Abstract: The rational design of molecular materials to control photophysical processes requires engineering excited-state carrier dynamics across the 10 nm to 1 μm length scale. While diffusion occurs over long length scales, the excitons only delocalize on short length scales due to the coupling between electronic and vibrational degrees-of-freedom. Here, we demonstrate that the locality of the excitons enables an adaptive Hierarchy of Pure States (adHOPS) method that is formally exact, embarrassingly parallel, and has size-invariant scaling. The size-invariant scaling of adHOPS allows for non-perturbative simulations of molecular aggregates with an arbitrary number of pigments in physically relevant parameter regimes. We provide proof-of-concept calculations on aggregates containing up to 1000 molecules and we expect that adHOPS will enable non-perturbative simulations of mesoscale quantum dynamics in molecular materials.

The rational design of molecules to control photophysical processes is essential for developing new organic materials for photonic, photocatalytic, opto-electronic, and light harvesting applications. The photophysics of molecular materials depends on the diffusion of excited-state carriers (e.g., electronic excitations, called ‘excitons’) on the 10 nm to 1 μm length scale. Spatially-resolved nonlinear spectroscopies can probe exciton dynamics on this mesoscale and examine the influence of material heterogeneity (e.g., grain boundaries and multi-particle interactions). Mesoscale simulations of quantum dynamics, however, have remained intractable due to the computational effort required to describe the interaction of electronic and vibrational degrees-of-freedom for thousands of molecules.

While exciton transport occurs over long length scales, the observation of ‘dynamic localization’ in non-linear spectroscopy implies that beyond a few hundred femtoseconds, excitons only delocalize over a few to tens of molecules. Here, we demonstrate that the locality of exciton wave functions in molecular materials can be used to construct a formally exact equation of motion with size-invariant scaling for large aggregates that is appropriate for mesoscale simulations.

Our approach is motivated by previous studies of localization in stochastic wave functions. Quantum State Diffusion (QSD) equations describe the time evolution of a quantum system coupled to a thermal environment using a density matrix composed of a non-interacting ensemble of stochastic pure states (ρ = ∑i |ψi⟩⟨ψi|). While unitary dynamics tend to disperse wave functions, in QSD simulations the thermal environment localizes wave functions. The localization of QSD trajectories has previously been used to accelerate calculations in the Markovian limit using a moving basis. The QSD equations can be extended to non-Markovian thermal environments (NMQSD) where they are equivalent to path integrals with the Feynman-Vernon influence functional. Suess et al. formally solved the NMQSD equations to give the Hierarchy of Pure States (HOPS). Like other QSD equations, thermal environments tend to cause localization within HOPS trajectories. To date, however, localization within HOPS has not been explored as an opportunity to accelerate formally exact simulations for quantum states coupled to non-Markovian environments.

We divide the exciton Hamiltonian into three parts

\[ H_T = \hat{H}_S \otimes \hat{I}_B + \hat{H}_{\text{int}} \otimes \hat{I}_B \]

where \( \hat{H}_S = \sum_n |n\rangle E_n \langle n| + \sum_{n \neq m} |n\rangle V_{n,m} \langle m| \) describes the electronic system and \( \hat{H}_B = \sum_n \hbar \omega_n (\hat{a}_n^\dagger \hat{a}_n + 1/2) \) represents the thermal environment arising from molecular vibrations. The influence of coupling between the electronic system and vibrational ‘bath’ (\( \hat{H}_{\text{int}} = \sum_{n,q} \kappa_{nq} \hat{L}_n \hat{q}_n \)) can be described in terms of the system-bath coupling operators (\( \hat{L}_n \)) and the two-point correlation functions

\[ \alpha_n(t) = \frac{1}{2\pi} \int_0^\infty d\omega J_n(\omega) \coth \left( \frac{\hbar \omega}{2k_B T} \right) \cos(\omega t) - i \sin(\omega t) \]

where T is the temperature and \( J_n(\omega) \) is the spectral density. In the following, we assume that each pigment has an independent thermal environment that drives fluctuations in excitation energy (i.e., \( \hat{L}_n = |n\rangle \langle n| \)). We describe the thermal environment of each pigment by a Drude-Lorentz spectral density

\[ J_n(\omega) = 2\lambda_n \gamma_n \frac{\omega}{\omega^2 + \gamma_n^2} \]

which, at high temperature (\( \beta \gamma < 1 \)), allows for a convenient exponential decomposition of the correlation function

\[ \alpha_n(t) = g_n e^{-\gamma_n t/\hbar} \]

where \( g_n = 2\lambda_n k_B T - i \lambda_n \gamma_n \).

We hypothesized that localization of the quantum state would result in a local structure of the HOPS equation of motion

\[ \frac{d\psi_i^{(k)}}{dt} = [-i\hat{H}_S - \vec{k} \cdot \vec{\gamma} - \Gamma_t + \sum_n \hat{L}_n (\vec{z}_{i,n} + \vec{\xi}_{i,n})] \psi_i^{(k)} + \sum_n \vec{k} |n\rangle \gamma_n \hat{L}_n \psi_i^{(k-\epsilon_n)} - \sum_n \gamma_n (\hat{L}_n - \langle \hat{L}_n \rangle) \psi_i^{(k+\epsilon_n)} \]

where the physical wave function is given by \( \hat{k} = 0 \) and higher-order auxiliary wave functions encode the feedback between the thermal environment and the system degrees-of-freedom. The interaction of a hierarchy wave function with itself (eq. first line) incorporates both the unitary dy...
namics arising from $\hat{H}_S$ and a stochastic noise term ($z_{n,t}$) defined by the ensemble averages: $E[z_{n,t}] = 0$, $E[z_{n,t}z_{m,t}] = 0$, and $E[z_{n,t}z_{m,t}] = \alpha_n(t-s)$. The HOPS equation is discussed in detail along with the definitions for all terms in the Supplementary Information.

The HOPS equation of motion is formally exact in the complete basis set limit. It is convenient to think of HOPS calculations as depending on two basis sets: the hierarchy basis and the state basis. The complete state basis is a finite set of vectors that span the Hilbert space of the system. The complete hierarchy basis is, however, an infinite set of auxiliary wave functions by keeping auxiliaries with a sum of indices smaller than a threshold value ($\sum \vec{k}[n] \leq k_{\text{max}}$). Convergence is guaranteed for sufficiently large $k_{\text{max}}$, but the depth of the hierarchy required to reach convergence can be prohibitive.

In HOPS calculations, localization in the state basis induces localization in the hierarchy basis. Fig. 1 shows a localized HOPS trajectory in which an excitation flits between site 3 and 2. The occupation of the auxiliary wave functions track with the population of the true wave function - i.e., the auxiliary wave functions associated with the thermal environment of site 2 (e.g., $[0,1,0,0,0]$) are only occupied when site 2 is occupied in the true wave function (green shaded region). This locality in the hierarchy arises from the combination of two effects. First, every auxiliary wave function is damped (eq. (4)), $-\vec{k} \cdot \vec{r} \psi^{(\vec{k})}$ and requires a constant source term to maintain a finite amplitude. Second, because the system-bath coupling operator is a site-projection operator ($L_n = |n\rangle \langle n|)$, a localized wave function only contributes amplitude to auxiliary wave functions with an index that differs by $\pm 1$ in an occupied site (i.e., $L_n \psi^{(\vec{k})} \neq 0$).

The central challenge to leveraging the local structure of HOPS is time-evolving a basis set that captures the dynamics while limiting the size of the basis.

We establish the essential basis set elements at each time point by ensuring that the derivative error

$$\|D_t - D_t^a\| \leq \delta$$

is below a given threshold ($\delta$), where $D_t$ is the derivative vector calculated in the full basis and $D_t^a$ is calculated in the adaptive basis. In the Supplementary Information, we present the expressions for the derivative error arising from neglecting elements in the state or hierarchy basis, assuming that the system-bath coupling operators are site projection operators ($L_n = |n\rangle \langle n|)$.

Our adaptive HOPS (adHOPS) algorithm neither assumes nor imposes locality. Rather, the adaptive basis takes advantage of whatever locality arises during the simulation. If the full hierarchy is required to satisfy the derivative error bound, adHOPS smoothly reverts to a HOPS calculation. As a result, adHOPS remains formally exact - the adaptive basis represents a time-dependent truncation of hierarchy elements, and $\delta$, like $k_{\text{max}}$, is a convergence parameter.

![Figure 1](image.png) Localization in a single HOPS trajectory. (a) Contour map of site populations. (b) Norm-squared of auxiliary wave functions for a two-dimensional subset of the hierarchy associated with site 2 (column) and site 3 (row). Panels are labelled by their index vector ($\vec{k}$). The shaded region represents time-period when site 2 is occupied. The physical wave function ($\hat{\psi} = 0$) shows the populations of site 2 and 3 as the green and blue lines, respectively. Parameters: $V = 10 \text{ cm}^{-1}$, $\lambda = 50 \text{ cm}^{-1}$, $\gamma = 50 \text{ cm}^{-1}$, $T = 295 \text{ K}$, $k_{\text{max}} = 10$, and $\delta = 10^{-4}$.

![Figure 2](image.png) Comparing HOPS and adHOPS for a linear chain. (a) Site 3 population dynamics for HOPS (black line) and adHOPS (green line). (b) Mean adaptive error as a function of $\delta$. The grey region represents error beneath the statistical error for a $10^4$ trajectory ensemble. (c) Ensemble distribution of the adaptive hierarchy size as a function of $\delta$. Parameters: $V = 50 \text{ cm}^{-1}$, $\lambda = 50 \text{ cm}^{-1}$, $\gamma = 50 \text{ cm}^{-1}$, $T = 295 \text{ K}$, $k_{\text{max}} = 10$, and $N_{\text{traj}} = 10^4$.

For a five-site linear chain, adHOPS calculations converge rapidly with respect to the derivative error bound and require a small fraction of the full HOPS basis. Fig. 2 shows the comparison between HOPS (black line) and adHOPS (green line) population dynamics of the initially excited pigment (site 3). For $\delta = 10^{-1}$, the adaptive basis set is so small that the calculation shows no excitation transport. Smaller values of $\delta$ improve the description, and by $\delta = 10^{-3}$ no deviations are visible by eye. Fig. 2 shows the mean adaptive error as a function of $\delta$. In the grey region the adaptive error is smaller than the statistical error associated with the $10^4$ trajectory ensemble. We measure the size of the hierarchy basis for a single trajectory by the average number of
auxiliary wave functions required across time points. Fig. 2 plots the ensemble distribution of the hierarchy size as a function of δ. For δ = 10^-3, most adHOPS trajectories require 10^7 auxiliaries on average, or approximately 1% of the 9 × 10^3 auxiliaries required for a HOPS calculation. Improving the accuracy of the calculation by decreasing δ two orders of magnitude only requires about four times as many auxiliaries. The other kinds of errors that occur in both HOPS and adHOPS simulations, including statistical error from a finite number of trajectories and hierarchy error from the finite k_{max} value, are reported in the Supplementary Information.

The essential advantage of adHOPS is the fundamentally different scaling that it achieves for both the hierarchy truncation depth (k_{max}) and the number of pigments (N_{pig}).

One persistent challenge for hierarchical methods, such as HOPS, is the formidable computational scaling with increasing depth of the hierarchy which often precludes demonstrations of convergence. Though our adHOPS method was inspired by localization, it dramatically reduces the computational scaling with increasing k_{max} even when the exciton is fully delocalized. Fig. 3a compares HOPS and adHOPS dynamics with increasing coupling, and Fig. 3b shows the corresponding hierarchy size as a function of k_{max}. By V = 5α the coherent beats in the site 3 population report a wave function that is coherently oscillating across 5 sites. While the HOPS hierarchy (black line) scales as \left<N_{pig}+k_{max}\right>, the adHOPS hierarchy (green line) scales much more slowly. For large k_{max}, these adHOPS calculations have approximately linear scaling and it is straightforward to perform calculations with previously inconceivable k_{max} values, such k_{max} = 20, which allows for computationally tractable demonstrations of convergence with respect to hierarchy depth.

The second perpetual challenge for formally-exact methods, such as HOPS, is the formidable computational scaling with increasing depth of the hierarchy which often precludes demonstrations of convergence. Though our adHOPS method was inspired by localization, it dramatically reduces the computational scaling with increasing k_{max} even when the exciton is fully delocalized. Fig. 3a compares HOPS and adHOPS dynamics with increasing coupling, and Fig. 3b shows the corresponding hierarchy size as a function of k_{max}.

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Figure 3. Comparing dynamics and hierarchy size of HOPS (black) and adHOPS (green) for different coupling strengths. (a) Site 3 population dynamics when k_{max} = 10. (b) Size of the hierarchy as a function of maximum depth (k_{max}). Other parameters: λ = 50 cm\(^{-1}\), γ = 50 cm\(^{-1}\), T = 295 K, δ = 10^{-3}, and N_{trajectories} = 10^4.

The second perpetual challenge for formally-exact methods is their inability to scale to a large number of pigments. For localized excitons, our adHOPS method achieves size-invariant scaling and can simulate an arbitrary number of pigments. Fig. 3 compares the average size of the system (top) and hierarchy (bottom) basis for HOPS (black) and adHOPS (colored) as a function of the number of pigments in a linear chain. The explosion in the number of auxiliary wave functions in the hierarchy with increasing N_{pig} causes calculations to be numerically intractable for even relatively modest numbers of pigments. The hierarchy basis size for adHOPS calculations, on the other hand, increases much more slowly. Moreover, the plateau in the size of the adHOPS basis, beginning on the order of 10-100 pigments, indicates the onset of size-invariant scaling and allows for calculations on scales that were previously unachievable.

By resolving these long-standing challenges of hierarchical and formally exact methods, adHOPS is a significant advance for mesoscale quantum dynamics. As a proof-of-concept, the inset of Fig. 4 reports the exciton diffusion coefficient calculated for a 10^3 pigment chain using a linear fit to the mean-squared displacement of the excitation in terms of the spacing between molecules (l_0). Parameters: λ = 50 cm\(^{-1}\), γ = 50 cm\(^{-1}\), T = 295 K, k_{max} = 10, and δ = 3 × 10^{-4}.

To summarize, our adaptive HOPS (adHOPS) algorithm:

1. is a formally exact solution to the time evolution of a quantum state coupled to a non-Markovian thermal reservoir,
2. is embarrassingly parallel, and
3. achieves size-invariant scaling for large systems.

This combination of properties allows us to perform non-perturbative simulations involving an arbitrary number of
pigments in physically relevant parameter regimes, thus laying a foundation for mesoscale quantum simulations of molecular materials. We note that the adHOPS method makes no approximations about the molecular vibrations beyond the usual linear-response and Gaussian approximations that allow for a harmonic description of the thermal environment. The exponential decomposition of the correlation function can always be performed, though there is substantial discussion about the most efficient scheme. Thus, the main approximation in adHOPS is the assumption that the system-bath coupling operator is a site-projection operator \( \mathcal{L}_n = |n\rangle \langle n| \). We are currently working to remove this approximation and develop an adHOPS scheme for general system-bath coupling operators.

Looking forward, we expect adHOPS will dramatically simplify running non-perturbative calculations on a variety of challenging molecular materials, including photosynthetic membranes, molecular thin films, and organic photovoltaic heterojunctions. On the other hand, the extent to which adHOPS, or a related algorithm, can accelerate calculations in the vibronic transport regime, where a large number of exponential components are required to describe the correlation function, is an open question.

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Supporting Information Available

The following files are available free of charge. The following files are available free of charge.

- Supplementary Information.pdf: This document contains the explanation and complete definition of the non-linear HOPS equation; explanation of the statistical, hierarchy, and time-step errors; the expressions for evaluating derivative error terms; description of the adaptive error distribution in the ensemble.
- mesohops.zip: This is the source code used for all HOPS and adHOPS calculations performed here. It is equivalent to MesOhops V1.00 (https://github.com/mesosciencelab/mesohops, commit: 86e991917e9e57d63dfc9b5e140d1f6112544f98).

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