correction can be very useful in systems with multiple baths. As an example we have simulated the site populations dynamics of an LHClII 7-mer subcomplex, composed of the 602a, 603a, 608b, 609b, 610a, 611a and 612a chromophores, at $T = 150$ K, with the chromophore baths described by the single Debye spectral density model from Ref. 13 with $\lambda_D = 220$ cm$^{-1}$ and $\omega_D = 357.68$ cm$^{-1}$. The initial system condition was set as the highest energy excitonic state. This is shown in Fig. 3 where it
FIG. 3. A comparison of the original and new low temperature corrections for the LHCII 7-mer site populations at 150K for long time dynamics up to $t = 20$ ps (left), and short time dynamics up to $t = 3$ ps (left). Converged results use the new correction with $\Gamma_c = 1980 \text{ cm}^{-1}$, which has contributions from ADOs with up to $L = \sum \gamma k n \gamma k = 5$ and $M = 3$, and the other results $\Gamma_c = 1320 \text{ cm}^{-1}$, which have contributions from ADOs with up to $L = 3$ and $M = 2$. The colours correspond to: blue 602a, red 603a, gold 608b, purple 609b, green 610a, cyan 611a, and burgundy 612a.

can be seen that for the same size of hierarchy, again using the Matsubara decomposition scheme with a frequency cut-off, the new low temperature correction yields more accurate the long time populations and short-time dynamics for this model compared to the converged results.

In conclusion, we have shown that using Nakajima-Zwanzig theory we can obtain corrections for truncation of the HEOM which restore consistency with the weak-coupling quantum master equation at all temperatures. This correction scheme is found to improve convergence of the HEOM in several cases, with negligible additional computational effort. The new scheme also removes instabilities in the HEOM in some cases, and can be seen as complementary to other approaches, which have recently been proposed. Finally, this correction scheme can be easily implemented in existing HEOM codes, and can easily be extended to other forms of the HEOM, such as those which employ a Padé expansion for the bath correlation functions.

ACKNOWLEDGEMENTS

TPF kindly thanks David Limmer for his comments on the manuscript. TPF was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, CPIMS Program Early Career Research Program under Award No. DE-FOA0002019.

SUPPORTING INFORMATION

The supporting information includes more details of the relationship between the HEOM low-temperature termination schemes and the weak-coupling quantum master equation, an exploration of using Redfield theory instead of Nakajima-Zwanzig theory to terminate the HEOM, and a description of the adaptive short iterative Arnoldi algorithm used to propagate the equations of motion in this work.

DATA AVAILABILITY

Data presented in the paper are available from the author upon a reasonable request. Code used to perform the simulations is publicly available at https://github.com/tomfay/heom-lab.

1. Y. Tanimura and R. Kubo, “Time Evolution of a Quantum System in Contact with a Nearly Gaussian-Markoffian Noise Bath,” J. Phys. Soc. Japan 58, 101–114 (1989).
2. Y. Tanimura, “Numerically “exact” approach to open quantum dynamics: The hierarchical equations of motion (HEOM),” J. Chem. Phys. 135, 020901 (2020).
3. Q. Shi, L. Chen, G. Nan, R.-X. Xu, and Y. Yan, “Efficient hierarchical Liouville space propagator to quantum dissipative dynamics,” J. Chem. Phys. 150, 084105 (2009).
4. A. Ishizaki and Y. Tanimura, “Quantum dynamics of system strongly coupled to low-temperature colored noise bath: Reduced hierarchy equations approach,” J. Phys. Soc. Japan 74, 3131–3134 (2005).
5. S. Nakajima, “On Quantum Theory of Transport Phenomena,” Prog. Theor. Phys. 20, 948–959 (1958).
6. R. Zwanzig, “Ensemble method in the theory of irreversibility,” J. Chem. Phys. 33, 1338–1341 (1960).
7. H. Mori, “Transport, Collective Motion, and Brownian Motion,” Prog. Theor. Phys. 33, 423–455 (1965).
8. H. Takahashi and Y. Tanimura, “Open Quantum Dynamics Theory of Spin Relaxation: Application to g SR and Low-Field NMR Spectroscopies,” J. Phys. Soc. Japan 89, 064710 (2020).
9. Y. Tanimura and P. G. Wolynes, “Quantum and classical Fokker-Planck equations for a Gaussian-Markovian noise bath,” Phys. Rev. A 43, 4131–4142 (1991).
10. R.-X. Xu, P. Cui, X.-Q. Li, Y. Mo, and Y. Yan, “Exact quantum master equation via the calculus on path integrals,” J. Chem. Phys. 122, 041103 (2005).
11. A. G. Dijkstra and V. I. Prokhorenko, “Simulation of photo-excited adenine in water with a hierarchy of equations of motion approach,” J. Chem. Phys. 147, 064102 (2017).
12. H. C. H. Chan, O. E. Gamel, G. R. Fleming, and K. B. Whaley, “Single-phonon absorption by single photosynthetic light-harvesting complexes,” J. Phys. B At. Mol. Opt. Phys. 51, 054002 (2018).
13. C. Kreisbeck, T. Kramer, and A. Aspuru-Guzik, “Scalable High-Performance Algorithm for the Simulation of Exciton Dynamics. Application to the Light-Harvesting Complex II in the Presence of Resonant Vibrational Modes,” J. Chem. Theory Comput. 10, 4045–4054 (2014).
14. S. Dunn, R. Tempelaur, and D. R. Reichman, “Removing instabilities in the hierarchical equations of motion: Exact and approximate projection approaches,” J. Chem. Phys. 150, 184109 (2019).
15. T. Li, Y. Yan, and Q. Shi, “A low-temperature quantum Fokker-Planck equation that improves the numerical stability of the hierarchical equations of motion for the Brownian oscillator spectral density,” J. Chem. Phys. 156, 064107 (2022).
16. J. Johansson, P. Nation, and F. Nori, “QuTiP 2: A Python framework for the dynamics of open quantum systems,” Comput. Phys. Commun. 184, 1234–1240 (2013).
17. T. Ikeda and G. D. Scholes, “Generalization of the hierarchical equations of motion theory for efficient calculations with arbitrary correlation functions,” J. Chem. Phys. 152, 204101 (2020).
18. pyrho: A python package for reduced density matrix techniques,” https://github.com/berkelbach-group/pyrho.
19. J. Hu, M. Luo, F. Jiang, R.-X. Xu, and Y. Yan, “Padé spectrum decompositions of quantum distribution functions and optimal hierarchical equations of motion construction for quantum open systems,” J. Chem. Phys. 134, 244106 (2011).
Supporting Information to “Note: A simple improved termination scheme for the hierarchical equations of motion”

Thomas P. Fay
Department of Chemistry, University of California, Berkeley, CA 94720, USA

S.1. RELATIONSHIP TO THE WEAK-COUPLING MASTER EQUATION

We can directly apply Markovian second order Nakajima-Zwanzig theory to the full system+bath Hamiltonian with the projection operator \( \mathcal{P} = \hat{\rho}_b \text{Tr}_b[\cdot] \) to obtain a weak-coupling quantum master equation which is valid at all temperatures.\(^1\)\(^\text{3}\) The relaxation superoperator \( \mathcal{R} \) is given by

\[
\mathcal{R}\hat{\sigma} = -\int_0^\infty \text{d}t \text{Tr}_b[[\hat{\mathcal{V}}\hat{B}, \hat{L}_{+}]_t[\hat{\mathcal{V}}\hat{B}, \hat{\sigma}\hat{\rho}_b]]
\]

\[
= -\int_0^\infty \text{d}t \mathcal{V}^\times \text{Tr}_b[\hat{B}e^{(\hat{L}_{+})_t}[\hat{\mathcal{V}}\hat{B}, \hat{\sigma}\hat{\rho}_b]]
\]

\[
= -\int_0^\infty \text{d}t \mathcal{V}^\times e^{\hat{L}_{+}t} \text{Tr}_b[\hat{B}(t)[\hat{\mathcal{V}}\hat{B}, \hat{\sigma}\hat{\rho}_b]]
\]

\[
= -\int_0^\infty \text{d}t \mathcal{V}^\times e^{\hat{L}_{+}t}(\text{Tr}_b[\hat{B}(t)\hat{\mathcal{B}}\hat{\rho}_b]\hat{\mathcal{V}}\hat{\sigma}-\text{Tr}_b[\hat{B}(t)\hat{\mathcal{B}}\hat{\rho}_b]\hat{\sigma}\hat{\mathcal{V}})
\]

\[
= -\int_0^\infty \text{d}t \mathcal{V}^\times e^{\hat{L}_{+}t}(C(t)\hat{\mathcal{V}}\hat{\sigma}-C(t)^*\hat{\sigma}\hat{\mathcal{V}})
\]  

(\text{S.1})

where \( \mathcal{V}^\times = [\hat{\mathcal{V}}, \cdot] \), and \( \hat{L}_{+} = -\frac{\text{i}}{\hbar}[\hat{H}_b, \cdot] \). Inserting the decomposition of \( C(t) \) and \( C(t)^* = \sum_{k=0}^{\infty} \bar{a}_k e^{-\beta E_k t} \), and inserting the eigen-decomposition of \( \hat{L}_{+} = \sum_{k=0}^{\infty} \lambda_k \hat{L}_{+}^{-1} \lambda_k \), we obtain

\[
\mathcal{R} = \sum_{k=0}^{\infty} \mathcal{L}_{-}\mathcal{L}_{+}^{-1}(E_{k}\mathcal{V}_{k} - \lambda_{k})^{-1}\mathcal{L}_{k+}
\]  

(\text{S.2})

which is exactly \( \Xi_{m=0} \) with \( k_c = 0 \). Within the secular approximation, when the system bath coupling is weak and coherences and populations decouple in the system energy eigenbasis \( |E_n\rangle \), the energy eigenstate population transfer rates satisfy detailed balance.\(^4\)

\[
\frac{\mathcal{R}_{E_n E_m}}{\mathcal{R}_{E_m E_n}} = e^{-\beta(E_{n}-E_{m})}.
\]  

(\text{S.3})

For the standard low-temperature correction, when \( k_c = 0 \) we have\(^5\)

\[
\Xi_{0}\hat{\sigma} = -\int_0^\infty \text{d}t \mathcal{V}^\times (C(t)\hat{\mathcal{V}}\hat{\sigma}-C(t)^*\hat{\sigma}\hat{\mathcal{V}}),
\]  

(\text{S.4})

which is not consistent with the weak-coupling master equation except in the high temperature limit. This means the standard low-temperature correction to the HEOM breaks down in the low temperature limit when \( k_c = 0 \), even for arbitrarily weak system-bath coupling.

S.2. THE REDFIELD CORRECTION SCHEME

Using the projection operator formalism describing in the main note, we can also obtain a Redfield correction scheme by instead using the second order time-convolutionless quantum master equation\(^6\) in the Markovian limit with the same projection operator on the ADOs. The Redfield superator is obtained as

\[
\mathcal{K} = \int_0^\infty \text{d}t \mathcal{P}\mathcal{V} e^{\mathcal{L}_{+}t}\mathcal{V} e^{-\mathcal{L}_{+}t}\mathcal{P},
\]  

(\text{S.5})

\(^{a)}\text{Electronic mail: tom.patrick.fay@gmail.com}\)
FIG. S.1. Convergence of the site 1 population dynamics, $(1 + \langle \sigma_z(t) \rangle)/2$, for the spin boson model with $\beta \epsilon = 20$, $\beta \Delta = 5$, $\beta \hbar \omega_D = 2$, $\beta \lambda_D = 0.5$, comparing the RF and NZ2 correction schemes.

FIG. S.2. Convergence of the HEOM dynamics for the spin boson model with $\beta \epsilon = 15$, $\beta \Delta = 5$, $\beta \hbar \omega_D = 5$, $\beta \lambda_D = 2.5$, comparing the RF and NZ2 correction schemes. The $\Gamma_c = 6\omega_D$ results contain explicit modes up to $M = 5$, and for $\Gamma_c = 12\omega_D$ up to $M = 6$.

which gives the following low temperature correction term,

$$\Xi_n = \sum_{k=M+1}^{\infty} \mathcal{L}_k \Pi_0 (J_k \circ \Pi_0^{-1} \mathcal{L}_{k+1} \Pi_1) \Pi_1^{-1}$$  \hspace{1cm} (S.6)

where $\circ$ denotes the element-wise (Schur) product, and $J_k$ is defined by

$$[J_k]_{n,m} = \frac{1}{v_k - (\lambda_{s,n} - \lambda_{s,m})}.$$  \hspace{1cm} (S.7)

where $\lambda_{s,n}$ is the nth eigenvalue of the system Liouvillian, $\mathcal{L}_s = -i[\hat{H}_s, \cdot]$. Analogously the RF truncation correction is

$$\Xi_n^{\text{trunc}} = \sum_{k \in \lambda_{\text{max}}} (n_k + 1) \mathcal{L}_k \Pi_0 (J_k \circ \Pi_0^{-1} \mathcal{L}_{k+1} \Pi_1) \Pi_1^{-1}.$$  \hspace{1cm} (S.8)

In Figs. S.1 and S.2 we compare the Redfield (RF) and second order Nakajima-Zwanzig (NZ2), correction schemes for the models presented in the main note. For both the low reorganisation energy spin-boson model (Fig. S.1) and the stronger higher reorganisation energy case (Fig. S.2) the RF scheme is less accurate and in the latter case it is unstable, and breaks down at even shorter times than the original low-temperature correction scheme without any truncation corrections. Also in the LHCII 7-mer model (results in Fig. S.1) the RF scheme has larger errors at short and long times than the NZ2 scheme, with very little difference between the RF and original low temperature correction scheme.
FIG. S.3. A comparison of the original and new low temperature corrections for the LHCII 7-mer site populations at 150K, comparing the RF and NZ2 correction schemes. Converged results use the new correction with $\Gamma_c = 1980$ cm$^{-1}$, which has contributions from ADOs with up to $L = 5$ and $M = 3$, and the other results $\Gamma_c = 1320$ cm$^{-1}$, which have contributions from ADOs with up to $L = 3$ and $M = 2$. The colours correspond to: blue 602a, red 603a, gold 608b, purple 609b, green 610a, cyan 611a, and burgundy 612a.

S.3. ADAPTIVE SHORT-ITERATIVE ARNOLDI INTEGRATION SCHEME

All of the results presented here are obtained by integrating the HEOM with an adaptive short-iterative Arnoldi algorithm. The HEOM is first expressed as

$$\frac{d}{dt}|\rho(t)\rangle = L|\rho(t)\rangle.$$  \hspace{1cm} (S.9)

At a given $t_0$ the $k$-dimensional Krylov subspace is constructed iteratively using the Arnoldi algorithm. This subspace $\mathcal{K}_k$ spans the set of vectors $\{|\rho(t_0)\rangle, L|\rho(t_0)\rangle, \ldots, L^{k-1}|\rho(t_0)\rangle\}$, and its basis is denoted $\mathcal{B}_k = \{|q_j\rangle|j = 0, \ldots, k-1\}$. The basis is constructed by setting

$$|q_0\rangle = \frac{1}{\|\rho(t_0)\|} |\rho(t_0)\rangle$$ \hspace{1cm} (S.10)

$$|q_j\rangle = \frac{1}{\|L|q_{j-1}\rangle - \sum_{i=0}^{j-1} |q_i\rangle \langle q_i|L|q_{j-1}\rangle\|} \left(\langle q_j|L|q_{j-1}\rangle - \sum_{i=0}^{j-1} |q_i\rangle \langle q_i|L|q_{j-1}\rangle\right) \text{ for } j = 1, \ldots, k-1$$ \hspace{1cm} (S.11)

Using the Arnoldi algorithm the matrix representation of $L$ on $\mathcal{K}_k$ in basis $\mathcal{B}_k$, denoted $L_k$, which has upper Hessenberg form, can be constructed at the same time as $\mathcal{B}_k$. The full algorithm for $j \geq 0$ for this procedure is

$$|q_{j+1}\rangle \leftarrow |q_j\rangle$$

$$[L_k]_{i,j} \leftarrow \langle q_i|q_{j+1}\rangle \text{ for } i = 0, \ldots, j$$

$$|q_{j+1}\rangle \leftarrow |q_{j+1}\rangle - \sum_{i=0}^{j} [L_k]_{i,j} |q_i\rangle$$ \hspace{1cm} (S.12)

$$[L_k]_{j+1,j} \leftarrow \|q_{j+1}\|$$

$$|q_{j+1}\rangle \leftarrow |q_{j+1}\rangle / \|L_k\|_{j+1,j}$$

The low-dimensional representation of $|\rho(t)\rangle$ is then propagated exactly with

$$c_k(t_0 + \delta t) = \exp(L_k \delta t)c_k(t_0)$$ \hspace{1cm} (S.13)

where $c_{k,j}(t_0) = \delta_{j,0}\|\rho(t_0)\|$, and $|\rho(t_0 + \delta t)\rangle \approx \sum_j c_{k,j}(t_0 + \delta t)|q_j\rangle$. This approximation is accurate to order $k - 1$, and as $\delta t$ increases so does the error, so the subspace needs to be reconstructed iteratively to propagate the state to long times. In the adaptive version of this we employed, we simultaneously propagate $c_k(t)$ and $c_{k+1}(t)$, and recompute the Krylov subspace when

$$\frac{\|c_k(t_0 + \delta t) - c_{k+1}(t_0 + \delta t)\|}{\|c_k(t_0 + \delta t)\|} > \epsilon$$ \hspace{1cm} (S.14)
where $\epsilon$ is a convergence parameter (here $c_k(t_0 + \delta t)$ is implicitly padded with a zero at the end to calculate the difference). In the calculations presented here $k = 16$ and $\epsilon = 10^{-10}$ are used.

Vector representations of observables $\{v_O\}$ can be computed when $K_k$ is constructed and observables can be obtained as

$$\langle O(t) \rangle = \langle O^\dagger \rho(t) \rangle = v_O^\dagger \cdot c(t)$$

(S.15)

without needing to reconstruct $|\rho(t)\rangle\rangle$.

---

1. S. Nakajima, “On Quantum Theory of Transport Phenomena,” Prog. Theor. Phys. 20, 948–959 (1958).
2. R. Zwanzig, “Ensemble method in the theory of irreversibility,” J. Chem. Phys. 33, 1338–1341 (1960).
3. H. Mori, “Transport, Collective Motion, and Brownian Motion,” Prog. Theor. Phys. 33, 423–455 (1965).
4. R. Zwanzig, Nonequilibrium Statistical Mechanics (Oxford University Press, 2001).
5. H. Takahashi and Y. Tanimura, “Open Quantum Dynamics Theory of Spin Relaxation: Application to $\mu$ SR and Low-Field NMR Spectroscopies,” J. Phys. Soc. Japan 89, 064710 (2020).
6. H. P. Breuer, B. Kappler, and F. Petruccione, “The Time-Convolutionless Projection Operator Technique in the Quantum Theory of Dissipation and Decoherence,” Ann. Phys. (N. Y.) 291, 36–70 (2001).
7. W. T. Pollard and R. A. Friesner, “Solution of the Redfield equation for the dissipative quantum dynamics of multilevel systems,” J. Chem. Phys. 100, 5054–5065 (1994).