Juxtaposing density matrix and classical path-based wave packet dynamics

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In many physical, chemical, and biological systems energy and charge transfer processes are of utmost importance. To determine the influence of the environment on these transport processes, equilibrium molecular dynamics simulations become more and more popular. From these simulations, one usually determines the thermal fluctuations of certain energy gaps, which are then either used to perform ensemble-averaged wave packet simulations, also called Ehrenfest dynamics, or to employ a density matrix approach via spectral densities. These two approaches are analyzed through energy gap fluctuations that are generated to correspond to a predetermined spectral density. Subsequently, density matrix and wave packet simulations are compared through population dynamics and absorption spectra for different parameter regimes. Furthermore, a previously proposed approach to enforce the correct long-time behavior in the wave packet simulations is probed and an improvement is proposed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4723669>]

I. INTRODUCTION

Reduced density matrix methods are often used to describe the quantum dynamics in open systems.^{1–3} For these calculations a Hamiltonian and spectral densities have to be specified beforehand, which may come from experiments or atomistic simulations. An alternative approach would be *ab initio* studies of the electronic and nuclear degrees of freedom (DOFs), but these are usually prohibitively expensive for large systems such as pigment-protein complexes.⁴ A further possibility is mixed quantum-classical dynamics in which one couples a few selected quantum DOFs to a large set of classical modes. Using such approaches one can include quantum effects in otherwise classical simulations, like classical molecular dynamics (MD) simulations, and enable the treatment of quantum phenomena such as charge and energy transfer.

A large variety of mixed quantum-classical approaches exists. Among the most well-known and used ones are the mean-field Ehrenfest dynamics^{5–8} and the surface hopping approach including its fewest switches variant.^{9,10} In both approaches the time-dependent Schrödinger equation is integrated using a time-dependent Hamiltonian which is derived from the motions of the classical DOFs. Furthermore, an ensemble average is needed in both schemes to obtain physically meaningful quantities. In the standard Ehrenfest and surface hopping approaches the classical forces are altered due to the dynamics in the quantum system, i.e., the so-called back reaction of the quantum onto the classical system is included. Both the Ehrenfest and surface hopping scheme have their advantages and drawbacks. Surface hopping approaches do not properly account for decoherence effect while in the Ehrenfest scheme no appropriate thermal equilibrium distri-

bution is reached in the long-time limit. Another stochastic approach for modelling exciton dynamics is the Haken-Strobl-Reineker model^{11,12} in which the bath fluctuations are assumed to be Gaussian white noise. Within a similar approach colored but dichotomic noise can be treated.^{13,14} Due to the classical nature of the baths in the Haken-Strobl-Reineker model and its colored noise variant this ingredient also leads to an equal population of the different exciton states at long times.

In the present study, we will mainly focus on the Ehrenfest approach for which many variants have been developed (see, e.g., Refs. 5–8 and 15–17 and references therein). Herein, we select a variant of the Ehrenfest approach in which the back reaction of the quantum onto the classical system is neglected. This limitation is certainly only reasonable for small coupling values between the classical and the quantum systems, but has the clear advantage that the classical dynamics can be performed using standard MD codes. The approximation of a ground-state, classical MD has recently been applied to vibrational relaxation,^{18,19} charge,^{20–22} and excitation energy transfer.^{23–27} The limitations of this scheme are obvious though might not be that severe for many systems.

One goal of the present study is to compare ensemble-averaged wave packet dynamics with reduced density matrix dynamics. The reasoning behind this investigation is the following: using a classical MD simulation one can determine the fluctuations of the atoms belonging to the subsystem of interest, e.g., a chromophore. Subsequent electronic structure calculations yield a time series of energy gap fluctuations of this subsystem. This time series can now be used in two alternative ways: either directly in ground-state classical-path Ehrenfest dynamics, or to determine spectral densities which are in turn key ingredients for density matrix approaches. One of the aims of this investigation is to test whether, and in which parameter regimes, these two different routes yield

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the same or similar results. A comparison of Ehrenfest dynamics and exact quantum dynamics has been performed earlier²⁸ showing a good performance of the Ehrenfest dynamics concerning coherent dynamics. In addition to some recent reports,^{29,30} a more detailed analysis is performed in the present study. To be able to perform these tests, we generate random site energies based on a Drude spectral density. As a first analysis the spectral density is reproduced from the site energy trajectories of different lengths. This study yields an estimate how accurately one can determine spectral densities based on finite length trajectories as done for realistic systems.^{31–38}

Density matrix dynamics are obtained by using the Drude spectral densities with the hierarchy equations of motion (HEOM).^{39–46} The HEOM are a set of coupled equations that describes the non-Markovian time evolution of a system coupled to a bosonic bath. Although the method is computationally costly, the HEOM includes no assumption of the relative strength of intra-system and system-bath interactions, and correctly describes quantum coherence in the system.⁴⁷ These properties have made it attractive for comparison with other methods, such as mean-field Ehrenfest dynamics.^{29,40,45,47}

In addition to comparing the results of density matrix calculation with those of mean-field Ehrenfest dynamics, the results from a temperature-corrected Ehrenfest dynamics variant are also investigated. This scheme, by Bastida *et al.*,^{48–51} introduced an additional correction factor to fulfill detailed balance and leads to the correct thermal distribution at long times. An improved version of this algorithm will be proposed and tested.

II. MODEL HAMILTONIAN FOR EXCITON TRANSFER

As we will analyze the agreement between the density matrix results and the ensemble-averaged wave packet approach for an excitonic system, we want to review the microscopic origin to highlight important details for the analysis of the two approaches.³ The Hamiltonian of a molecular aggregate, H_{agg} , is constructed from the contributions of the individual molecules, H_m , and the couplings among these molecules denoted as V_{mn}

$$H_{agg} = \sum_m H_m(\mathbf{r}, \mathbf{R}) + \sum_{m \neq n} V_{mn}(\mathbf{r}, \mathbf{R}). \quad (1)$$

In this expression, $\mathbf{r}$ and $\mathbf{R}$ denote the electronic and nuclear DOFs, respectively. Assuming the Born-Oppenheimer approximation the electronic part of the individual pigments, $H_m^{(el)}$, can be solved using

$$H_m^{(el)}(\mathbf{R})\varphi_{ma}(\mathbf{r}_m; \mathbf{R}) = \epsilon_{ma}(\mathbf{R})\varphi_{ma}(\mathbf{r}_m; \mathbf{R}). \quad (2)$$

Here φ_{ma} and ϵ_{ma} denote the wave function and the energy of the electronic state a , respectively. For simplicity we restrict ourselves to the ground and first excited states of the electronic system in this investigation, i.e., each pigment is described by a two-level system with $a = g$ or $a = e$. The electronic ground state of the aggregate is therefore given by

$$|0\rangle = \prod_n |\varphi_{ng}\rangle. \quad (3)$$

Consequently a single excitation at site m can be written as

$$|m\rangle = |\varphi_{me}\rangle \prod_{n \neq m} |\varphi_{ng}\rangle. \quad (4)$$

Within the single-exciton manifold the completeness relation reads $\sum_m |m\rangle\langle m| = 1$. The Hamiltonian of the full system, including the electronic and nuclear parts, can be decomposed into

$$H_{agg} = H_{agg}^{(0)} + H_{agg}^{(1)}. \quad (5)$$

In this expression, the first term describes the system with the electronic part in the ground state while the second term corresponds to the case when one electronic excitation is present in the system. The corresponding ground-state Hamiltonian is given by

$$\begin{aligned} H_{agg}^{(0)} &= \sum_m H_{mg}|0\rangle\langle 0| \\ &= (T_{nuc}(\mathbf{R}) + V_{nuc-nuc}(\mathbf{R}) + \epsilon_{mg}(\mathbf{R}))|0\rangle\langle 0| \end{aligned} \quad (6)$$

with T_{nuc} and $V_{nuc-nuc}$ being the kinetic energy of the nuclei and their nuclei-nuclei potential, respectively. The second term in Eq. (5) describes the excited state Hamiltonian

$$H_{agg}^{(1)} = \sum_m (H_{mg} + \epsilon_{me}(\mathbf{R}) - \epsilon_{mg}(\mathbf{R}))|m\rangle\langle m|. \quad (7)$$

A property used below is the site energy

$$E_m = \epsilon_{me}(\mathbf{R}_0) - \epsilon_{mg}(\mathbf{R}_0), \quad (8)$$

which corresponds to the excitation energy needed to excite molecule m from the ground to the first excited state while being in the equilibrium nuclear configuration $\mathbf{R}_0$. The changes of the site energies for varying nuclear configurations are in the following referred to as site energy fluctuations given by

$$\Delta E_m(t) = \epsilon_{me}(\mathbf{R}(t)) - \epsilon_{mg}(\mathbf{R}(t)) - E_m. \quad (9)$$

Below we review two alternative approaches how to describe the motion of an electronic excitation in a molecular aggregate. We would like to point out that the relevant DOFs in these methods are the excitons and the environmental DOFs consist of the atoms including the electrons in their ground electronic state.

III. EXCITATION TRANSFER DYNAMICS

A. Reduced density matrix approach

Due to the size of the molecular aggregates and their environment which we would like to investigate, it is not possible to treat all DOFs of the system on the same footing. Therefore, it is common practice to split the Hamiltonian $\hat{H}$ into a system part $\hat{H}_S$ and a bath part $\hat{H}_B$

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{H}_S(\mathbf{r}) + \hat{H}_B(\mathbf{R}) + \hat{H}_{SB}(\mathbf{r}, \mathbf{R}). \quad (10)$$

The system-bath coupling Hamiltonian $\hat{H}_{SB}$ can be written as a sum of products of system and bath operators. The latter one is denoted by $\hat{\Phi}_j$ while the former one is supposed to be site diagonal for an excitonic system³

$$\hat{H}_{SB} = \sum_j \hat{\Phi}_j |j\rangle\langle j|. \quad (11)$$

In this form there is an interaction between the bath and the system at site j only if an excitation is present.

If in addition to the relevant system described by $\hat{\rho}$, an environmental bath is present, which is described by its density matrix $\hat{R}$, then the density matrix $\hat{W}$ of a complete but uncorrelated system can be written as $\hat{W} = \hat{\rho} \otimes \hat{R}$. Its time evolution is described by the Liouville-von Neumann equation

$$\frac{\partial}{\partial t} \hat{W}(t) = -i\hat{\mathcal{L}}\hat{W}(t), \quad \hat{\mathcal{L}}\bullet = \frac{1}{\hbar}[\hat{H}, \bullet]. \quad (12)$$

The time evolution of the reduced density matrix of the system, $\hat{\rho}(t)$, is calculated by taking the average of the total system density matrix over the bath DOFs,²

$$\hat{\rho}(t) = \langle \hat{W}(t) \rangle_B = \left\langle \exp\left(-\frac{i}{\hbar} \int_0^t ds \hat{\mathcal{L}}\right) \right\rangle_B \hat{\rho}(0) = \langle \hat{\mathcal{U}} \rangle_B \hat{\rho}(0). \quad (13)$$

Various methods have been derived to treat this equation. For example, the propagator $\langle \hat{\mathcal{U}} \rangle_B$ can be determined using a path integral formalism⁵² or with alternative approaches such as the HEOM,^{39,44,45} employed here.

For the system Hamiltonian we assume a time-independent tight-binding model, with site energies E_i at site i and intersite couplings V_{ij} , given by

$$\hat{H}_S = \sum_{i=1}^N E_i |i\rangle \langle i| + \sum_{i=1}^N \sum_{j=1}^N V_{ij} |i\rangle \langle j|. \quad (14)$$

The bath is treated as a collection of harmonic oscillators

$$\hat{H}_B = \sum_{\xi} \left(\frac{\hat{p}_{\xi}^2}{2m_{\xi}} + \frac{m_{\xi} \omega_{\xi}^2 \hat{x}_{\xi}^2}{2} \right) \quad (15)$$

with p_{ξ} , x_{ξ} , ω_{ξ} , and m_{ξ} denoting the momenta, displacements around the equilibrium, frequencies, and masses of the bath oscillators. In addition to the site-local assumption discussed above in Eq. (11), the bath part of the system-bath coupling Hamiltonian is assumed to be linear in the bath coordinates

$$\hat{H}_{SB} = \sum_j \hat{X}_j |j\rangle \langle j| = \sum_j \sum_{\xi} c_{j\xi} \hat{x}_{\xi} |j\rangle \langle j|. \quad (16)$$

In this expression the constants $c_{j\xi}$ define the coupling strengths of the bath oscillators to the system. By taking the bath average, all information concerning the system-bath coupling is given by the so-called spectral density

$$J_j(\omega) = \sum_{\xi} \frac{c_{j\xi}^2}{2m_{\xi}\omega_{\xi}} \delta(\omega - \omega_{\xi}). \quad (17)$$

Denoting the inverse temperature by $\beta = 1/(k_B T)$ the spectral density $J_j(\omega)$ at site j can be determined as^{3,32,35}

$$J_j(\omega) = \frac{2}{\pi\hbar} \tanh\left(\frac{\hbar\omega\beta}{2}\right) \int_0^{\infty} dt \cos(\omega t) C_j(t). \quad (18)$$

This relation combines a energy gap autocorrelation function $C_j(t) = \langle \Delta E_j(t) \Delta E_j(0) \rangle$ with the spectral density. We note that the spectral density in the Caldeira-Leggett model $J_{CL,j}(\omega)$ is connected to the present form by $J_{CL,j}(\omega) = \frac{\pi}{\hbar} J_j(\omega)$. Often analytical forms of the spectral density are

assumed, such as the Drude form used below. In other cases spectral densities are estimated based on experimental data⁵³ or determined using MD simulations.^{31–38}

B. Ensemble-averaged wave packet dynamics

To derive the equations for the ensemble-averaged wave packet approach, we first take a look at the time-dependent Schrödinger equation for the complete system of relevant system plus bath

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle = (\hat{H}_S + \hat{H}_B + \hat{H}_{SB}) |\Psi(t)\rangle. \quad (19)$$

In this equation, the state of the complete system $|\Psi\rangle$ is a product of the state of the relevant system $|\Psi^S\rangle$ and the bath $|\Psi^B\rangle$ leading to

$$i\hbar \frac{\partial}{\partial t} |\Phi^S\rangle |\Phi^B\rangle = \hat{H}_S |\Psi^S\rangle |\Psi^B\rangle + \hat{H}_B |\Psi^S\rangle |\Psi^B\rangle + \hat{H}_{SB} |\Psi^S\rangle |\Psi^B\rangle. \quad (20)$$

At this point we deviate from the standard Ehrenfest dynamics and neglect the effect of the system on the bath, yielding

$$i\hbar \frac{\partial}{\partial t} |\Psi^B(t)\rangle = \hat{H}_B |\Psi^B(t)\rangle. \quad (21)$$

In this approximation the bath always stays in equilibrium if initially in equilibrium. As with perturbative approaches, where this is also one of the basic assumptions,³ the present approach will not be able to handle strongly coupled system-bath configurations. Taking the expectation value with respect to the bath in a mean-field manner, Eq. (20) reduces to a system Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi^S(t)\rangle = (\hat{H}_S + \langle \Psi^B | \hat{H}_{SB} | \Psi^B \rangle) |\Psi^S(t)\rangle. \quad (22)$$

Together with Eqs. (11) and (14) one can therefore define an effective Hamiltonian for the relevant system as

$$\begin{aligned} \hat{H}_S^{\text{eff}} &= \hat{H}_S + \sum_m \langle \Psi_B(t) | \hat{\Phi}_m | \Psi_B(t) \rangle |m\rangle \langle m| \\ &= \sum_m (E_m + \Delta E_m(t)) |m\rangle \langle m| + \sum_{n \neq m} V_{nm} |n\rangle \langle m|. \end{aligned} \quad (23)$$

In this expression, the term $\Delta E_m(t) = \langle \Psi_B(t) | \hat{\Phi}_m | \Psi_B(t) \rangle$ describes fluctuations of the site energies due to the coupling to the environment. To determine this time-dependent term one needs to solve the bath Schrödinger Eq. (21) in parallel to the Schrödinger equation of the relevant system using the effective Hamiltonian.

As the bath DOFs are assumed to be harmonic, their expectation values of positions and momenta follow Newton's classical equations of motion. This property provides a straightforward bridge to approximate the quantum bath by a classical one. At the same time one has to keep in mind that such a classical bath includes a high-temperature limit and does not obey detailed balance.⁵⁴ In several recent reports, the classical bath has been described by equilibrium molecular dynamics simulations.^{31–38} Since these simulations determine thermal fluctuations around the equilibrium positions,

the harmonic approximation is fulfilled at least for a part of the DOFs in MD simulations.

To be able to describe the dissipative energy or charge transfer in a molecular system, in an initial step ground-state MD simulations of the pigments in their environments are performed. The resulting trajectories are used to compute the the energy gap between ground and excited state, and the corresponding fluctuations. Subsequently, one solves the time-dependent Schrödinger equation, Eq. (22), employing the energy gap fluctuations. Finally, an ensemble average over different samples of the classical trajectory is performed, achieving the charge or energy transfer observable A in the respective system

$$\langle A \rangle = \frac{1}{N_\alpha} \sum_{\alpha=1}^{N_\alpha} \langle \Psi_\alpha^S(t) | A | \Psi_\alpha^S(t) \rangle = \overline{\langle \Psi^S(t) | A | \Psi^S(t) \rangle} \quad (24)$$

with N_α being the number of samples.

IV. COMPARING DENSITY MATRIX AND WAVE PACKET DYNAMICS: TWO-SITE SYSTEM

In this section a simple model system, i.e., the two-site model coupled to a thermal bath, is employed to compare the density matrix and ensemble-averaged wave packet approaches. The system Hamiltonian of the form (14) with the two energies, E_1 and E_2 , and coupling $V_{12} = V_{21} = V$. The baths of both sites are assumed to be uncorrelated, i.e., each site has its own spectral density $J_i(\omega)$. To facilitate a direct comparison between density matrix and wave packet approaches, a bath is chosen which can be described easily in both formalisms. To this end, the Drude model for the spectral density is used³

$$J_i(\omega) = \frac{2}{\pi} \lambda_i \gamma_i \frac{\omega}{\omega^2 + \gamma_i^2}. \quad (25)$$

In this expression, γ_i is related to the width of the spectral density and λ_i denotes the reorganization energy of the bath. The latter quantity can be calculated from spectral density using

$$\lambda_i = \int_0^\infty \frac{J_i(\omega)}{\omega} d\omega. \quad (26)$$

For an harmonic bath the correlation functions of the site energies are connected to the spectral density through an integral expression which can be evaluated analytically in the high-temperature limit, i.e., classical³

$$C_i(t) = \langle \Delta E_i(t) \Delta E_i(0) \rangle \\ = \hbar \int_0^\infty d\omega J_i(\omega) \coth\left(\frac{\hbar\omega\beta}{2}\right) \cos(\omega t) = \frac{2\lambda_i}{\beta} e^{-\gamma_i t}. \quad (27)$$

Thus the Drude spectral density corresponds to an exponentially decaying correlation function.² The task is therefore to create trajectories of site energy fluctuations which yield exponentially decaying correlation functions. A Gaussian random number generator with exponentially correlated numbers can be used to produce the fluctuations.⁵⁵ For the present study we generated energy trajectories with 1 fs

FIG. 1. Numerical estimates of the spectral density for different numbers of samples and different time steps. The analytical form is indistinguishable from the numerical results with $dt = 0.1$ fs and 5000 samples.

time steps to mimic the behavior in molecular systems like light-harvesting systems. In a first step the correspondence between the Drude spectral density and the fluctuations was investigated. To this end we used the inverse relation to Eq. (27), i.e., Eq. (18). As an example we used a spectral density with $\lambda = 50$ cm⁻¹ and $1/\gamma = 25$ fs and evaluate the correlation function at $T = 300$ K. In Fig. 1, the spectral densities determined from a different number of 200 fs long trajectories with different time step are shown. If high-energy components are involved in the spectral density as for the algebraically decaying Drude form, rather small time steps are necessary to reproduce the correct high-frequency behavior, i.e., the exponential decay of the correlation function needs to be properly sampled using small time steps. At the same time, one needs to average over a large number of independent short trajectories where the correlation is clearly distinguishable from numerical noise. To this end one can use certain sampling tricks such as shifted windows along a long trajectory.⁵⁶ This example shows that one should be rather careful over-interpreting little wiggles in spectral densities obtained with too poor sampling and might as well be a problem in the determination of spectral densities from MD simulations.^{31–38} In the present case, the root mean square deviation from the known analytic form of the spectral density decays reciprocally proportional to the number of sampling points (data not shown).

In the following, the density matrix and wave packet dynamics are compared for a specific model system. To parametrize the two-site model we fixed the values of the coupling between the sites to $V = 100$ cm⁻¹, temperature to $T = 300$ K ($k_B T/V \approx 2$), and the correlation time to $1/\gamma = 100$ fs. The population at the sites corresponds to the diagonal elements of the system density matrix and can be written in terms of the wave packet as

$$\rho_{nn}(t) = \overline{\langle n | \Psi^S(t) \rangle \langle \Psi^S(t) | n \rangle}. \quad (28)$$

In Fig. 2 we compare the density matrix and Ehrenfest dynamics for four different reorganisation energies λ for the case of a vanishing average site energy difference, i.e., $\Delta E = E_1 - E_2 = 0$. For small reorganisation energies the

FIG. 2. Population of the excited site for different reorganization energies λ and equal average site energies.

agreement is excellent. Small deviations start to show up at longer times which is in part due to the finite number of 5000 samples. For $\lambda = V$ the agreement is still good and starts to deteriorate for larger system-bath coupling strengths. This disagreement is due to the neglect of the back reaction of the quantum onto the classical system needed for strong system-bath coupling. Nevertheless, the method reaches the correct thermal equilibrium for long times so that the disagreement for the strongest coupling case is at intermediate times.

The situation is slightly different for unequal average site energies, here $\Delta E = V$. In Fig. 3 the initial agreement is again good but for larger times it becomes clear that the populations from the varying approaches reach different limits. The correct thermal equilibrium population is approached for the case of density matrix dynamics, while for Ehrenfest dynamics, equal populations for both sites are reached, i.e., both populations go to 0.5. Nevertheless, the initial dephasing behaviour is again rather accurately reproduced using the Ehrenfest dynamics. It is quite rewarding to see that, when using the proper procedure, both approaches indeed yield very similar results.

FIG. 3. Population of the excited site for different reorganization energies λ and a difference in average site energies of $\Delta E = V = 100 \text{ cm}^{-1}$.

V. ABSORPTION

Within the usual perturbative coupling to the electromagnetic field the linear absorption line-shape $I(\omega)$ can be calculated from the Fourier transform of the dipole-dipole correlation function as^{3,40}

$$I(\omega) \propto \text{Re} \int_0^\infty dt e^{i\omega t} \text{tr}\{\rho^{\text{eq}}[\hat{\mu}(t), \hat{\mu}]\}. \quad (29)$$

In this expression $\hat{\mu}(t)$ denotes the dipole operator which is evolving according to the Hamiltonian of the unperturbed system and initially corresponds to $\hat{\mu}(0) = \sum_n |n\rangle\langle 0|$. The equilibrium density matrix of the complete system is denoted by ρ^{eq} . To be able to easily compare line shapes among different theoretical approaches and experiment, one usually normalizes all spectra to a maximum peak height equal to unity, i.e., prefactors are neglected. In case of the ensemble-averaged wave packet scheme one obtains²⁹

$$I(\omega) \propto \text{Re} \int_0^\infty dt e^{i\omega t} \sum_{m=1}^2 \overline{\langle m|\Psi(t)\rangle\langle\Psi(t)|0\rangle}. \quad (30)$$

In this expression, the initial condition $\langle m|\Psi(t)\rangle\langle\Psi(t)|0\rangle = 1$ is assumed along with identical transition dipole moments on both sites m and one simply adds the lineshapes from individual excitations of the sites (see Ref. 29 for a more detailed discussion).

Concerning the scenario of equal average site energies and a small reorganisation energy, the agreement between the density matrix and wave packet-based approaches is excellent as can be seen in Fig. 4. The deviations start to grow for larger reorganisation energies though both schemes basically yield very similar broad line shapes for large reorganisation energies. The situation changes with the implementation of a site energy difference. As discussed above, the population dynamics for these cases show different long-time behaviors. This difference also manifests itself in the absorption line shapes. At the lowest reorganisation energy shown in Fig. 4 a low energy peak is present in the wave packet-based calculations which is much smaller in the density matrix formalism. For the intermediate reorganisation energy there is still a more pronounced shoulder in the wave packet-based outcome. The difference between the two approaches in the case of the largest reorganisation energy, where there is only a single, broad absorption line, is not much larger than in the case of a vanishing site energy difference. So in total, the difference between the two schemes gets more smeared out for larger coupling strengths to the environment.

VI. TEMPERATURE-CORRECTED WAVE PACKET APPROACH

One of the major drawbacks of the ensemble-averaged wave packet approach is its implicit high-temperature restriction. Attempts have been made to overcome this limitation. Here we test and improve the scheme by Bastida *et al.*^{48–51} As discussed above, we have to solve the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi^S(t)\rangle = \hat{H}_S^{\text{eff}} |\Psi^S(t)\rangle \quad (31)$$

FIG. 4. Absorption line shapes with $\Delta E = 0$ (left) and $\Delta E = V$ (right) for three different values of the reorganization energy. The solid lines represent the wave packet results and the dashed lines those from the density matrix theory. The different reorganisation energies are indicated by the color code: black $\lambda = 20 \text{ cm}^{-1}$, red $\lambda = 50 \text{ cm}^{-1}$, and blue $\lambda = 500 \text{ cm}^{-1}$.

with the effective Hamiltonian defined in Eq. (23) and then perform an ensemble average. In the following we expand the time-dependent state $|\Psi^S(t)\rangle$ in terms of the time-independent excitonic eigenstates $|\alpha\rangle$ of the system Hamiltonian $\hat{H}_S$

$$|\Psi^S(t)\rangle = \sum_{\alpha} c_{\alpha}(t) |\alpha\rangle. \quad (32)$$

This relation leads to coupled equations for the time-dependent expansion coefficients

$$i\hbar \frac{\partial}{\partial t} c_{\alpha}(t) = \varepsilon_{\alpha} + \sum_{\beta} J_{\alpha\beta}(t) c_{\beta}(t) \quad (33)$$

with the matrix elements of the system-bath coupling Hamiltonian

$$\begin{aligned} J_{\alpha\beta}(t) &= \langle \alpha | \langle \Psi^B | \hat{H}_{SB} | \Psi^B \rangle | \beta \rangle \\ &= \sum_{m,n} c_m^{\alpha} c_n^{\beta} \langle m | \langle \Psi^B | \hat{H}_{SB} | \Psi^B \rangle | n \rangle. \end{aligned} \quad (34)$$

Here, the time-independent decomposition of the excitonic states in terms of site-local state $|m\rangle$ was used

$$|\alpha\rangle = \sum_m c_m^{\alpha} |m\rangle. \quad (35)$$

Using the site-local form of the system-bath coupling Eq. (16), this matrix element becomes

$$J_{\alpha\beta}(t) = \sum_j c_j^{\alpha} c_j^{\beta} \langle \Psi_B(t) | \hat{\Phi}_j | \Psi_B(t) \rangle = \sum_j c_j^{\alpha} c_j^{\beta} \Delta E_j(t). \quad (36)$$

Again, as discussed above, the $\Delta E_j(t)$ denote fluctuations of the site energies and therefore the $J_{\alpha\beta}(t)$ are the corresponding counterparts in the excitonic picture. The probability to find the wave packet at site m is given by

$$P_m(t) = |\langle m | \Psi \rangle|^2 = \left| \sum_{\alpha} c_m^{\alpha} c_{\alpha}(t) \right|^2. \quad (37)$$

To reproduce a physical ensemble the wave packet propagation has to be performed on sufficient number of trajectories and subsequently averaged.

As can be seen in Eq. (33) the fluctuations in the excitonic representation, i.e., the $J_{\alpha\beta}(t)$, induce couplings between the time-independent excitonic states of H_S . If these fluctuations are classical and result, e.g., from MD simulations, the fluctuations lead to an equal distribution of the population among the excitonic states in the long-time limit. This result is the expected high-temperature limit. However, the appropriate thermal equilibrium distribution of populations in the excitonic states is given by the Boltzmann distribution

$$|c_{\alpha}^{eq}|^2 = \frac{e^{-\varepsilon_{\alpha}/k_B T}}{\sum_{\alpha} e^{-\varepsilon_{\alpha}/k_B T}}. \quad (38)$$

To improve this temperature behavior we follow a method proposed by Bastida and co-workers.^{48–51} In this method Fermi's golden rule, i.e., the assumption that the rate is proportional to the square of the coupling, is employed. To fulfill detailed balance, a quantum-correction factor is, thus, introduced into the coupling. Several of such factors exist in literature.⁵⁷ As introduced by Bastida and co-workers^{48–51} only the so-called standard correction factor is described below but tests with the harmonic, the Schofield, and Egelstaff variants⁵⁷ performed very similarly for the present system. To this end, the couplings between the quantum system and classical system are modified by the so-called standard temperature-dependent quantum correction factor

$$J_{\alpha\beta}^{tc} = \left(\frac{2}{1 + e^{-\hbar\omega_{\alpha\beta}/k_B T}} \right)^{1/2} J_{\alpha\beta}, \quad \hbar\omega_{\alpha\beta} = \varepsilon_{\alpha} - \varepsilon_{\beta}. \quad (39)$$

This factor ensures that detailed balance is fulfilled and therefore the correct equilibrium distribution is reached. The drawback of this correction is the asymmetry of the coupling matrix $J_{\alpha\beta}^{tc} \neq J_{\beta\alpha}^{tc}$. In order to restore symmetry, symmetry-corrected couplings are introduced as^{48–51}

$$\begin{aligned} J_{\alpha\beta}^{stc} &= J_{\beta\alpha}^{stc} = |c_{\beta}| J_{\alpha\beta}^{tc} - |c_{\alpha}| J_{\beta\alpha}^{tc}, \quad \varepsilon_{\alpha} > \varepsilon_{\beta}, \\ J_{\alpha\alpha}^{stc} &= J_{\alpha\alpha}. \end{aligned} \quad (40)$$

The corrected coupling matrix is real and symmetric and thus the norm and the total energy of the wave function will be conserved. The non-diagonal matrix elements vanish when

the populations reach equilibrium which can be proven using Eqs. (38)–(40).

The aforementioned approach by Bastida and co-workers^{48–51} has the drawback that it does not reproduce the high-temperature limit. Therefore, we propose a modification of this scheme by introducing an additional normalization

$$J_{\alpha\beta}^{ntc} = J_{\beta\alpha}^{ntc} = \frac{|c_\beta|J_{\alpha\beta}^{tc} - |c_\alpha|J_{\beta\alpha}^{tc}}{|c_\beta| - |c_\alpha|},$$

$$E_\alpha > E_\beta \quad \text{and} \quad |c_\alpha| \neq |c_\beta|,$$

$$J_{\alpha\beta}^{ntc} = J_{\beta\alpha}^{ntc} = (J_{\alpha\beta}^{tc} + J_{\beta\alpha}^{tc})/2,$$

$$E_\alpha > E_\beta \quad \text{and} \quad |c_\alpha| = |c_\beta|,$$

$$J_{\alpha\alpha}^{ntc} = J_{\alpha\alpha}.$$

In the high-temperature limit $J_{\alpha\beta}^{ntc}$ equals $J_{\beta\alpha}^{ntc}$, i.e., $J_{\alpha\beta}^{ntc} = J_{\beta\alpha}^{ntc} = J_{\alpha\beta} = J_{\beta\alpha}$, and therefore the same is true for the normalized coupling coefficients $J_{\alpha\beta}^{ntc}$ while not being true for $J_{\alpha\beta}^{stc}$. Thus, the normalized version results in the standard Ehrenfest method in the limit of high temperatures for which it performs very accurately as shown above. In principle, the additional normalization can lead to very high-coupling values when the two respective coefficients approach equal values. To avoid the singularity, the coupling value for equal coefficients needs to be set to a large but finite value. In our tests with several thousand trajectories this case was never reached. If situations are approached in which the coefficients are very close in absolute value, the resulting large coupling value leads to a fast change in populations and therefore rapidly changing coefficients avoiding the singularity.

For unequal average site energies of $\Delta E = V$ the results are shown in Fig. 5. This corresponds to the case shown in Fig. 3 for the standard Ehrenfest approach. The difference between the temperature-corrected version of Bastida and co-workers^{48–51} and the standard Ehrenfest approach for the present system is actually rather small for the times shown in Fig. 5. The former does reach the correct thermal distribution for long times (data not shown) while in the presented

FIG. 5. Excitation dynamics calculated using the temperature-corrected wave packet approach and the present normalized version thereof compared with the density matrix results for a difference in average site energies of $\Delta E = V = 100 \text{ cm}^{-1}$.

FIG. 6. Coherence between the two sites in site representation. The red dashed line shows the density matrix results, the black solid the standard Ehrenfest without back reaction, blue dash-dotted the temperature-corrected version and the green dotted line the normalized temperature-corrected variant. 50 000 samples were used to minimize the wiggles due to poor sampling.

results the major visible difference are for larger reorganization energies at which the temperature-corrected version reaches populations below the equi-distribution value of 0.5. The situation is different for the normalized version of the same approach proposed in Eq. (41). This version results in much larger changes compared to the standard Ehrenfest approach. The relaxation rate is very similar to the converged results obtained using the HEOM. At the same time it is visible that the dephasing rate of the newly proposed version is too large, i.e., the oscillations decay too fast while at the same time the oscillation frequency is slightly shifted. This change in coherent dynamics is certainly caused by changing the coupling constant through the correction factors but cannot be avoided using the present scheme. Thus forcing the temperature-corrected version to reproduce the high-temperature limit leads to quite accurate relaxation but too fast dephasing. More work is needed to improve this scheme though it might already be useful in estimating improved relaxation rates from ensemble-averaged wave packet dynamics.

Another property, which can be determined to test the accuracy of the different versions is the coherence. The coherence between two sites in a quantum system corresponds to the off-diagonal elements of the density matrix in site representation

$$\rho_{nm}(t) = \overline{\langle n | \Psi(t) \rangle \langle \Psi(t) | m \rangle}, \quad n \neq m. \quad (42)$$

In Fig. 6, the coherence between the two sites is shown in site representation. One has to note that the coherences vanish in the thermal equilibrium in the excitonic picture. With finite electronic coupling between the sites this property leads to finite coherences in site representation for long times. However, in the standard Ehrenfest scheme these site coherences go to zero at long times. This behavior improves for the temperature-corrected version and for the normalized version, where values close to the ones from the density matrix calculations are obtained.

VII. CONCLUSIONS

Starting from the energy gap fluctuations one can use either a density matrix method or the mean-field Ehrenfest method without back reaction to obtain the respective quantum dynamics in the system. In a first step, we analyzed how many points along an energy gap trajectory one needs to reproduce a known spectral density. This study indicates that rather good sampling is necessary for an accurate reproduction of a spectral density.

For weak to moderate system-bath coupling strengths, Ehrenfest dynamics (here without back reaction) and the density matrix calculations nicely agree, especially if the site energies are equal. As expected, Ehrenfest dynamics does not produce the correct steady-state values in the long-time limit, particularly in describing quantum coherence between two sites or when their site energies are different. This drawback is also reflected in the absorption spectra. For small reorganization energies there is a clearly visible deviation of the absorption spectra if the average site energies are different. For strong system-bath coupling, however, these differences are hidden by the broad, featureless absorption peak.

To overcome the drawback of the long-time Ehrenfest dynamics, Bastida *et al.*^{48–51} introduced a correction factor which leads to the fulfillment of detailed balance. The comparison with the density matrix calculations showed that the correct thermal equilibrium distribution is obtained but at a much too slow rate. Surprisingly, the scheme by Bastida *et al.* does not yield the correct high-temperature limit though this limit is fine in the standard Ehrenfest approach. Therefore, this latter flaw was removed in the present study and shown that the improved approach yields relaxation rates much closer to that of the density matrix results. Unfortunately, this correction also worsens the agreement at short times, i.e., the dephasing became too strong. Nevertheless, this approach produces much more favorable results for the off-diagonal terms of the density matrix in site representation. While in standard Ehrenfest dynamics these coherences vanish in the long-time limit, using the modified correction one reaches values close to the correct ones.

Finally, we want to emphasize one point which has not been mentioned so far. Combined molecular dynamics and quantum chemistry calculations yield not only time-series of site energy fluctuations but also couplings, transition dipole moments, etc. In principle, one could introduce spectral densities for all these fluctuating quantities but these additional properties would lead to very complex density matrix equations. In ensemble-averaged wave packet calculations all these fluctuating quantities can be used directly when solving the time-dependent Schrödinger equation. This advantage certainly makes Ehrenfest dynamics and all its variants attractive despite its limitations.

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