Coarse-grained representation of the quasi adiabatic propagator path integral for the treatment of non-Markovian long-time bath memory

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The description of non-Markovian effects imposed by low frequency bath modes poses a persistent challenge for path integral based approaches like the *iterative* quasi-adiabatic propagator path integral (*i*QUAPI) method. We present a novel approximate method, termed mask assisted coarse graining of influence coefficients (MACGIC)-*i*QUAPI, that offers appealing computational savings due to substantial reduction of considered path segments for propagation. The method relies on an efficient path segment merging procedure via an intermediate coarse grained representation of Feynman-Vernon influence coefficients that exploits physical properties of system decoherence. The MACGIC-*i*QUAPI method allows us to access the regime of biological significant long-time bath memory on the order of hundred propagation time steps while retaining convergence to *i*QUAPI results. Numerical performance is demonstrated for a set of benchmark problems that cover bath assisted long range electron transfer, the transition from coherent to incoherent dynamics in a prototypical molecular dimer and excitation energy transfer in a 24-state model of the Fenna-Matthews-Olson trimer complex where in all cases excellent agreement with numerically exact reference data is obtained. *Published by AIP Publishing*. [<http://dx.doi.org/10.1063/1.4984075>]

I. INTRODUCTION

Phenomena like energy relaxation dynamics and irreversible decoherence are decisively determined by the interaction of a quantum system with its environment. The formally exact solution presented by Feynman and Vernon for the dynamics of a quantum system coupled to a bath of harmonic oscillators¹ provides a rigorous theoretical framework in the form of the time non-local Feynman-Vernon influence functional for the description of decoherence of molecular systems in condensed phase.^{2–5} Recent 2D experiments in the optical domain⁶ performed on photosynthetic light harvesting complexes⁷ have provided real time access to decoherence dynamics in condensed phase. While the initial interpretation of these experiments in terms of long lived electronic coherences questioned the conventional view that quantum coherence is efficiently quenched,⁵ the origin and functional role of the observed coherent dynamics are a matter of substantial debate^{8,9} (see Ref. 10 for a recent review). Despite conflicting views, the experimental findings initiated substantial theoretical effort aimed at the thorough description of the excitonic dynamics in photosynthetic light harvesting complexes.

Challenges arise from the fact that biological systems are often characterized by intersite and system bath couplings of similar magnitude (≈ 10 – 100 cm^{−1})¹¹ that impose comparable correlation time scales of system and environment. Therefore the Born-Markov approximation is no longer valid^{12,13} and the dynamics is characterized by pronounced non-Markovian behavior.¹⁴ The finite bath memory time induced non-Markovian effects can lead to an alteration of

transfer rates and decoherence.^{15–20} For situations where the harmonic bath can be expanded in a sum of exponentials, the hierarchy of equation of motion (HEOM) method^{21,22} recently gained substantial attention due to its ability to provide numerical exact simulations of quantum dissipative dynamics. Graphical processor unit accelerated codes made the real-time quantum dynamics of photosynthetic light harvesting complexes, like the Fenna-Matthews-Olson (FMO) complex, accessible.^{23,24} However, the HEOM is numerically demanding for large scale systems and long bath correlation times. Moreover the HEOM method converges slowly for low temperatures²⁵ and large reorganization energies.²⁶

A numerically exact approach to describe quantum dynamics subject to a dissipative environment is given by the quasi-adiabatic propagator path integral (QUAPI) method that employs, similar to path integral Monte-Carlo^{27,28} and HEOM methods,^{21,22} the time nonlocal Feynman-Vernon influence functional as a starting point for derivation. By noting a vanishing correlation of well separated time points due to the decay of memory imposed by the influence functional, an *iteratively* constructed multi-time propagator tensor was developed^{3,29–31} that correlates all time points within a finite memory time (*i*QUAPI). An improvement of the *i*QUAPI method (see Ref. 32 for an overview) was presented in the form of the on-the-fly filtered propagator path selection³³ that avoids the necessity of *a priori* importance sampling of path segments by Monte-Carlo methods. Propagator renormalization techniques proposed in Ref. 34 employ a non-uniform propagation time-grid with high accuracy for small memory times, and increased time steps for long memory times, where the bath response function changes only slowly. Generalizations of the *i*QUAPI method to multiple bosonic or fermionic reservoirs have been presented.^{35–37}

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The *i*QUAPI has been successfully applied to describe dissipative electron transfer dynamics and provides robust solutions for weak (non-adiabatic) and strong coupling (adiabatic) regimes as well as super-exchange mediated charge transfer reactions.^{31,38,39} In general applications benefit from a limited size of the system Hamiltonian or its sparse structure thereby inherently reducing the number of relevant path segments. A valuable verification of *i*QUAPI against an exact solution has been presented for a parametrically driven dissipative quantum harmonic oscillator demonstrating the applicability for continuous potentials.⁴⁰ The numerical equivalence of *i*QUAPI to the cumulant time-nonlocal master equation has further been demonstrated⁴¹ and *i*QUAPI has been applied to the investigation of excitonic dynamics in a model of the FMO monomer complex.⁴² The inherent discrete variable representation (DVR) of *i*QUAPI allows to treat real space coordinates apart from the harmonic approximation.^{43,44} The *i*QUAPI method thus offers an efficient way for propagating the reduced density matrix, provided that the bath induced memory is limited to ≈ 10 -20 propagation time steps. Limitations arise for “sluggish” environments characterized by slow bath modes strongly coupled to the system that require long memory times. Even for such challenging situations, *i*QUAPI results have been presented.^{39,45} Moreover the system Hamiltonian of typical photosynthetic complexes is often of substantial size [e.g., 24 bacteriochlorophyll (BChl) chromophores for the FMO trimer complex⁴⁶⁻⁴⁸], which are characterized by intersite couplings of varying magnitude which requires a substantial number of path segments for convergence due to population branching among multiple sites.

Here, we present an approximate algorithm that systematically converges to the exact *i*QUAPI limit and allows us to treat situations where the bath is characterized by slow relaxation time scales. We extend the appealing multiple time step propagator renormalization technique proposed by Makri³⁴ to an intermediate coarse grained representation of the influence functional (cf. Sec. II C). This representation provides an efficient quadrature of the bath response on a non-uniform time-grid which serves as an auxiliary mask for a merging procedure of path segments that substantially reduces their number. The employed on-the-fly filtered propagator path selection further avoids the necessity of Monte-Carlo importance sampling of path segments. The introduced approximate coarse grained representation of the influence functional exploits physical properties of system decoherence imposed by finite memory time and offers appealing computational savings. We demonstrate the applicability of the algorithm to the weak-to-intermediate coupling regime with a transition from coherent to incoherent dynamics, a situation typically found in photosynthetic complexes like the FMO complex. The new method makes substantial sizes of the system Hamiltonian accessible for approximate *i*QUAPI propagations of the reduced density matrix. We present benchmark results on prototypical model systems of multi-site charge transfer (Sec. III A) and excitation energy transfer (EET) (Sec. III B). Moreover the promising scaling behavior of the algorithm allows us to explore convergence properties and investigate population dynamics in a model Hamiltonian of the FMO trimer complex consisting of 24 states (Sec. III C).

II. THEORY

We start by briefly recapturing the working equations of the *i*QUAPI method for the description of open quantum systems, a detailed derivation can be found in Refs. 32 and 49.

A. Iterative quasi adiabatic propagator path integral (*i*QUAPI)

Within the theory of open quantum systems,¹³ the complete system consisting of many degrees of freedom is divided into a low-dimensional quantum system H_s that is coupled via the system bath interaction H_{sb} to a bath H_b ,

$$H = H_s + H_b + H_{sb}. \quad (1)$$

We assume a bath of Q harmonic oscillators, characterized by masses m , momenta p , frequencies ω , and positions x . Further we assume that the bath is bilinearly coupled via the coupling constants c_j to the collective system coordinate(s) s of the quantum system. The Hamiltonian in this widely used Caldeira-Legett model then takes the form^{13,50}

$$H = H_s + \sum_j \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left(x_j - \frac{c_j s}{m_j \omega_j^2} \right)^2 \right]. \quad (2)$$

Equation (2) includes the counterterm quadratic in s that accounts for renormalization of the potential. By redefining the system potential with respect to the adiabatic reference⁴⁴ and expressing the quantum system in terms of M eigenstates $|u\rangle$ of one-dimensional “lattice sites,” the Hamiltonian takes the form⁴⁹

$$H_s = \sum_{n=1}^M \sum_{n'=1}^M h_{nn'} |u_n\rangle \langle u_{n'}|, \quad (3)$$

$$H_{sb} = - \sum_{j=1}^Q c_j x_j \sum_{n=1}^M s_n |u_n\rangle \langle u_n|, \quad (4)$$

$$H_b = \sum_{j=1}^Q \left(\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 x_j^2 \right). \quad (5)$$

Time-dependent state populations, coherences, and system observables can be calculated from the reduced density matrix $\tilde{\rho}(t)$ by taking the trace over the bath degrees of freedom

$$\tilde{\rho}(t) = \text{Tr}_b \left[e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar} \right]. \quad (6)$$

Instead of considering Q harmonic oscillators explicitly, all relevant bath information is incorporated in the spectral density function (specified below, cf. Sec. II C 2)

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j). \quad (7)$$

Employing a factorized initial density matrix, the DVR of system coordinates s and discretizing the time-evolution of $\tilde{\rho}$ in N steps of size $\Delta t = t/N$, Eq. (6) can be expressed in discrete path integral representation

$$\begin{aligned} \langle u_{k_N^+} | \tilde{\rho}(t) | u_{k_N^-} \rangle &= \sum_{k_0^+}^M \sum_{k_1^+}^M \cdots \sum_{k_{N-1}^+}^M \sum_{k_0^-}^M \sum_{k_1^-}^M \cdots \sum_{k_{N-1}^-}^M \\ &\times S(s_{k_0^+}, \dots, s_{k_N^+}; t) I(s_{k_0^-}, \dots, s_{k_N^-}; t), \quad (8) \end{aligned}$$

with $[s_{k_j^+}, j = 0, \dots, N]$ and $[s_{k_j^-}, j = 0, \dots, N]$ denoting coordinate points at time $j\Delta t$ on forward and backward discretized path segments, respectively. The short-time system propagator S accounts for forward- and backward-time propagation of the initial reduced system density matrix $\tilde{\rho}(0)$,

$$S(s_{k_0^+}, \dots, s_{k_N^+}; t) = \langle u_{k_0^+} | \tilde{\rho}(0) | u_{k_0^-} \rangle \prod_{j=1}^N S_{k_j}(s_{k_j^+}, s_{k_{j-1}^+}) \quad (9)$$

with

$$S_{k_j}(s_{k_j^+}, s_{k_{j-1}^+}) = \langle u_{k_j^+} | e^{-iH_s \Delta t / \hbar} | u_{k_{j-1}^+} \rangle \langle u_{k_{j-1}^-} | e^{iH_s \Delta t / \hbar} | u_{k_j^-} \rangle. \quad (10)$$

Note that in Eq. (10) only neighboring time points are coupled by the short-time system propagator (time locality).

The time non-local Feynman-Vernon influence functional I ,

$$\begin{aligned} I(s_{k_0^+}, \dots, s_{k_N^+}; t) &= \prod_{j=0}^N \prod_{j'=0}^j I_{k_j k_{j'}}(s_{k_j^+}, s_{k_{j'}^+}) \\ &= \exp \left\{ -\frac{1}{\hbar} \sum_{j=0}^N \sum_{j'=0}^j (s_{k_j^+} - s_{k_{j'}^+}) \right. \\ &\quad \left. \times (\eta_{jj'} s_{k_{j'}^+} - \eta_{jj'}^* s_{k_{j'}^-}) \right\}, \end{aligned} \quad (11)$$

accounts for the effects of the bath on the system dynamics.¹ Here, $\eta_{jj'}$ denotes influence coefficients as discretized analog of the bath response function⁴⁹ (see Appendix). Influence coefficients $\eta_{jj'} (j \neq j')$ introduce time non-locality by connecting time steps j and j' within the finite memory time.³ Coefficients with $j/j' = 0$ describe the start of dynamics from a bath at equilibrium, whereas coefficients with $j/j' = N$ are required for endpoint propagations. Inclusion of independent baths is possible by extending the 1-dimensional lattice coordinates s into multiple dimensions α each affected by an uncorrelated set of influence coefficients $\eta^{(\alpha)}$ arising from independent spectral density functions

$$\begin{aligned} I(s_{k_0^+}, \dots, s_{k_N^+}; t) &= \exp \left\{ -\frac{1}{\hbar} \sum_{\alpha} \sum_{j=0}^N \sum_{j'=0}^j (s_{k_j^+, \alpha} - s_{k_{j'}^+, \alpha}) \right. \\ &\quad \left. \times (\eta_{jj'}^{(\alpha)} s_{k_{j'}^+, \alpha} - \eta_{jj'}^{(\alpha)*} s_{k_{j'}^-, \alpha}) \right\}, \end{aligned} \quad (12)$$

where the relation to the spin-boson model with a single collective bath has been discussed in Ref. 36.

The direct application of Eq. (8) is limited to short propagation times and few quantum states due to the exponential increase in the number of contributing path segments (M^{2N}). By noting that the bath correlation of distant points in time decreases with increasing time gap and can be effectively truncated beyond a certain memory time $\tau_M = \Delta k_{\max} \Delta t$, an effective propagator functional tensor can be iteratively constructed that includes forward and backward path segments of length $\Delta k_{\max}$.^{3,29,30} The propagator tensor of size $L \times L$ with $L = M^{2\Delta k_{\max}} \ll M^{2N}$ is then iteratively applied to propagate in steps of $\Delta k_{\max} \Delta t$ beyond the memory time. Considering a cut off for long-distance interactions the size of the propagator tensor can be further reduced to $M^{2\Delta k_{\max}+2}$.³⁰

Further reduction in the number of contributing path segments is possible by employing a filtered propagator functional (FPF).^{49,51} Here a weight threshold θ is introduced and contributing path segments are selected according to their weight [i.e., the absolute value of the summand of Eq. (8)] thereby reducing the number of contributing path segments to $L_{FPF} \ll M^{2\Delta k_{\max}}$. The FPF method couples the considered L_{FPF} path segments to all possible L_{FPF} paths when propagating the system through τ_M resulting in overall $\mathcal{O}(L_{FPF}^2)$ scaling.⁴⁹ It was demonstrated that the fraction of high-weight path segments is in general small and that neglecting low-probability path segments allows for considerable savings while retaining high accuracy.⁵¹ By monitoring the norm of the quantum system, systematic convergence of results can be obtained. Path segment selection is performed *a priori* by Monte-Carlo importance sampling.

B. On-the-fly filtered propagator functional

On-the-fly path filtering allows to avoid Monte-Carlo importance sampling prior to the propagation of the reduced density matrix.³³ Within the on-the-fly FPF approach, the system is propagated in steps of Δt and the influence functional [Eq. (11)] is factorized in a history term and a memory term,

$$I(s_{k_0^+}, \dots, s_{k_N^+}; t) = \prod_{j=0}^{N-1} \prod_{j'=0}^j I_{k_j k_{j'}}(s_{k_j^+}, s_{k_{j'}^+}) \prod_{j'=0}^N I_{k_N k_{j'}}(s_{k_N^+}, s_{k_{j'}^+}). \quad (13)$$

The history term includes interactions between past time points (j, j') and the memory term accounts for interactions of the present time point N with past time points j' .

Equation (8) is expressed as a sum over all possible $L = M^{2(N-1)}$ forward and backward path segments $\mathbf{p}_i$ that contribute to the propagator $\mathfrak{P}$ connecting history time points to the present time point (memory terms) and to the history terms $\mathfrak{H}$ until time $t = (N-1)\Delta t$:

$$\langle u_{k_N^+} | \tilde{\rho}(t) | u_{k_N^-} \rangle = \sum_{i=1}^L \mathfrak{H}(\mathbf{p}_i) \mathfrak{P}(\mathbf{p}_i, k_N^{\pm}). \quad (14)$$

The history term has the form

$$\mathfrak{H}(\mathbf{p}_i) = \langle u_{k_0^+} | \tilde{\rho}(0) | u_{k_0^-} \rangle \prod_{j=1}^{N-1} S_{k_j}(s_{k_j^+}, s_{k_{j-1}^+}) \prod_{j=0}^{N-1} \prod_{j'=0}^j I_{k_j k_{j'}}(s_{k_j^+}, s_{k_{j'}^+}) \quad (15)$$

and the propagator term is given by

$$\mathfrak{P}(\mathbf{p}_i, s_{k_N^+}) = S_{k_N}(s_{k_N^+}, s_{k_{N-1}^+}) \prod_{j'=0}^N I_{k_N k_{j'}}(s_{k_N^+}, s_{k_{j'}^+}). \quad (16)$$

Taking into account a finite memory time $\tau_M = \Delta k_{\max} \Delta t$ allows to merge the path segments that coincide during memory time and differ in time steps before $t - \tau_M$, thereby keeping the number of path segments approximately constant when propagating beyond τ_M (cf. Sec. III, Fig. 1). The number of path segments can again be further reduced by employing the filtered propagator functional that discards path segments with weight below a threshold θ (see above).

FIG. 1. Schematic representation of merging procedure of path segments in on-the-fly filtered propagator functional (OFPF) (top) and in mask assisted coarse graining of influence coefficients (MACGIC) (middle and bottom): three exemplary forward paths A, B, and C of a 3-state system with $\Delta k_{\max} = 5$. Top: the OFPF method uses all $\Delta k_{\max}$ time steps during memory time (light grey) and path segments A and B are merged. Middle: MACGIC merging procedure using a mask of $k_{\text{eff}} = 3$ (blue), paths segments A, B, and C are merged. Bottom: schematic representation of $\eta(\Delta k)$ obtained via piecewise constant approximation with three discontinuities (green); the shaded area determines the quality of the approximate $\eta(\Delta k)$ representation with respect to $|\eta_{kk'}|$ (red).

The resulting on-the-fly filtered propagator functional (OFPF) propagates each path segment independently through τ_M which results in $\mathcal{O}(\Delta k_{\max}^2 L_{\text{OFPF}} M^2)$ scaling. This numerical advantage comes at the expense of comparing and reindexing of path segments that coincide within τ_M . The employed *radix* sorting algorithm⁵² scales linear with the number of path segments [$\mathcal{O}(\Delta k_{\max} L_{\text{OFPF}})$]. The overall scaling of the OFPF method can thus be reduced to linear with the number of path segment L_{OFPF} for $\Delta k_{\max}, M \ll L_{\text{OFPF}}$ and avoids Monte-Carlo importance presampling.

C. Mask assisted coarse graining of influence coefficients (MACGIC)

The treatment of “sluggish” solvents characterized by low-frequency modes and corresponding long-time bath imposed memory poses a special challenge to the *iQUAPI* method. The presented extension of the OFPF method employs an efficient quadrature of the bath response function on a non-uniform time-grid³⁴ thereby reducing the number of considered path segments substantially. The central idea of the new algorithm relies on the observation that an approximation of the bath response function requires denser temporal sampling for short correlation times, i.e., closely spaced quadrature points, whereas the spacing of quadrature points can be increased at long correlation times, where the bath response

function approaches zero and shows only slow temporal variation.

1. Mask assisted path merging

Let us first recall the path segment merging procedure of the OFPF algorithm (Fig. 1, top). Here individual path segments that coincide within the memory time $\tau_M = \Delta k_{\max} \Delta t$ are merged by propagating in single time steps Δt beyond τ_M (cf. path segments A and B). In the proposed mask assisted coarse graining of influence coefficients (MACGIC)-*iQUAPI* algorithm, we introduce a coarse grained filter mask function $\mathfrak{M}$ that represents the influence coefficients $\eta_{kk'}$ on a non-uniform time grid of size k_{eff} (schematically highlighted in blue in Fig. 1, middle). We now perform a path segment merging procedure on the coarse grained temporal grid specified by mask $\mathfrak{M}$ thereby effectively reducing the number of distinguishable path segments to $M^{2k_{\text{eff}}} \leq M^{2\Delta k_{\max}}$. Path segments, originally defined on the uniform time grid spanning memory time $\tau_M = \Delta k_{\max} \Delta t$, that coincide for coarse grained grid points specified by mask function $\mathfrak{M}$ are merged by selecting and retaining the path segment with highest weight and summing the complex weight of all merged path segments, in analogy to the OFPF algorithm.³³ For the limiting case of $k_{\text{eff}} = \Delta k_{\max}$, the MACGIC-*iQUAPI* method is identical to the OFPF algorithm, whereas for $k_{\text{eff}} < \Delta k_{\max}$, the number of path segments is reduced significantly.

As in OFPF, we achieve an additional reduction in the number of path segments by retaining only these with weight above a threshold θ (cf. filtered propagator functional above). In principle, the filtering can be applied prior or after the mask assisted merging procedure described above. We have chosen an implementation where path selection via the weight criterion θ is performed prior to the merging procedure. This results in a more aggressive reduction in the number of path segments and an optimal performance of MACGIC-*iQUAPI* as the merging and sorting procedure is performed on an already reduced set of path segments. We note that for converged simulations (in weight threshold parameter θ , memory time $\Delta k_{\max} \Delta t$ and $k_{\text{eff}} \rightarrow \Delta k_{\max}$), the order of mask assisted merging and filtering of the propagator functional yield identical results.

2. Mask selection procedure

So far we have not specified the precise definition of the coarse grained mask function $\mathfrak{M}$. The performance of the MACGIC-*iQUAPI* algorithm is strongly affected by a careful definition of $\mathfrak{M}$ via coarse grained quadrature points k_{eff} where the number of possible realizations is given by

$$\binom{\Delta k_{\max}}{k_{\text{eff}}} = \frac{\Delta k_{\max}!}{k_{\text{eff}}!(\Delta k_{\max} - k_{\text{eff}})!}. \quad (17)$$

We consider commonly employed spectral densities of Ohmic type^{31,38,41,44}

$$J(\omega) = 2\pi\omega\xi e^{-\omega/\omega_c} \quad (18)$$

and Drude-Lorentz form^{41,42}

$$J(\omega) = 2\lambda \frac{\omega\gamma}{\omega^2 + \gamma^2}. \quad (19)$$

In Eq. (18) ξ denotes the dimensionless Kondo parameter and ω_c is the cutoff frequency. The Drude-Lorentz case [Eq. (19), over-damped Brownian oscillator model] is specified by the reorganization energy λ and oscillator time scale γ , respectively.

For both types of spectral densities, the magnitude of the discretized bath response function $|\eta_{kk'}|$ decays monotonically where an initial fast decay is followed by a slowly decaying tail (cf. Fig. 1, bottom). The sparse distribution of mask quadrature points should thus reproduce the shape of the bath response function as close as possible in order to facilitate a correct description of the system dynamics. A mask $\mathfrak{M}$ close to optimum can be obtained by assuming a piecewise constant approximation $\eta(\Delta k)$ to the magnitude (i.e., absolute value) of the discretized bath response function $|\eta_{kk'}|$ in the range $0 - \Delta k_{\max}$. Here $\Delta k = k - k'$ denotes the lag of influence functional coefficients. $\eta(\Delta k)$ discontinuously switches for every $\Delta k \in \mathfrak{M}$. The mask function $\mathfrak{M}$ with k_{eff} elements is then optimized by minimizing the penalty function

$$P(\mathfrak{M}) = \sum_{k-k'=0}^{\Delta k_{\max}} (|\eta_{kk'}| - \eta(\Delta k))^2. \quad (20)$$

We have numerically verified that minimization of $P(\mathfrak{M})$ for the approximate, piecewise constant discretized bath response function $\eta(\Delta k)$ yields a close to optimal representation of the original bath response function $\eta_{kk'}$. In particular, we have systematically compared exact *iQUAPI* simulations for small model systems with Ohmic and Drude-Lorentz type spectral densities to all possible combinations of the mask function $\mathfrak{M}$. The performance of the mask function $\mathfrak{M}$ obtained with the piecewise constant approximation is found to be reliable within the top 2% of all possible masks and the results systematically converge to the exact *iQUAPI* reference result for increasing $k_{\text{eff}} \rightarrow \Delta k_{\max}$. The employed piecewise constant function approximates the decay of the absolute value of complex valued $\eta_{kk'}$ coefficients. For the investigated spectral densities of Ohmic and Drude-Lorentz type [Eqs. (18) and (19), respectively], this approach yields excellent results. By considering the real part of the complex valued influence coefficients, results of similar accuracy can be obtained, while a piecewise constant approximation to the imaginary part yields mask functions of reduced accuracy due to the oscillatory behavior of the imaginary part (cf. inlay in Fig. 2). The mask selection can thus be understood as selecting the complex correlations $\eta_{kk'}$ that resemble closest classical correlations $|\eta_{kk'}|$. In that sense, those quantum path segments are selected which are close to path segments subject to classical noise. The described careful selection of $\mathfrak{M}$ allows for an accurate description of long-time bath memory and captures the fast decay of influence functional coefficients for early correlation times due to a finer distribution of quadrature points while effectively limiting the number of considered path segments to $M^{2k_{\text{eff}}} \ll M^{2\Delta k_{\max}}$.

We note that the mask function $\mathfrak{M}$ requires optimization for every set of parameters ($\Delta k_{\max}$, k_{eff} , Δt , $\beta = 1/k_B T$ with k_B being the Boltzmann constant and temperature T) and spectral density $J(\omega)$. However the required effort is negligible

FIG. 2. Top: population dynamics of the seven-state model of bath assisted long range electron transfer; red—MACGIC-*iQUAPI* with $\Delta k_{\max} = 40$ and mask size $k_{\text{eff}} = 4$; black—OFPF reference results with $\Delta k_{\max} = 40$; blue—OFPF results with $\Delta k_{\max} = 4$; black arrows denote the canonical equilibrium population of high and low energy states, respectively. The inlay shows the decay of DVR influence functional coefficients $\eta_{kk'}$ (red—absolute value, blue solid—real part, blue dotted—imaginary part), green points mark the significant path segments of the mask function $\mathfrak{M}$. Bottom: number of considered path segments, grey vertical lines denote bath memory times $4\Delta t$ and $40\Delta t$, respectively.

compared to the obtained savings in CPU time for $k_{\text{eff}} < \Delta k_{\max}$. Furthermore the approach allows us to reduce memory requirements significantly as the number of path segments is substantially reduced. In the current implementation, path segments are stored as vectors of short integer data type (2 byte per entry) of length $2\Delta k_{\max}$ (forward and backward path) and probability amplitudes for every path segment are stored as double precision complex numbers (16 byte). The described merge and sort algorithm requires for an allocation of twice the memory for every path segment, resulting in total memory requirements of $2 \cdot (2 \cdot 2\Delta k_{\max} + 16)$ byte per path segment. For exemplary $\Delta k_{\max} = 40$, this yields 352 byte per path segment or $\approx 3\,000\,000$ path segments per GB memory.

As will be demonstrated in Sec. III, the developed MACGIC-*iQUAPI* method allows for the description of long memory times on the order of hundred time steps Δt with accuracy that can be systematically improved towards the full *iQUAPI* result while at the same time reducing the number of path segments substantially. During propagation through the first memory time interval τ_M , sub-exponential growth of the number of path segments can be obtained.

III. RESULTS

In the following, the MACGIC-*i*QUAPI method is tested on benchmark systems where accurate numerical results are available.^{39,53,54} The examples cover a variety of parameter regimes and are characterized by increasing complexity. We start by considering the “natural regime” of *i*QUAPI, i.e., bath assisted long range electron transfer in the moderate-to-strong system-bath coupling regime (Sec. III A). We further consider different regimes of excitation energy transfer (EET) traditionally described by HEOM methods. Starting from a prototypical model dimer (Sec. III B), we further demonstrate the numerical efficiency of the MACGIC-*i*QUAPI method for a model of the FMO trimer complex consisting of 24 BChl chromophores (Sec. III C).

A. Bath assisted long range electron transfer

We start with the investigation of long range electron transfer dynamics with the MACGIC-*i*QUAPI method in order to compare the accuracy and performance to the converged *i*QUAPI results reported by Lambert *et al.*³⁹ We consider an extended multi-state system characterized by a tight-binding-like Hamiltonian of the form

$$H_s = \begin{pmatrix} E_1 & V & 0 & 0 & 0 & 0 & 0 \\ V & E_2 & V & 0 & 0 & 0 & 0 \\ 0 & V & E_2 & V & 0 & 0 & 0 \\ 0 & 0 & V & E_2 & V & 0 & 0 \\ 0 & 0 & 0 & V & E_2 & V & 0 \\ 0 & 0 & 0 & 0 & V & E_2 & V \\ 0 & 0 & 0 & 0 & 0 & V & E_2 \end{pmatrix}. \quad (21)$$

Interaction with environment degrees of freedom is modeled by a bath characterized by an Ohmic spectral density [cf. Eq. (18)]. Model parameters are taken from Ref. 39 and summarized in Table I. In the considered regime of bath-assisted long-range electron transfer,⁵⁵ the employed propagation time step $\Delta t = 0.8$ in combination with a small cutoff frequency $\omega_c = 0.4$ induces non-negligible system-bath correlation up to 40 time steps ($\Delta k_{\max} = 40$). The slow decay of the discretized bath response function (cf. inlay of Fig. 2) imposes long-time bath memory that, as will be shown below, affects the charge transport dynamics rather significantly.

Figure 2, top presents the dynamics of site populations simulated with the OFPF method (cf. Sec. II B) as a reference, which are compared to the results obtained with the MACGIC-*i*QUAPI method (black and red lines, respectively). We note that the OFPF results accurately reproduce the state populations reported by Lambert *et al.*³⁹ on the basis of a

memory propagator matrix that avoids on-the-fly reindexing of paths. Excellent agreement is observed for intermediate state populations as well as the long time populations already by employing a coarse grained mask $k_{\text{eff}} = 4$ (cf. the inlay of Fig. 2). The decay of the initially populated state 1 leads to a transient increase of state 2 population, while equilibrium between iso-energetic states is observed in the long time limit. The long time bath memory substantially affects population dynamics as can be recognized by comparison to simulations that cover the memory kernel only partially ($\Delta k_{\max} = 4$, blue lines). In this case, we observe qualitatively different population dynamics and no correct equilibrium in the long time limit. As intersite couplings are substantially smaller than the E_1 - E_2 energy gap, population dynamics is mediated by the bath dynamics³⁹ thereby accelerating depopulation of site 1 if the entire memory time is taken into account ($\Delta k_{\max} = 40$). The slow bath dynamics further affects subsequent transfer steps where non-equilibrium bath fluctuations mediate transfer, demonstrating the effect of long-time bath memory on charge transport dynamics.

The long-time bath memory necessitates for $\Delta k_{\max} = 40$ in OFPF and MACGIC-*i*QUAPI simulations in order to achieve convergence. Due to the structure of the system Hamiltonian [Eq. (21)] where only nearest neighbor states are weakly coupled, the employed weight threshold $\theta = 5 \cdot 10^{-9}$ acquires about $4 \cdot 10^6$ paths in the OFPF method (black line in Fig. 2, bottom; CPU time $\approx 206\,662$ s on a 16 core Intel Xeon E5-2650v2 processor). During initial propagation, the number of path segments increases exponentially, while beyond the memory time $\tau_M = \Delta k_{\max} \Delta t = 32$ the number of selected paths stays approximately constant in the OFPF simulations due to merging of indistinguishable path segments.³³ The moderate increase in the number of path segments due to population redistribution among all seven states for $t = 100$ -3000 a.u. demonstrates the on-the-fly capabilities of the algorithm. The MACGIC-*i*QUAPI algorithm with a sparse representation of significant path segments ($k_{\text{eff}} = 4$; red line in Fig. 2, bottom) exploits the advantages of the OFPF treatment (notice the modest increase in selected paths for $t = 100$ -3000 a.u.) while allowing to reduce the computational cost substantially (number of path segments $L_{\text{MACGIC}} \approx 3400$, CPU time ≈ 136 s). As the entire bath memory ($\Delta k_{\max} = 40$) is covered, the long time population dynamics is reproduced within 1% root-mean-square deviation (RMSD) compared to the converged OFPF results. For comparison, the reduced $\Delta k_{\max} = 4$ treatment (light blue line in Fig. 2, bottom) requires a similar number of path segments (5600, CPU time ≈ 84 s) but the inferior description of long time bath memory results in a qualitatively wrong description of population transfer dynamics. For the MACGIC-*i*QUAPI method, we observe a sub-exponential increase in the number of path segments during the first memory time τ_M . We note that in the considered model population of the initially excited site 1 is distributed and delocalized over multiple states, which leads to an increase-only behavior of selected path segments during the propagation. A modification considering a final trap state would similarly allow to reduce the number of path segments during the propagation upon population trapping.

TABLE I. Model parameters [cf. Eqs. (21) and (18)] of bath assisted long range electron transfer (units scaled with respect to $E_1 = 1$; $\hbar = 1$).

E_1	1	$\Delta k_{\max}$	4-40
E_2	0	k_{eff}	4-40
V	-0.025	Δt	0.8
β	2	τ_M	32
ω_c	0.4		
ξ	0.3	θ	$5 \cdot 10^{-9}$

TABLE II. Model parameters for excitation energy transfer in a molecular dimer.

ΔE (cm ⁻¹)	100	$\Delta k_{\max}$	30-100
V_{12} (cm ⁻¹)	100	Δt (fs)	20-6
γ (cm ⁻¹)	53.08	τ_M (fs)	600
T (K)	300	k_{eff}	12
λ (cm ⁻¹)	2-500	θ	10^{-7} - $5 \cdot 10^{-9}$

B. Excitation energy transfer (EET) in a molecular dimer

We proceed by considering EET in a prototypical model dimer, characterized by the energy gap ΔE and intersite coupling V_{12} (model parameters are taken from Ishizaki and Fleming,⁵³ cf. Table II). We consider a Drude-Lorentz spectral density [Eq. (19), overdamped Brownian oscillator model] where values of the reorganization energy λ are varied in the range 2-500 cm⁻¹. The considered regime of EET can thus be classified as weakly adiabatic ($\gamma^{-1} = 100$ fs, $\gamma/V_{12} = 0.53$).⁵⁶ In this regime, Redfield theory has been demonstrated to be of limited accuracy for $\lambda \geq 20$ cm⁻¹,¹⁴ and the parameter setting constitutes a typical benchmark scenario for numerical exact and approximate theories.^{41,48,53,57-61}

Figure 3 presents the population of the initially excited site 1 with λ varying by more than two orders of magnitude. For small values of λ (2-20 cm⁻¹), the repeatedly reported long lived quantum coherent oscillations can be identified that are quenched as λ approaches the magnitude of the intersite coupling V_{12} ($\lambda = 100$ cm⁻¹). In the investigated parameter regime, short-time oscillations and long-time population transfer of HEOM reference calculations⁵³ are reproduced with high accuracy (<2% RMSD, cf. red and black lines

FIG. 3. Excitation energy transfer (EET) in a molecular dimer (characterized by the population of site 1) for different values of the reorganization energy λ : black—reference HEOM data reported by Ishizaki and Fleming;⁵³ red—MACGIC-*i*QUAPI results with $k_{\text{eff}} = 12$, $\theta = 10^{-7}$, $\Delta k_{\max} \leq 100$ ($\tau_M = 600$ fs); green—MACGIC-*i*QUAPI results with $k_{\text{eff}} = 20$, $\theta = 5 \cdot 10^{-9}$, $\Delta k_{\max} = 100$ ($\tau_M = 600$ fs). The propagation time step Δt is 20, 10, and 6 fs for $\lambda = 2 - 20$ cm⁻¹, $\lambda = 100$ cm⁻¹, and $\lambda = 500$ cm⁻¹, respectively.

in Fig. 3). The employed $k_{\text{eff}} = 12$ allows for an efficient coarse graining of the influence functional covering in total $\tau_M = \Delta k_{\max} \Delta t = 600$ fs with $\Delta k_{\max} = 30$ -100. Quantitative agreement to HEOM reference results can be systematically achieved for $k_{\text{eff}} = 20$ and a weight selection threshold $\theta = 5 \cdot 10^{-9}$ that accounts for path segments of lower weight (cf. green line in Fig. 3 and Table IV).

Recalling that *i*QUAPI performs especially well in the intermediate-to-strong coupling regime ($\lambda = 100$ -500 cm⁻¹), we find that the number of path segments can be substantially reduced by the MACGIC-*i*QUAPI method and reasonable accuracy is already obtained with 80 000 paths ($\lambda = 500$ cm⁻¹). Note, that the applicability of the *i*QUAPI method is limited in this regime due to the long-time memory kernel extending over $\Delta k_{\max} = 100$ propagation time steps. In the weak coupling (Redfield) regime ($\lambda = 2$ -20 cm⁻¹), the influence of bath memory is reduced and accordingly the memory time for the employed spectral density can be shortened to ≈ 200 fs (not shown), confirming the weak to vanishing non-Markovian character and validity of the Born-Markov approximation.¹³ By extending the memory time to 600 fs, as might be required for more complex structured spectral densities, still quantitative agreement with reference dynamics can be obtained. It is noteworthy that in such a case (long time memory, small reorganization energy), a substantial amount of path segments is required to describe the very weakly damped population oscillations. In particular, ≈ 15 000 000 path segments are selected from all $2^{2 \cdot 12} \approx 1.68 \cdot 10^7$ possible combinations ($\lambda = 2$ cm⁻¹, cf. Table IV). In summary, we could demonstrate that MACGIC-*i*QUAPI facilitates simulations in the weak-to-intermediate coupling regime of EET subject to long-time bath memory with high accuracy and numerical stability where convergence can be systematically improved.

C. Fenna-Matthews-Olson (FMO) trimer complex

The Fenna-Matthews-Olson (FMO) complex is one of the most studied pigment-protein complexes with the function to transfer excitation energy towards a reaction center.^{11,62} Recent experimental findings that were interpreted in terms of long-lived coherent exciton dynamics⁷ have subsequently been questioned^{8,9} as part of an intense debate about the possible origin of the observed coherent dynamics.¹⁰ Due to the attracted substantial theoretical interest,¹³ models of the FMO complex have been established as a benchmark for sophisticated theoretical methods beyond the Born-Markov approximation. The FMO complex consists of three symmetry equivalent subunits (PDB code: 3ENI)⁴⁶ where each monomeric subunit contains eight BChl chromophores. In particular, the existence of the eighth BChl has only recently been discovered⁴⁶ and its impact on EET dynamics elucidated.^{47,63}

We proceed by presenting results on EET dynamics in the FMO trimer complex for which up to now only few results have been reported.^{48,54} We consider a model of the FMO trimer complex at physiological temperature (300 K) with site energies and intra-monomer couplings of the 24-state Hamiltonian reported in Refs. 47 and 48, respectively [see Appendix, Eqs. (A7)–(A9)]. In this model, site energies vary over ≈ 500 cm⁻¹

TABLE III. Parameters of the 24-state model of the FMO trimer complex.

γ (cm ⁻¹)	106	$\Delta k_{\max}$	30
T (K)	300	Δt (fs)	10
λ (cm ⁻¹)	35	τ_M (fs)	300
		k_{eff}	2-10
		θ	10^{-7} – 10^{-8}

and inter-chromophore couplings are on the order <80 cm⁻¹. In comparison to the nearest neighbor coupling Hamiltonian employed for the simulation of bath assisted long range electron transfer [cf. Sec. III A, Eq. (21)], we recognize a more complex coupling pattern in the FMO model with excitonic couplings of various magnitudes giving rise to different relaxation channels and time scales. Inter-monomer couplings are in the 1-10 cm⁻¹ range and introduce weak coupling of the three symmetry equivalent monomer subunits. We assume an identical and uncorrelated bath for every site³⁶ characterized by a Drude-Lorentz type spectral density [Eq. (19)] that induces long time bath memory on a 300 fs time scale ($\Delta k_{\max} = 30$, cf. Table III for model parameters). Due to the long memory time, perturbative master equations that assume system-bath adiabaticity are unable to describe the considered parameter setting.^{14,54} We note that the simplified shape of the spectral density here poses a serious limitation. Individual underdamped modes in spectral densities of the FMO complex have been identified^{64–66} with the potential to alter the population dynamics.⁶⁷ Here we employ a spectral density of Drude-Lorentz type for direct comparability to HEOM benchmark results.⁵⁴

We start by discussing the convergence of short time dynamics ($t < 0.5$ ps) upon excitation of BChl 1 by varying the number of quadrature points k_{eff} to represent the coarse grained influence functional (Fig. 4, top). The very recently reported HEOM results on the FMO trimer complex⁵⁴ serve as a reference for presented results. For $k_{\text{eff}} = 2$ (light red line) we notice substantial deviations to the HEOM reference. Deviations appear for both, the coherent population beating as well as the population of BChl 1 after 0.5 ps. An improved representation of the discretized bath response function ($k_{\text{eff}} = 4$) converges the limiting population at 0.5 ps; however, the damped population oscillations around 150 fs are still underestimated ($\approx 4\%$). An increase of $k_{\text{eff}} = 6$ improves the description of coherence dynamics within the memory time $\tau_M = 300$ fs and allows to reproduce the coherent feature at 150 fs already with 2% accuracy. Finally, converged results can be achieved with $k_{\text{eff}} = 8$ allowing for quantitative agreement with the HEOM reference. Further increase of k_{eff} shows no noticeable effect on population dynamics demonstrating the systematic convergence properties of the MACGIC-*i*QUAPI algorithm. We notice that for the presented short time dynamics, norm conservation $>99\%$ is achieved for converged results. Similarly, reduced density matrix coherences appear converged on this level of theory.

The numerical performance of the introduced algorithm is demonstrated by analyzing the number of path segments considered in the propagator functional (Fig. 4, bottom and Table IV). We observe an approximately linear scaling of runtime with the number of path segments while the number of

selected path segments increases by a factor of roughly three for every four quadrature points added to the coarse grained representation of the influence functional (corresponding to, e.g., $k_{\text{eff}} = 2$ to $k_{\text{eff}} = 4$ as forward and backward paths are considered). Note that this factor is strongly system dependent and will decrease for tight-binding-like Hamiltonians and increase for excitonically coupled systems of various magnitudes and coupling pattern complexity. For the converged simulations ($k_{\text{eff}} = 8$, $\theta = 10^{-7}$), 13×10^6 path segments are considered, requiring 24 520 s runtime on a 16 core CPU (≈ 109 CPU hours) per 0.5 ps propagation time of the 24-state FMO model.

For completeness and comparison to the wealth of available data (see, e.g., Refs. 42 and 68–70), we simulated the EET dynamics of the FMO monomeric subunit upon the excitation of BChl 1 ($T = 77$ K, data not shown) employing a seven-site Hamiltonian suggested by Adolphs and Renger.⁷¹ In this model, the initially coherent dynamics appears more pronounced (in part due to lower temperature). We find that for the derived settings of the FMO trimer model ($\Delta k_{\max} = 30$, $k_{\text{eff}} = 8$, $\theta = 10^{-7}$), converged results can be obtained also for the FMO monomer at reduced temperature and that the repeatedly reported oscillatory short time dynamics is reproduced with high accuracy. Compared to the FMO trimer model, we recognize that a larger number of path segments is selected ($L_{\text{MACGIC}} = 7.38 \cdot 10^7$, Table IV) confirming

FIG. 4. EET dynamics in the 24-state model of the FMO trimer complex ($T = 300$ K): top—short time population dynamics of BChl 1 for varying k_{eff} ($\theta = 10^{-7}$, cf. Table III); reference HEOM results⁵⁴ are given as black line; bottom—number of selected path segments for increasing k_{eff} .

the observation of Sec. III B where for the description of coherent dynamics significant numbers of path segments had to be considered. For assessment, an OFPF treatment ($\Delta k_{\max} = k_{\text{eff}} = 30$) selects $\approx 10^8$ path segments within initial 14 time steps where, within the memory time, the number of path segments still grows exponentially. Accordingly $\Delta k_{\max}$ is limited to ≈ 15 in the OFPF algorithm on typical available hardware (≈ 100 GB RAM) prohibiting to cover the entire memory time (300 fs) with a sufficiently small propagation time step determined by the energy spectrum of the system Hamiltonian.

It was suggested^{42,54} that the degree of coherent dynamics substantially depends on the identity of the initially excited BChl chromophore within the FMO complex. Figure 5 shows the short time dynamics of the 24-site FMO trimer model after the excitation of BChl 1, 6, 7, or 8, respectively. For all initial conditions, the converged influence functional representation derived above allows us to successfully describe the dynamics ($k_{\text{eff}} = 8$, $\Delta k_{\max} = 30$, Table IV). For the excitation of BChl 1, we observe coherent population transfer to BChl 2 with the latter reaching a maximum population after ≈ 100 fs, followed by slower population transfer to BChl 3 and 8 [Fig. 5(a)]. We note that the secondary transfer dynamics proceeds incoherent due to reduced intermolecular couplings (< 24 cm⁻¹, cf. Appendix) compared to the appreciable excitonic coupling of BChl 1 and 2 (80 cm⁻¹). A similar scenario is observed

for population relaxation subsequent to initial excitation of BChl 6. Here BChl 6 and 5 form an excitonically coupled pair of chromophores with oscillating population dynamics on the 200 fs time scale [Fig. 5(b)]. Due to the appreciable coupling to BChl 4, the oscillatory dynamics between BChl 6 and 5 is quenched substantially faster than for the BChl 1–BChl 2 dimer, and followed by relaxation towards BChl 3 as lowest energy state.

In contrast, initial excitation of BChl 7 or BChl 8 [Figs. 5(c) and 5(d), respectively] is quenched by slower population transfer to acceptor chromophores. Excitation of BChl 7, as highest energy chromophore, results in non-exponential population transfer to the strongly coupled BChl 4–BChl 6 dimer within the first 100 fs, followed by incoherent population redistribution among BChls [Fig. 5(c)]. Excitation of BChl 8 is quenched incoherently via the BChl 1–BChl 2 dimer and subsequently redistributed to the low-energy BChl 3 on a picosecond time scale [Fig. 5(d)]. The incoherent dynamics can be rationalized by the smaller inter-chromophore couplings and substantial detuning that impose slower relaxation dynamics between BChl 8 and 1 or BChl 7 and 4, respectively (cf. Appendix).

Figure 6 presents the long time EET equilibration dynamics of the 24-site FMO trimer model simulated with decreased $k_{\text{eff}} = 4$ but tighter weight selection threshold $\theta = 10^{-8}$

FIG. 5. EET dynamics in the 24-state model of the FMO trimer complex ($T = 300$ K) for initial excitation of BChl 1 (a), 6 (b), 7 (c), and 8 (d). $k_{\text{eff}} = 8$, $\theta = 10^{-7}$, cf. Table III.

FIG. 6. Long time EET dynamics in the 24-state model of the FMO trimer complex ($T = 300$ K) for initial excitation of BChl 1 (a), BChl 6 (b), and BChl 8 (c), respectively. The population of all 24 states is shown for initial excitation of BChl 1 of FMO monomer 2 (d); $k_{\text{eff}} = 8$, $\theta = 10^{-7}$, cf. Table III.

(cf. Table III). These settings allow for acceptable conservation of norm (87% after 20 ps) and reasonable computational efficiency ($\approx 10\,000\,000$ path segments, $\approx 308\,000$ s runtime on a 16 core Intel Xeon E5-2650v2 CPU @ 2.60 GHz), long time path integral populations have been renormalized prior to comparison to the HEOM reference.⁵⁴ We find that MACGIC-*i*QUAPI results reproduce accurately the reported HEOM data (1.5% RMSD) for both, population redistribution on the low ps time scale and equilibrium populations after 20 ps. We observe that upon excitation of BChl 1, 6, or 8 [Figs. 6(a)–6(c)], the non-equilibrium population is redistributed on the sub-picosecond time scale between discrete BChl molecules, followed by intermediate equilibration within a monomeric FMO sub-unit on a ≈ 2 –5 ps time scale. The weak inter-complex coupling imposes an additional time scale of dynamics that leads to a redistribution of population over the full FMO trimer complex within 10–20 ps [Fig. 6(d)]. Populations after 20 ps are independent of the initially excited BChl molecule and reflect the symmetry equivalence between BChl molecules of individual FMO sub-units. Accordingly, the MACGIC-*i*QUAPI algorithm facilitates the description of EET dynamics initially characterized as coherent dynamics, coupled to steady-state equilibration in the incoherent regime of Förster energy transfer.

IV. DISCUSSION AND CONCLUSIONS

In this contribution, we have introduced the approximate MACGIC-*i*QUAPI method that extends the applicability of numerical exact path integral quantum dynamics to system Hamiltonians of appreciable size and the relevant intermediate regime of system bath coupling, being similar in magnitude to inter-chromophore couplings and energetic bias. In this regime, no separation of time scales is present and methods that rely on the Born-Markov approximation are of limited applicability. The approach relies on an intermediate coarse grained representation of influence functional coefficients that allows us to reduce the number of considered path segments substantially. In contrast to the original *i*QUAPI method^{3,30,49,51} and its on-the-fly variant OFPF,³³ the definition of the coarse grained mask function constitutes a new parameter set that is of crucial importance for performance where the mask size is controlled by the effective number k_{eff} of coarse grained quadrature points. For $k_{\text{eff}} \rightarrow \Delta k_{\text{max}}$, systematic convergence towards the exact *i*QUAPI result can be obtained. For optimal mask functions, the distribution of coarse grained quadrature points reflects the physical properties of the bath response function, i.e., an initial fast decay is represented by closely spaced quadrature

points, followed by a slowly decaying tail that can be represented by fewer quadrature points. The presented algorithm for the optimization of the mask function assumes a piecewise constant approximation of discretized influence functional coefficients and is computationally efficient. The technique of mask assisted coarse graining of influence coefficients (MACGIC) yields a set of primarily relevant path segments employed for propagation in discrete time steps Δt that allows to extend the considered memory time to $\approx$ hundred of time steps.

We have demonstrated for a benchmark set of prototypical model systems that the time evolution of the reduced density matrix can be simulated in excellent agreement to numerical exact reference *i*QUAPI and HEOM results. The numerical examples covered a variety of parameter regimes of increasing complexity, i.e., bath assisted long range electron transfer in the moderate to strong system-bath coupling regime (Sec. III A), the transition from coherent to incoherent EET dynamics in a prototypical model dimer (Sec. III B) and the dependence of EET dynamics on initial excitation conditions in a model of the FMO trimer complex consisting of 24 BChl chromophores (Sec. III C). We could comprehensively demonstrate that the MACGIC-*i*QUAPI method allows to interpolate between the weak (Redfield limit), intermediate, and strong (Förster limit) system bath coupling regime. We note that efficient non-perturbative methods are very much needed even if the dynamics is Markovian but when the substantial coupling strength to the bath does not permit a perturbative treatment, e.g., the simulation of exciton dynamics in the FMO complex.⁷²

Common spectral densities of Ohmic and Drude-Lorentz form have been investigated where with the employed piecewise constant approximation of the discretized response function reliable mask functions close to optimum could be obtained. We note that the current approach as well as traditional path integral schemes is not limited to those forms of the spectral density.^{31,64,73} Structured spectral densities are common for many biological environments and play an important role in the dynamics.^{65–67} Established numerical exact methods such as HEOM suffer from an exponential increase of memory requirements when including complex spectral densities and convergence is challenging for strong system bath coupling/large reorganization energies.^{26,66,74,75} Path integral methods can in principle handle arbitrary spectral densities³¹ but, without further approximations, suffer from exponential growth in the number of path segments with increasing memory time.³⁴ The developed method provides a promising

starting point for the treatment of structured spectral densities as the efficient path selection procedure allows access to long-time bath memory. Preliminary test simulations with log-normal spectral densities⁷⁶ appear promising, a detailed investigation of the performance of the MACGIC-*i*QUAPI method for structured spectral densities with long time memory will be given in future work.

The introduced method provides access to the dissipative quantum dynamics of appreciable sized system Hamiltonians. In particular, we could demonstrate excellent agreement with converged HEOM benchmark results⁵⁴ for model Hamiltonians as large as a 24-state model of the FMO trimer complex. This model neglects trapping of excitation energy at the reaction center. Bearing this fact in mind, the long time equilibration within the FMO trimer complex presented here and in Ref. 54 might not resemble the actual situation found under operation conditions of the FMO—reaction center core complex.^{77,78} An explicit coupling to exciton states of the reaction center and concomitant charge separation^{79–82} would allow to quantify energy conversion efficiency of the transfer cascade which is an exciting avenue of future research. The developed MACGIC-*i*QUAPI method here provides a rigorous framework for the investigation of integrated light-harvesting—reaction center core complexes that are characterized by intersite and system bath couplings of similar magnitude, complex structured spectral densities, and substantial reorganization energies of charge separated states.

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APPENDIX: EXPRESSIONS OF INFLUENCE FUNCTIONAL COEFFICIENTS AND MODEL HAMILTONIANS

1. Explicit expressions of influence functional coefficients $\eta_{jj'}$

The Feynman-Vernon influence functional coefficients have the form (cf. Ref. 3):

If $0 < j' < j < N$,

$$\eta_{jj'} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) e^{\beta \hbar \omega / 2}}{\omega^2 \sinh(\beta \hbar \omega / 2)} \sin^2(\omega \Delta t / 2) e^{-i \omega \Delta t (j - j')}. \quad (\text{A1})$$

If $0 < j' = j < N$,

$$\eta_{jj} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) e^{\beta \hbar \omega / 2}}{\omega^2 \sinh(\beta \hbar \omega / 2)} (1 - e^{-i \omega \Delta t}). \quad (\text{A2})$$

If $j = j' = 0$ or $j = j' = N$,

$$\eta_{00} = \eta_{NN} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) e^{\beta \hbar \omega / 2}}{\omega^2 \sinh(\beta \hbar \omega / 2)} (1 - e^{-i \omega \Delta t / 2}). \quad (\text{A3})$$

If $0 = j' < j < N$,

$$\eta_{j0} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) e^{\beta \hbar \omega / 2}}{\omega^2 \sinh(\beta \hbar \omega / 2)} \sin(\omega \Delta t / 4) \sin(\omega \Delta t / 2) e^{-i \omega (j \Delta t - \Delta t / 4)}. \quad (\text{A4})$$

TABLE IV. Parameter settings and comparison of filtered propagator functional (FPF) and MACGIC-*i*QUAPI method.

M	τ_M (fs/a.u.)	$\Delta k_{\max}$	k_{eff}	θ	$M^{2\Delta k_{\max}}$	$M^{2k_{\text{eff}}}$	L_{MACGIC}	CPU Time (s/step)	Figures
2	600	30	12	10^{-7}	$1.15 \cdot 10^{18}$	$1.68 \cdot 10^7$	$1.46 \cdot 10^7$	17.9	3(a)
2	600	30	12	10^{-7}	$1.15 \cdot 10^{18}$	$1.68 \cdot 10^7$	$1.18 \cdot 10^7$	11.3	3(b)
2	600	60	12	10^{-7}	$1.33 \cdot 10^{36}$	$1.68 \cdot 10^7$	$1.02 \cdot 10^6$	1.41	3(c)
2	600	100	12	10^{-7}	$1.61 \cdot 10^{60}$	$1.68 \cdot 10^7$	$7.90 \cdot 10^4$	0.22	3(d)
2	600	100	20	$5 \cdot 10^{-9}$	$1.61 \cdot 10^{60}$	$1.10 \cdot 10^{12}$	$7.48 \cdot 10^6$	20.7	3(d)
7	32	40	40	$5 \cdot 10^{-9}$	$4.05 \cdot 10^{67}$	$4.05 \cdot 10^{67}$	$4.06 \cdot 10^6$	8.27	2
7	32	4	4	$5 \cdot 10^{-9}$	$5.76 \cdot 10^6$	$5.76 \cdot 10^6$	$5.53 \cdot 10^3$	3.34 (ms)	2
7	32	40	4	$5 \cdot 10^{-9}$	$4.05 \cdot 10^{67}$	$5.76 \cdot 10^6$	$3.32 \cdot 10^3$	5.40 (ms)	2
7	300	30	8	10^{-7}	$5.08 \cdot 10^{50}$	$3.32 \cdot 10^{13}$	$7.38 \cdot 10^7$	85.5	(Not shown)
24	300	30	2	10^{-7}	$6.50 \cdot 10^{82}$	$3.32 \cdot 10^5$	$7.45 \cdot 10^4$	2.62	4
24	300	30	4	10^{-7}	$6.50 \cdot 10^{82}$	$1.10 \cdot 10^{11}$	$1.39 \cdot 10^6$	48.0	4
24	300	30	6	10^{-7}	$6.50 \cdot 10^{82}$	$3.65 \cdot 10^{16}$	$5.94 \cdot 10^6$	203	4
24	300	30	8	10^{-7}	$6.50 \cdot 10^{82}$	$1.21 \cdot 10^{22}$	$1.36 \cdot 10^7$	463	4
24	300	30	10	10^{-7}	$6.50 \cdot 10^{82}$	$4.02 \cdot 10^{27}$	$2.80 \cdot 10^7$	732	4
24	300	30	8	10^{-7}	$6.50 \cdot 10^{82}$	$1.21 \cdot 10^{22}$	$1.36 \cdot 10^7$	463	5(a)
24	300	30	8	10^{-7}	$6.50 \cdot 10^{82}$	$1.21 \cdot 10^{22}$	$2.21 \cdot 10^7$	678	5(b)
24	300	30	8	10^{-7}	$6.50 \cdot 10^{82}$	$1.21 \cdot 10^{22}$	$1.69 \cdot 10^7$	576	5(c)
24	300	30	8	10^{-7}	$6.50 \cdot 10^{82}$	$1.21 \cdot 10^{22}$	$7.70 \cdot 10^6$	231	5(d)
24	300	30	4	10^{-8}	$6.50 \cdot 10^{82}$	$1.10 \cdot 10^{11}$	$1.03 \cdot 10^7$	130	6(a) and 6(d)
24	300	30	4	10^{-8}	$6.50 \cdot 10^{82}$	$1.10 \cdot 10^{11}$	$1.04 \cdot 10^7$	153	6(b)
24	300	30	4	10^{-8}	$6.50 \cdot 10^{82}$	$1.10 \cdot 10^{11}$	$1.02 \cdot 10^7$	151	6(c)

If $0 < j' < j = N$,

$$\eta_{Nj'} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) e^{\beta \hbar \omega / 2}}{\omega^2 \sinh(\beta \hbar \omega / 2)} \sin(\omega \Delta t / 4) \sin(\omega \Delta t / 2) e^{-i\omega(t-j'\Delta t - \Delta t / 4)}. \quad (\text{A5})$$

If $j' = 0$ and $j = N$,

$$\eta_{N0} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) e^{\beta \hbar \omega / 2}}{\omega^2 \sinh(\beta \hbar \omega / 2)} \sin^2(\omega \Delta t / 4) e^{-i\omega(t - \Delta t / 2)}. \quad (\text{A6})$$

2. Model Hamiltonian of the 24-state FMO trimer complex

The model Hamiltonian of the 24-state FMO trimer complex was constructed with monomer site energies taken from Ref. 47 and reported inter-chromophore couplings of Ref. 48 (in cm^{-1}),

$$H_M = \begin{pmatrix} 186.0 & -80.3 & 3.5 & -4.0 & 4.5 & -10.2 & -4.9 & 21.0 \\ -80.3 & 81.0 & 23.5 & 6.7 & 0.5 & 7.5 & 1.5 & 3.3 \\ 3.5 & 23.5 & 0.0 & -49.8 & -1.5 & -6.5 & 1.2 & 0.7 \\ -4.0 & 6.7 & -49.8 & 113.0 & -63.4 & -13.3 & -42.2 & -1.2 \\ 4.5 & 0.5 & -1.5 & -63.4 & 65.0 & 55.8 & 4.7 & 2.8 \\ -10.2 & 7.5 & -6.5 & -13.3 & 55.8 & 89.0 & 33.0 & -7.3 \\ -4.9 & 1.5 & 1.2 & -42.2 & 4.7 & 33.0 & 492.0 & -8.7 \\ 21.0 & 3.3 & 0.7 & -1.2 & 2.8 & -7.3 & -8.7 & 218.0 \end{pmatrix}. \quad (\text{A7})$$

The excitonic couplings of monomeric FMO subunits were taken from Ref. 48 (in cm^{-1}),

$$H_C = \begin{pmatrix} 1.0 & 3.0 & -0.6 & 0.7 & 2.3 & 1.5 & 0.9 & 0.1 \\ 1.5 & -0.4 & -2.5 & -1.5 & 7.4 & 5.2 & 1.5 & 0.7 \\ 1.4 & 0.1 & -2.7 & 5.7 & 4.6 & 2.3 & 4.0 & 0.8 \\ 0.3 & 0.5 & 0.7 & 1.9 & -0.6 & -0.4 & 1.9 & -0.8 \\ 0.7 & 0.9 & 1.1 & -0.1 & 1.8 & 0.1 & -0.7 & 1.3 \\ 0.1 & 0.7 & 0.8 & 1.4 & -1.4 & -1.5 & 1.6 & -1.0 \\ 0.3 & 0.2 & -0.7 & 4.8 & -1.6 & 0.1 & 5.7 & -2.3 \\ 0.1 & 0.6 & 1.5 & -1.1 & 4.0 & -3.1 & -5.2 & 3.6 \end{pmatrix}. \quad (\text{A8})$$

The model Hamiltonian H_S of 24-state FMO trimer complex finally reads

$$H_S = \begin{pmatrix} H_M & H_C & H_C^\dagger \\ H_C^\dagger & H_M & H_C \\ H_C & H_C^\dagger & H_M \end{pmatrix}. \quad (\text{A9})$$

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