Non-Markovian Quantum State Diffusion for Temperature-Dependent Linear Spectra of Light Harvesting Aggregates

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Non-Markovian Quantum State Diffusion (NMQSD) has turned out to be an effective method to calculate excitonic properties of aggregates composed of organic chromophores, taking into account the strong coupling of electronic transitions to vibrational modes of the chromophores. In this paper we show how to calculate linear optical spectra at finite temperatures in an efficient way. To this end we map a finite temperature environment to the zero temperature case using the so-called thermofield method. The zero temperature case equations can then be solved efficiently by standard integrators. As an example we calculate absorption and circular dichroism spectra of a linear aggregate. The formalism developed can be applied to calculate arbitrary correlation functions.

I. INTRODUCTION

Linear optical spectroscopy is an important tool to obtain information about multichromophoric complexes like J-aggregates [1–6] or photosynthetic light harvesting complexes [7–10]. In particular the combination of linearly polarized spectra and circular dichroism spectra (difference of absorption of left and right circularly polarized light) allows one to draw many conclusions about the (often unknown) arrangement of the chromophores [8, 11] or to extract unknown electronic transition energies [8, 10].

The fact that already linear spectroscopic techniques may reveal many properties of such chromophore complexes is based on the strong transition dipole-dipole interaction between the chromophores which leads to excitonic eigenstates of the aggregate where the excitation is coherently delocalized over several chromophores (monomers). These delocalized eigenstates depend on the arrangement of the chromophores, since the dipole-dipole interaction depends strongly on the distance and orientation of the monomers. If the transition energies of different chromophores are out of resonance the delocalization length is typically reduced. In addition the absorption strength of the eigenstates depends on the relative orientation of the chromophores participating in the coherently delocalized eigenstates. From linear spectra one can thus gain valuable insight into the arrangement of the chromophores and the transition energies of the chromophores.

The interpretation of measured spectra can, however, be complicated because of often strong coupling of an electronic excitation to internal vibrations and other environmental degrees of freedom and one has to be careful not to draw conclusions solely based on an electronic theory [11].

We have studied the influence of vibrations on molecular aggregates using various methods (e.g. direct diagonalization [12], phenomenological Green operator approach or sum rules [3]). Recently we have adopted the so-called Non-Markovian Quantum State Diffusion (NMQSD) approach [13–15], which allows one to treat aggregates where the excitations couples to a structured spectral density (which can e.g. describe, damped vibrational modes of the chromophores).

The NMQSD method is based on an open system approach. In the present work we will take the open system to consist of the electronic states of the chromophores, as we have done in Refs. [16–20]. Note that one can also make different choices for the system, e.g. including some vibrational modes explicitly [18]. In the NMQSD approach a stochastic Schrödinger equation is derived which lives only in the space of the system degrees of freedom. Averaging over the stochastic trajectories allows in principle to obtain exactly the reduced density operator of the system and expectation values of operators in the system space.

While for transfer of excitation the inclusion of stochastic terms in the NMQSD wave function equation is fundamental [16–18], it turned out that for absorption from the ‘total ground state’ (i.e. zero temperature) the stochastic noise terms do not enter explicitly the relevant propagation [16, 18] and only a single trajectory (without noise) needs to be propagated.

In the present work, we will show that the same formulation can be found for finite temperatures through a mapping to temperature zero, which was introduced for the NMQSD approach in Refs. [21, 22]. We will adopt this treatment in our calculations of the optical properties.

The paper is organized as follows: In the following section II the model Hamiltonian used to describe the aggregate is introduced. Then in section III we present our method for the calculation of linear spectra. First the general definitions of absorption and circular dichroism are given, then the thermofield approach providing the mapping to temperature zero is briefly reviewed. In the following subsections III B and III C the calculation of spectra within the NMQSD approach is derived. In subsection III D we summarize our main results.
In section IV we apply the method to calculate absorption and CD spectra of helical aggregates.
Throughout the paper we set $\hbar = 1$ and $k_B = 1$.

II. THE AGGREGATE HAMILTONIAN

We consider an aggregate consisting of $N$ monomers, labeled by $n = 1, \ldots, N$.

A. The monomer

For each monomer $n$ we take into account its electronic ground state $|\phi_n^g\rangle$ and one excited electronic state $|\phi_n^e\rangle$. The transition energy between these two states is denoted by $\epsilon_n$. Each monomer has a collection of vibrational modes comprising internal ones as well as modes of the local environment of the chromophore. We will refer to these degrees of freedom as “the bath”. We choose the vibrational modes to be harmonic and consider a linear coupling of the electronic excitation of monomer $n$ to these bath degrees of freedom (making contact to previous work [23, 30]). The Hamiltonian of monomer $n$ is then given by

$$H_n = H_n^g|\phi_n^g\rangle\langle\phi_n^g| + H_n^e|\phi_n^e\rangle\langle\phi_n^e|,$$

(1)

with the Hamiltonian of the vibrations in the electronic ground state

$$H_n^g = \sum_{\lambda} \omega_{n\lambda} a_{n\lambda}^\dagger a_{n\lambda}$$

(2)

The electronic ground state of the aggregate is then taken as the product $|\phi_n^g\rangle = \prod_{m=1}^{N} |\phi_m^g\rangle$.

of the electronic ground states $|\phi_n^g\rangle$ of all individual monomers. A state of the aggregate in which only monomer $n$ is electronically excited and all other monomers are in their electronic ground state we denote by

$$|\pi_n\rangle = |\phi_n^e\rangle \prod_{m \neq n} |\phi_m^g\rangle.$$  

(5)

We expand the aggregate Hamiltonian w.r.t. the states Eqs. (4) and (5) and neglect states with more than one electronic excitation on the aggregate. Thus we obtain the Hamiltonian

$$H = H^g|g_{ei}\rangle\langle g_{ei}| + H^e$$

(6)

for the aggregate, with the electronic ground state Hamiltonian

$$H^g = \sum_{n=1}^{N} H_n^g = \sum_{n=1}^{N} \sum_{\lambda} \omega_{n\lambda} a_{n\lambda}^\dagger a_{n\lambda} \equiv H_{env}$$

(7)

and the electronically excited state Hamiltonian

$$H^e = \sum_{n=1}^{N} \left( H_n^e + \sum_{\lambda \neq n} H_{\lambda}^e \right) |\pi_n\rangle\langle\pi_n| + \sum_{n,m=1}^{N} V_{nm} |\pi_n\rangle\langle\pi_m|.$$  

(8)

The matrix element $V_{nm}$, causing electronic excitation to be transferred from monomer $n$ to monomer $m$ via transition dipole-dipole interaction, is taken to be independent of nuclear coordinates (note that $H_n^g$ and $H_n^e$ depend on nuclear coordinates through Eqs. (2) and (3)). With the Hamiltonians of the monomers Eqs. (2) and (3) we can write Eq. (5) as

$$H^e = H_{sys} + H_{int} + H_{env},$$

(9)

with the purely electronic “system” part

$$H_{sys} = \sum_{n=1}^{N} \epsilon_n |\pi_n\rangle\langle\pi_n| + \sum_{n,m=1}^{N} V_{nm} |\pi_n\rangle\langle\pi_m|,$$

(10)

and a part $H_{env}$ describing the “bath” of vibrational modes given by Eq. (7).

The coupling of electronic excitation to these vibrations is expressed through

$$H_{int} = \sum_{n=1}^{N} L_n \sum_{\lambda} \kappa_{n\lambda} (a_{n\lambda}^\dagger + a_{n\lambda})$$

(11)

with the system operator $L_n = -|\pi_n\rangle\langle\pi_n|$. Note that also the inclusion of off-diagonal coupling terms

$$H_{off} = \sum_{n,m=1}^{N} \sum_{\lambda} \kappa_{nm\lambda} (a_{n\lambda}^\dagger a_{m\lambda} + a_{n\lambda} a_{m\lambda})$$

(12)

with $L_{nm} = -\frac{1}{2} (|\pi_n\rangle\langle\pi_m| + |\pi_m\rangle\langle\pi_n|)$ is possible. The generalization of the following equations to this case is
straightforward. However, for readability we restrict ourselves to the diagonal coupling terms Eq. (11) and also assume that the baths are uncorrelated.

It is convenient to define the so-called spectral density \( J_n(\omega) = \pi \sum_\lambda |\kappa_{n\lambda}|^2 \delta(\omega - \omega_{n\lambda}) \). (13) Later, \( J(\omega) \) will be considered as a continuous function of frequency.

C. Transition dipole operator

The transition dipole operator \( \hat{\mu}_n \) of monomer \( n \) is assumed to be independent of nuclear (environmental) coordinates and is written as

\[
\hat{\mu}_n = \mu_n (|\phi_n^e\rangle \langle \phi_n^e| + |\phi_n^g\rangle \langle \phi_n^g|).
\] (14)

Here, \( \mu_n \) denotes the transition dipole moment of monomer \( n \) (see e.g. Ref. \[31\]). The dipole operator of the aggregate is given by the sum

\[
\hat{\mu} = \sum_n \hat{\mu}_n.
\] (15)

III. CALCULATION OF LINEAR OPTICAL SPECTRA

The transition strength for the linear optical spectra that we will consider in the following can be obtained from a half-sided Fourier transformation \[18\]

\[
F(\omega) = \text{Re} \int_0^{\infty} dt e^{i\omega t} c(t).
\] (16)

The explicit form of the correlation function \( c(t) \) will be specified below for the case of absorption and circular dichroism. The total initial state of system and bath prior to light absorption is taken as

\[
\rho_0 = |\psi_0\rangle \langle \psi_0| \otimes \rho(\beta),
\] (17)

where the aggregate is in its electronic ground state Eq. (2) and the bath is in a thermal state at temperature \( T \), i.e.

\[
\rho(\beta) = \frac{e^{-\beta H_{\text{env}}}}{\text{tr}_{\text{env}} \{ e^{-\beta H_{\text{env}}} \}}.
\] (18)

with the inverse temperature \( \beta = 1/T \). In Eq. (18), \( \text{tr}_{\text{env}} \) denotes the trace over the bath degrees of freedom.

In order to calculate the correlation function \( c(t) \) in Eq. (18), we introduce a correlation operator \( C(t) \) in the electronic system defined by

\[
C(t) \equiv \text{tr}_{\text{env}} \{ (U^g)\dagger(t) U^c(t) \rho(\beta) \}.
\] (19)

with the propagators for system and bath,

\[
U^g(t) \equiv e^{-iH^g t},
U^c(t) \equiv e^{-iH^c t},
\] (20)

in the respective electronic states. In linear response theory, one can then calculate \( c(t) \) in Eq. (18) for the absorption spectrum of an isotropically oriented sample as

\[
c^{\text{Abs}}(t) = \text{tr}_{\text{sys}} \{ A^{\text{Abs}} C(t) \}
\] (21)

\[
= \sum_{nm} (A^{\text{Abs}})_{nm} \mathcal{C}_{nm}(t),
\] (22)

where \( A^{\text{Abs}} \) is a matrix in the electronic system with matrix elements

\[
(A^{\text{Abs}})_{nm} = \langle \pi_n | A^{\text{Abs}} | \pi_m \rangle = \mu_n \cdot \mu_m
\] (23)

and the dot denotes the real scalar product. Similarly, for the circular dichroism spectrum within the Rosenfeld formalism \[33\] one has

\[
c^{\text{CD}}(t) = \text{tr}_{\text{sys}} \{ A^{\text{CD}} C(t) \},
\] (24)

where the matrix elements of \( A^{\text{CD}} \) are given by

\[
(A^{\text{CD}})_{nm} = \langle \pi_n | A^{\text{CD}} | \pi_m \rangle = \bar{R}_{nm} \cdot (\hat{\mu}_n \times \hat{\mu}_m).
\] (25)

Here, \( \bar{R}_{nm} = \bar{R}_n - \bar{R}_m \) denotes the distance vector between monomers \( n \) and \( m \). The validity of the Rosenfeld approximation and a more appropriate formula for large aggregates with considerable excitonic delocalization are discussed in \[33\] and in appendix \[A\] where short derivations of \( c^{\text{Abs}}(t) \) and \( c^{\text{CD}}(t) \) can be found.

A. Thermofield method

To evaluate the expression \( C(t) \) defined in Eq. (19) we use the thermofield approach \[30\]. The thermal initial state \( \rho(\beta) \) of the environment is mapped onto the (pure) ground state \( |0(\beta)\rangle \) (later denoted as “thermal vacuum”) of an enlarged environment with suitably constructed creation and annihilation operators, as detailed below. The calculation of \( C(t) \), which will be discussed in the following section \[11\], then proceeds analogously to the temperature zero case \[10\], \[12\]. In this subsection we sketch briefly the procedure for the mapping to the enlarged bath, following the treatment of Refs. \[21\], \[22\].

First, in addition to the physical bath operators \( (a_{n\lambda}, a_{n\lambda}^+) \) one introduces independent ‘fictitious’ negative frequency bath operators \( (b_{n\lambda}, b_{n\lambda}^+) \) resulting in the expression

\[
\hat{H}_{\text{env}} \equiv \hat{H}_{\text{env}} + \hat{H}_b
\] (26)

for the new environmental Hamiltonian, with

\[
\hat{H}_b = \sum_{n=1}^N \sum_{\lambda} (-\omega_{n\lambda}) b_{n\lambda}^+ b_{n\lambda}
\] (27)
and the same numbers \( \omega_{n\lambda} \) as for the physical bath \( H_{\text{env}} \). With the bar, as in Eq. (26), we indicate that the Hamiltonian contains the additional \( b \)-bath. As a consequence, the number of degrees of freedom of the new bath Hamiltonian

\[
H_{\text{env}} = \sum_{n=1}^{N} \sum_{\lambda} \omega_{n\lambda} \left( a_{n\lambda}^\dagger a_{n\lambda} - b_{n\lambda}^\dagger b_{n\lambda} \right)
\]

(28)
is twice that of the original one. The desired state \( |0(\beta)\rangle \) in the doubled-bath Hilbert space is now constructed such that one recovers the correct thermal equilibrium state \( \rho(\beta) \) defined in Eq. (15) for the physical \( a \) bath after tracing out the fictitious \( b \) degrees of freedom, i.e.

\[
\rho(\beta) = \text{tr}_b |0(\beta)\rangle \langle 0(\beta)|.
\]

(29)

Note that the additional degrees of freedom do not alter the dynamics, because they are uncoupled from the physical ones. Through a (temperature-dependent) Bogoliubov transformation of the bath operators \( (a_{n\lambda}, a_{n\lambda}^\dagger) \) and \( (b_{n\lambda}, b_{n\lambda}^\dagger) \) one defines so-called thermal bath annihilation operators

\[
A_{n\lambda} = \sqrt{n_{n\lambda} + 1} a_{n\lambda} - \sqrt{n_{n\lambda}} b_{n\lambda}^\dagger
\]

\[
B_{n\lambda} = \sqrt{n_{n\lambda} + 1} b_{n\lambda} - \sqrt{n_{n\lambda}} a_{n\lambda}^\dagger
\]

(30)

and their corresponding adjoint creation operators. Here, \( n_{n\lambda} = \left( e^{2\beta \omega_{n\lambda}} - 1 \right)^{-1} \) is the mean thermal occupation number of the physical mode \( \lambda \) of monomer \( n \). All the bosonic, thermal operators \( A_{n\lambda} \) and \( B_{n\lambda} \) annihilate the thermal vacuum \( |0(\beta)\rangle \equiv |0\rangle_A |0\rangle_B \). Here \( |0\rangle_A, |0\rangle_B \) are shorthand notations for the product vectors of all environmental \( (A_{n\lambda}, A_{n\lambda}^\dagger) \) and \( (B_{n\lambda}, B_{n\lambda}^\dagger) \) oscillators being in their vacuum state respectively, i.e. \( |0\rangle_A = \prod_{n\lambda} |0\rangle_{n\lambda} \) (and the analogous expression for \( |0\rangle_B \)). The extended Hamiltonian with the untransformed bath operators expressed in terms of the thermal bath operators now reads

\[
\hat{H}^g = \hat{H}_{\text{env}} = \sum_{n=1}^{N} \sum_{\lambda} \omega_{n\lambda} \left( A_{n\lambda}^\dagger A_{n\lambda} - B_{n\lambda}^\dagger B_{n\lambda} \right)
\]

(31)

for the electronic ground state, whereas for the electronically excited state one obtains

\[
\hat{H}^e = \hat{H}_{\text{sys}} + \hat{H}_{\text{env}} + H_{\text{int}}
\]

(32)

with

\[
H_{\text{int}} = \sum_{n=1}^{N} \sum_{\lambda} \omega_{n\lambda} \times
\left( \sqrt{n_{n\lambda} + 1} (A_{n\lambda}^\dagger + A_{n\lambda}) + \sqrt{n_{n\lambda}} (B_{n\lambda}^\dagger + B_{n\lambda}) \right).
\]

(33)

\[\left|{\xi}\right\rangle = \frac{1}{\sqrt{\beta \omega}} \sum_{\lambda} \left|{\xi}_{n\lambda}\right\rangle, \]

B. Absorption in the NMQSD approach

To evaluate the expression Eq. (19) for the correlation operator \( C(t) \) we apply the thermofield approach outlined in the previous section and insert \( \rho(\beta) \) from Eq. (29) into Eq. (19) to obtain

\[
C(t) = \text{tr}_a \text{tr}_b \{ \langle U^g(t) | U^e(t) | 0(\beta) \rangle \langle 0(\beta) | \}
\]

(34)

Here, \( \text{tr}_a = \text{tr}_{\text{env}} \) denotes the trace over the original environmental degrees of freedom and \( \text{tr}_b \) is, as in Eq. (29), the trace over the negative frequency oscillators. Inserting \( \mathbb{1} = e^{iH_{\text{sys}}t} e^{-iH_{\text{sys}}t} \) where \( H_b \) is the Hamiltonian for the additional bath degrees of freedom defined in Eq. (29), between the two propagators and rearranging the trace yields

\[
C(t) = \text{tr}_a \text{tr}_b \{ \langle \hat{U}^e(t) | 0(\beta) \rangle \langle 0(\beta) | \langle \hat{U}^g(t) \rangle \}
\]

(35)

Analogous to Eq. (20) the propagators are defined as \( \hat{U}^g(t) = e^{-i\hat{H}^g t} \) and \( \hat{U}^e(t) = e^{-i\hat{H}^e t} \) with \( \hat{H}^g \) and \( \hat{H}^e \) given by Eqs. (31) and (32). Note that the trace is over the full doubled-bath Hilbert space. Since \( \langle 0(\beta) | \langle \hat{U}^g(t) \rangle = \langle 0(\beta) | \) performing the trace leads to

\[
C(t) = \langle 0(\beta) | \langle \hat{U}^e(t) | 0(\beta) \rangle.
\]

(36)

The aim in the following is to derive an evolution equation for \( C(t) \) that can be handled numerically in an efficient way. To this end we expand the environmental part of the Hilbert space in terms of Bargmann coherent states \( |{\xi}_{n\lambda}\rangle \)

\[
|{\xi}_{n\lambda}\rangle = \exp \left( \sum_{n\lambda} \left|{\xi}_{n\lambda}\right|^2/2 \right) |{\xi}_{n\lambda}\rangle,
\]

(37)

where we defined the reduced propagator

\[
G(t, \zeta^e, \zeta^g) = \langle \xi^e_\lambda | \rho(\beta) | \xi^g_\lambda \rangle.
\]

(38)

To obtain Eq. (32), we have made use of \( \langle 0(\beta) | \langle \xi^e_\lambda | \langle 0(\beta) \rangle = 1 \). \( G(t, \zeta^e, \zeta^g) \) is analytic in \( \zeta^e \) and \( \zeta^g \) because of the properties of the Bargmann states \( |{\xi}_{n\lambda}\rangle \). Therefore one can Taylor expand it with respect to these parameters resulting in

\[
G(t, \zeta^e, \zeta^g) = G(0)(t) + \sum_{n,\lambda} \left( G^{(1)}_{n\lambda}(t) \zeta^g_{n\lambda} + G^{(2)}_{n\lambda}(t) \zeta^e_{n\lambda} \right) + \ldots.
\]

(40)
Inserting this into Eq. (38) and noting that
\[ \int \frac{d^2s}{\pi} e^{-|s_{n\lambda}|^2} (\xi^*)^j = \delta_{j0} \] (the same also holds for integrals containing \( \zeta^* \)), one sees that only the zeroth-order term \( G^{(0)}(t) \) survives and one obtains
\[ C(t) = G^{(0)}(t). \] (41)

It has been shown in Ref. [21] that there exists an integro-differential equation for \( G(t, \zeta^*, \xi^*) \) (given also in appendix B) which can be used as a starting point to obtain \( G^{(0)}(t) \).

In this work, we will not present the general solution but, in order to simplify the notation, we will use the fact that for the present case where \( L_n = L_n^1 \) the general equation (33) can be written as (see Appendix B1)
\[ \partial_t G(t, z^*) = -iH_{sys} G(t, z^*) + \sum_n L_n z^*_{t,n} G(t, z^*) \]
- \sum_n L_n^1 \int_0^t ds \alpha_n(t-s) \frac{\delta}{\delta z_{t,n}} G(t, z^*) \]
with the initial condition \( G(0, z^*) = \mathbb{1}_{sys} \). Here
\[ \alpha_n(\tau) = \sum_\lambda |\kappa_{n\lambda}|^2 \left( \coth \left( \frac{\omega_{n\lambda}}{2T} \right) \cos(\omega_{n\lambda} \tau) - i \sin(\omega_{n\lambda} \tau) \right) \] (42)
is the bath correlation function of monomer \( n \) and
\[ z^*_{t,n} = -\frac{i}{\hbar} \sum_\mu g_{n\mu} e^{i\omega_{n\mu} t} z^*_{n\mu}, \] (43)
where \( z^*_{n\mu} \) is defined in appendix B1 and combines \( \kappa_{n\mu} \) and \( \zeta_{n\mu} \). The factors \( g_{n\mu} \) and frequencies \( \omega_{n\mu} \) are also defined in appendix B1.

In Refs. [12, 14, 21] the time-dependent complex numbers \( z^*_{t,n} \) play the role of stochastic processes driving the evolution of the system—a viewpoint that is not necessary for this paper. Nonetheless, later on in this work we will also call \( z^*_{t,n} \) a stochastic process.

It is important to note that the \( z^*_{n\mu} \) have the same basic properties as the \( \xi_{n\lambda} \) and \( \zeta_{n\lambda} \), in particular
\[ \int \frac{d^2s_{n\mu}}{\pi} e^{-|s_{n\mu}|^2} (z^*_{n\mu})^j = \delta_{j0}. \] From the above definition of the \( z^*_{t,n} \) it is clear that also \( G(t, z^*) \) is analytic in \( z^* \) and we can Taylor expand it resulting in
\[ G(t, z^*) = G^{(0)}(t) + \sum_{n_1\lambda_1} G^{(1)}_{n_1\lambda_1}(t) z^*_{n_1\lambda_1} \]
+ \sum_{n_1n_2\lambda_1\lambda_2} G^{(2)}_{n_1n_2\lambda_1\lambda_2}(t) z^*_{n_1\lambda_1} z^*_{n_2\lambda_2} + \ldots \] (45)

Note that the \( z^* \)-independent part \( G^{(0)}(t) \) is the same as in Eq. (40) and that Eq. (41) still holds. Analogous to Eqs. (38) and (39) we have
\[ C(t) = \int \frac{d^2z}{\pi} e^{-|z|^2} G(t, z^*) \] (46)
and
\[ G(t, z^*) \equiv \langle z | \mathcal{U}(t) | 0(\beta) \rangle. \] (47)

Using Eq. (42) we will in the following derive an evolution equation for \( C(t) \). Equation (42) is exact. It describes the full evolution of the electronic system in the excited state manifold coupled to the environment. Note, however, that the appearance of the functional derivative in Eq. (42) renders a general solution very difficult, even though for the case of absorption considered here we are only interested in \( G_0(t) \), which is independent of the complex numbers \( z^*_{t,n} \). There are only a few cases where exact solutions to Eq. (42) are known [21, 33, 40]. In general, it might not even be possible to derive an exact closed equation for \( C(t) = G_0(t) \), but we can still make use of the integrals over the environmental degrees of freedom in Eq. (38) in order to find a tractable expression for \( C(t) \) that does not involve the \( z^*_{t,n} \) anymore.

To achieve this, we first note that using Eq. (46) we find from the evolution equation (42) for the reduced propagator \( G(t, z^*) \) (for the considered case of self-adjointed coupling) the evolution equation
\[ \partial_t C(t) = \int \frac{d^2z}{\pi} e^{-|z|^2} \times \left( -iH_{sys} + \sum_n L_n z^*_{t,n} \right. \]
- \sum_n L_n^1 \int_0^t ds \alpha_n(t-s) \frac{\delta}{\delta z_{t,n}} G(t, z^*) \]
for the correlation operator \( C(t) \). Using
\[ \int \frac{d^2z}{\pi} e^{-|z|^2} (z^*_{t,n})^j = \delta_{j0}, \] the integrals in the first two terms can be performed and Eq. (46) can be rewritten to
\[ \partial_t C(t) = -iH_{sys} C(t) - \sum_n L_n^1 \int_0^t \frac{d^2z}{\pi} e^{-|z|^2} \]
\[ \times \int_0^t ds \alpha_n(t-s) \frac{\delta}{\delta z^*_{t,n}} G(t, z^*). \] (49)

The second term in Eq. (49) vanishes, because \( G(t, z^*) \) is analytic in \( z^* \) and thus its product with \( z^*_{t,n} \) is a sum of powers of the form \( (z^*_{t,n})^j \). The difficult third term still prevents us from having a closed equation for \( C(t) \). To tackle this problem we show two approaches, in the following, which lead to coupled systems of (infinitely many) equations from which \( C(t) \) can be approximated numerically.

C. Handling of the functional derivative

In the following we present two different ways how to treat the functional derivative appearing in Eq. (49) for the correlation operator \( C(t) \).
1. Functional expansion of auxiliary operators and Zeroth-Order Functional Expansion (ZOFE) approximation:

We follow [16, 18, 21, 38] and use the ansatz

$$\frac{\delta}{\delta z_{s,n}} G(t, z^*) \equiv O_n(t, s, z^*) G(t, z^*), \quad (50)$$

where we replace the action of the functional derivative on the reduced propagator $G(t, z^*)$ in Eq. (49) by a linear operator $O_n(t, s, z^*)$ in the electronic system that acts on $G(t, z^*)$. Here, the lower index $n$ at the operator $O_n(t, s, z^*)$ indicates that this operator is connected to the coupling operator $L_{1n}^\dagger$ of monomer $n$. Note that in our previous work [16, 20] we used an upper index instead.

For convenience we define the auxiliary operators

$$\tilde{O}_n(t, z^*) \equiv \int_0^t ds \, \alpha_n(t - s) O_n(t, s, z^*). \quad (51)$$

Then Eq. (49) can be written as

$$\partial_t \mathcal{C}(t) = -i H_{\text{sys}} \mathcal{C}(t) - \sum_n L_{1n}^\dagger \int d^2 z \frac{e^{-|z|^2}}{\pi} \times \bar{O}_n(t, z^*) G(t, z^*). \quad (52)$$

The operators $\tilde{O}_n(t, z^*)$ in Eq. (52) describe the coupling of monomer $n$ to its local environment and implicitly contain temperature through the environmental correlation function $\alpha_n(t - s)$ under the memory integral in Eq. (51). The evolution of $O_n(t, s, z^*)$ can be obtained [18, 21] from the consistency condition

$$\frac{d}{dt} \langle O_n(t, s, z^*) \psi(t, z^*) \rangle = \frac{\delta}{\delta z_{s,n}} \partial_t \langle \psi(t, z^*) \rangle. \quad (53)$$

We assume that $\bar{O}_n(t, z^*)$ is analytic in $z_{t,n}^*$ and expand it in a Taylor series w.r.t. the time-dependent complex numbers (stochastic processes) $z_{t,n}^*$:

$$\bar{O}_n(t, z^*) = \bar{O}_n^{(0)}(t) + \sum_{n_1} \int_0^t \bar{O}_n^{(1),n_1}(t, v_1) z_{v_1,n_1}^* dv_1$$

$$+ \sum_{n_1,n_2} \int_0^t \int_0^t \bar{O}_n^{(2),n_1,n_2}(t, v_1, v_2) z_{v_1,n_1}^* z_{v_2,n_2}^* dv_1 dv_2$$

$$+ \ldots, \quad (54)$$

with operator-valued expansion coefficients $\bar{O}_n^{(k),n_1,\ldots,n_k}(t, v_1, \ldots, v_k)$. For these expansion coefficients one can derive coupled differential equations describing their time evolution [41]. When evaluating the integral in Eq. (52) with the expansion Eq. (54) all terms with a $z_{t,n}^*$-dependence yield zero. This is because both $\bar{O}(t, z^*)$ as well as $G(t, z^*)$ are analytic in $z_{t,n}^*$ and therefore in the product $\bar{O}_n(t, z^*) G(t, z^*)$ only the combination of the two zeroth-order terms is left after the integration in Eq. (52). The resulting equation for the correlation operator $\mathcal{C}(t)$ reads

$$\partial_t \mathcal{C}(t) = \left(-i H_{\text{sys}} - \sum_n L_{1n}^\dagger \bar{O}_n^{(0)}(t)\right) \mathcal{C}(t), \quad (55)$$

with, indeed, only the $z^*$-independent zeroth-order O-Operator $\bar{O}_n^{(0)}(t)$. Note that although only $\bar{O}_n^{(0)}(t)$ contributes to the evolution equation for $\mathcal{C}(t)$, still $\bar{O}_n^{(0)}(t)$ has to be determined by solving the coupled hierarchy of equations resulting from Eqs. (53) and (54).

To obtain a numerically efficient method, previously we have applied an approximation [16, 41], which we denote as 'zeroth-order functional expansion' (ZOFE) approximation. For the case of absorption considered here this approximation amounts to neglecting the coupling of the zeroth order to the higher orders in the hierarchy. The operators $\bar{O}_n^{(0)}(t, s)$ are then determined by the auxiliary evolution equation

$$\partial_t \bar{O}_n^{(0)}(t, s) = -i \left[H_{\text{sys}}, \bar{O}_n^{(0)}(t, s)\right]$$

$$+ \sum_m \left[\pi_m \langle \pi_m | \bar{O}_m^{(0)}(t, s) \right], \quad (56)$$

with the initial condition $\bar{O}_n^{(0)}(s, s) = L_n = -\pi_n$. The operators $\bar{O}_n^{(0)}(t, s)$ are then determined by the auxiliary evolution equation

$$\partial_t \bar{O}_n^{(0)}(t, s) = -i \left[H_{\text{sys}}, \bar{O}_n^{(0)}(t, s)\right]$$

$$+ \sum_m \left[\pi_m \langle \pi_m | \bar{O}_m^{(0)}(t, s) \right], \quad (56)$$

with the initial condition $\bar{O}_n^{(0)}(s, s) = L_n = -\pi_n$.

For a practical implementation we expand the bath correlation functions $\alpha_n(t - s)$ given in Eq. (53) as sums of exponentials

$$\alpha_n(t - s) = \sum_j \alpha_{nj}(t - s), \quad (57)$$

where

$$\alpha_{nj}(\tau) = p_{nj} e^{i\omega_{nj} \tau}; \quad \tau \geq 0 \quad (58)$$

with complex frequencies $\omega_{nj} = \Omega_{nj} + i\gamma_{nj}$ and prefactors $p_{nj}$ that may also be complex.

2. Hierarchy of pure states (HOPS):

The method of the previous subsection relied on the ansatz Eq. (50) for the functional derivative $\frac{\delta}{\delta z_{s,n}}$ together with the assumption that $\bar{O}_n(t, z^*)$ be analytic in $z^*$. It is not a priori clear that this ansatz and this assumption are valid. Here we sketch briefly a scheme that does not use the ansatz Eq. (50) to treat the complicated last term in Eq. (48). It leads to an exact solution of the original problem, that can be handled numerically in an efficient way. Details can be found in Ref. [42].

In this scheme, termed hierarchy of pure states (HOPS) [42], one introduces a new operator for the whole memory integral in Eq. (48) and defines

$$\mathcal{G}_{\epsilon(n)}(t, z^*) \equiv \int_{-\infty}^{\infty} ds \alpha_{nj}(t - s) \frac{\delta}{\delta \bar{z}_{s,n}} G(t, z^*). \quad (59)$$
The integral boundaries 0 and $t$ from Eq. (42) are recovered later using the initial condition for $G(t, z^*)$ and requiring causality. The label ($e_{n,j}$) in Eq. (59) is a matrix that has dimension (number of monomers) $\times$ (number of terms in the bath correlation function). It has a 1 at position $(n,j)$ and is zero otherwise. In the following we will map this matrix onto a vector which we denote by $e_{n,j}$. For these operators $G(e_{n,j})(t, z^*)$ one can again derive an evolution equation that leads to a (formally exact) hierarchy of coupled equations of motion. For the bath correlation functions defined in Eqs. (57) and (58) one finds

$$\partial_t G^{(k)}(t, z^*) =$$

$$(-iH_{sys} + i \sum_{n,j} k_{n,j}(0) + \sum_n L_n z_{t,n}^{*} ) G^{(k)}(t, z^*)$$

$$+ \sum_n L_n \sum_j k_n(0) G^{(k-\varepsilon_n)}(t, z^*)$$

$$- \sum_n L_n \sum_j G^{(k+\varepsilon_n)}(t, z^*).$$

The vector $\vec{k}$ in Eq. (60) labels the different orders of the hierarchy (we speak of a term of $k$th order when $\sum_{n,j} k_{n,j} = k$). In Eq. (60) the $k$th order terms are connected to terms that differ by one order (as explained above $\varepsilon_n$ denotes the $n$th unit vector, where $n$ labels the monomers and $j$ the terms of the bath correlation function). This scheme (applied to wave functions instead of the reduced propagators) has been developed in [42]. There also an appropriate closure of the hierarchy is discussed.

Since all the $G^{(k)}(t, z^*)$ are analytic functions in $z_{t,n}^*$, one can use similar arguments as those leading from Eq. (54) to Eq. (55) to obtain an equation for $C(t)$ which is independent of the time-dependent complex numbers (stochastic processes) $z_{t,n}^*$. With the definition

$$C^{(k)}(t) = \int \frac{d^2z}{\pi} e^{-|z|^2} G^{(k)}(t, z^*)$$

one finds

$$\partial_t C^{(k)}(t) =$$

$$(-iH_{sys} + i \sum_{n,j} k_{n,j}(0) ) C^{(k)}(t)$$

$$+ \sum_n L_n \sum_j k_{n,j}(0) C^{(k-\varepsilon_n)}(t)$$

$$- \sum_n L_n \sum_j C^{(k+\varepsilon_n)}(t),$$

and the desired correlation operator $\bar{C}(t)$ is

$$\bar{C}(t) = C^{(0)}(t).$$

D. Summary of equations

We summarize the relevant equations that we will use to calculate the transition strength $F(\omega)$ for linear absorption and circular dichroism spectra. The transition strengths are calculated from

$$F(\omega) = \text{Re} \int_0^\infty dt e^{i\omega t} c(t)$$

with the correlation function

$$c(t) = \text{tr}_{sys} \left( AC(t) \right).$$

The matrix $A$ is different for absorption and circular dichroism and has the matrix elements:

$$A_{nm} = \begin{cases} \bar{\mu}_n \cdot \bar{\mu}_m & \text{absorption} \\
\bar{R}_{nm} \cdot (\bar{\mu}_n \times \bar{\mu}_m) & \text{circular dichroism} \end{cases}$$

In the present work we have discussed two possible approaches to calculate the correlation operator $C(t)$.

1. ZOFE approximation

In ZOFE approximation one has

$$\partial_t C(t) = \left( -iH_{sys} - \sum_n L_n O_n(0) \right) C(t)$$

with $C(0) = \mathbb{1}_{sys}$ (together with the approximate evolution equation (65) for $O_n(0)(t, s)$). In principle one can also include higher order terms (see [43]).

2. Hierarchy of pure states (HOPS)

For bath correlation functions of the form Eq. (57) with Eq. (58) one can find the exact hierarchy of equations

$$\partial_t C^{(k)}(t) =$$

$$(-iH_{sys} + i \vec{k} \cdot \vec{\omega}) C^{(k)}(t)$$

$$+ \sum_n L_n \sum_j k_{n,j}(0) C^{(k-\varepsilon_n)}(t)$$

$$- \sum_n L_n \sum_j C^{(k+\varepsilon_n)}(t),$$

and the desired correlation operator $C(t)$ is

$$C(t) = C^{(0)}(t).$$

with initial conditions $C^{(0)}(0) = \mathbb{1}_{sys}$ and $C^{(k)}(0) = 0$ ($k \neq 0$).

3. Propagation of vectors instead of a matrix

Note that one can also obtain $C(t)$ by independently propagating the initial states $|\pi_n\rangle$. The matrix elements $C_{nm}$ are then given by $\langle \pi_n | \psi^{(m)}(t) \rangle$, where $|\psi^{(m)}(t)\rangle$ denotes a vector obtained by propagating Eq. (67) or (68) for a vector instead of a matrix and with the initial condition $|\psi^{(m)}(0)\rangle = |\pi_m\rangle$. (See also appendix C where we use this scheme explicitly for a molecular dimer.)
IV. EXAMPLE CALCULATIONS

In this section we present calculated absorption and circular dichroism (CD) spectra to illustrate a typical situation for which the present approach can be used. We do not intend to give a detailed investigation of the validity of the ZOFE approximation or the speed of convergence of HOPS with the order of the hierarchy, here. Such studies have been presented in Refs [18, 43] and Ref. [42], respectively. All spectra shown in this work are calculated using the HOPS approach with order \( k = 10 \) [49].

We consider the simplest case of an aggregate, i.e. a dimer composed of two monomers. The interaction \( V_{12} = V_{21} \) between the two monomers in Eq. (8) or (10) we denote by \( V \). We take the transition energies and spectral densities to be equal for both monomers (\( \varepsilon_n = \varepsilon \) and \( \alpha_n(\tau) = \alpha(\tau) \)). In this work our concern is not the detailed investigation of the dependence of the spectra on the orientation of the monomers. Therefore we restrict the geometry of the dimer by taking the transition dipoles of the monomers perpendicular to the distance vector \( \vec{R} \equiv \vec{R}_{12} \) between them. Then the angle \( \theta \) between the monomers is sufficient to describe the geometry, which is sketched in Fig. 1. If \( \theta \) is not equal to 0 or \( \pi \) then the system has chirality and shows a CD signal.

The coupling to the (vibrational) environment we describe by a continuous spectral density. For the example calculations in this work the spectral density is chosen to be of the simple anti-symmetrized Lorentzian form

\[
J(\omega) = p \left( \frac{1}{(\omega - \Omega)^2 + \gamma^2} - \frac{1}{(-\omega - \Omega)^2 + \gamma^2} \right),
\]

(70) for which the corresponding bath correlation function is known analytically [44] as a sum of exponentials of the form Eq. (67). In order to calculate the bath correlation function for different temperatures, we use the method described in Ref. [45], which is based on a Padé approximation [40] of the hyperbolic cotangent appearing in Eq. (43). Note that in Ref. [45] a much larger class of spectral densities was suggested that allow for an analytic determination of the bath correlation function as such a sum of exponentials. Especially, the spectral densities considered there allow to describe superohmic behavior near \( \omega = 0 \). However, in this work, where we only want to present some examples, we consider the simple case Eq. (70). This spectral density Eq. (70) shows a linear increase for small \( \omega \) and falls off with the third power for large \( \omega \). This spectral density can be approximately interpreted as describing the coupling of an electronic transition to a damped molecular vibration with frequency \( \Omega \), where the damping is described by the constant \( \gamma \). Problems of this interpretation are discussed in Ref. [32].

The prefactor \( p \) is connected to the so-called reorganization energy \( E_r = \frac{1}{\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \) by \( p = E_r \gamma (\Omega^2 + \gamma^2)/\Omega \). Fig. 2 shows a plot of the spectral density for two different width parameters \( \gamma \). All quantities are expressed in units of the central frequency \( \Omega \).

In the following we present spectra of dimers as well as the corresponding spectra of the uncoupled monomers. Note that the ZOFE approximation is, in fact, exact for uncoupled monomers [13], but it badly fails in the dimer case for many of the parameters that we chose in this work, especially for the smaller value of \( \gamma \).

A. Temperature-dependent spectra

To demonstrate the influence of temperature we present some exemplary spectra that we obtain for the spectral density Eq. (70) at various temperatures. We take two Padé expansion terms for the hyperbolic cotan-
gent into account for all temperatures. Only for $T = 0.1$ and $\gamma = 0.3$ we take three expansion terms. We show absorption and circular dichroism (CD) spectra for two uncoupled (monomer case) and two coupled (dimer case) monomers at different temperatures for two spectral densities with width parameter $\gamma = 0.1$ (Fig. 3) and $\gamma = 0.3$ (Fig. 4). In the left column of each figure the linear absorption for $V = 0$, i.e. for uncoupled monomers, is shown. In the middle and right columns we plotted linear absorption and CD spectra for a dimer with $V = 0.5$ and $\theta = 70^\circ$. For non-interacting monomers, which do not possess a CD of their own, the CD vanishes, as expected. It is well known (and for the present formalism stated in appendix C) that for the chosen geometry the absorption and CD spectrum can be understood by considering the correlation functions of the symmetric and antisymmetric parts of the dimer wave function. In the absorption spectrum the angle $\theta$ enters as a weighting of the two contributions, in the CD spectra $\theta$ only scales the absolute values. Note that if the interaction between the monomers is of point-dipole-dipole type, then $\theta$ also enters in the interaction strength via $V \sim (1 - 3 \cos^2 \theta)/R^3$. We have chosen the sign of $V$ to be consistent with this type of interaction. The magnitude $\mu$ of the transition dipoles and the length $R$ of the distance vector between the two monomers, which only define a scale for the resulting spectra (see appendix C), we both set to one.

In the plots we show the symmetric and anti-symmetric contributions to the spectra (weighted by their $\theta$-dependent prefactor), which we obtain from Eq. (C9) for absorption and Eq. (C10) for CD, as colored lines (red and blue, respectively) and the resulting absorption and CD spectra as black curves. The absorption spectra are normalized to have an area of $2\pi$. Note that the integral over the CD spectra vanishes, as it should.

First we take a brief look at the situation for $V = 0$, i.e. uncoupled monomers, depicted in the left columns of Figs. 3 and 4. In Fig. 3 we see for the monomer case a ‘vibrational progression’ corresponding to the (broadened) mode $\Omega$ of the spectral density. With increasing temperature (from top to bottom) the spectrum becomes broader. Additionally, absorption at lower energies than the one of the dominating 0-0 transition of the mode $\Omega$ increases (hot bands).

Let us now consider the dimer case. We choose a positive dipole-dipole coupling $V = 0.5$ and an angle $\theta = 70^\circ$ between the monomer transition dipoles. Absorption and CD spectra for this case are shown in the middle (absorption) and right (CD) columns of Figs. 3 and 4. One sees that the dimer spectra contain a lot more structure compared with the monomer spectra. This complicates the interpretation of measured spectra, since one might for example interpret the second peak from the left as belonging to a vibrational progression with the lowest peak. Methods to extract the usually unknown geometry of the dimer with many vibrational modes from absorption and CD are discussed in Refs. 3, 11. As in the monomer case increasing the temperature leads to a broadening of the spectra.

For the larger value of the width parameter $\gamma$ we see in Fig. 4 that the features in the spectra are broadened and smeared out already for the lower temperatures so that less structure of the spectra is visible, as one expects.

V. CONCLUSIONS

In this work we have shown how to calculate linear optical spectra (in particular absorption and circular dichroism) of molecular aggregates using the NMQSD formalism. One key aspect was to demonstrate that, while the NMQSD formalism in general requires to calculate many stochastic trajectories, for the calculation of linear optical properties one deterministic propagation is sufficient. To this end we have mapped the finite temperature case to effective temperature zero equations for which the stochastics drop out. We have presented two methods (ZOFE and HOPS) to solve these equations. While HOPS allows for a numerically exact treatment, ZOFE is computationally much less demanding and yields in many situations of interest very good agreement with the exact result.

We have shown exemplarily for the case of a dimer how
these equations can be used.

The method presented here can easily be applied to other problems (beside the calculation of optical spectra). Basically our derivations shows how to calculate two-time correlation functions in an efficient way.

Appendix A: Correlation function

In this section, the expressions Eqs. (21) and (24) for the correlation function entering Eq. (16) for the absorption strength are derived. For linear absorption the orientation averaged dipole-autocorrelation function that needs to be evaluated \[47\] reads

\[ c^{\text{Abs}}(t) = \text{tr}_{\text{env}}\{ \langle g_{el}|\hat{\mu}(t) \cdot \hat{\mu}(0)|g_{el}\rangle \rho_{\text{env}} \}. \] (A4)

After expanding \( \hat{\mu} \) and \( U(t) \) in terms of the basis states \( |g_{el}\rangle \) and \( |\pi_n\rangle \) using Eqs. (A3) and (20), equation (A4) simplifies to

\[ c^{\text{Abs}}(t) = \sum_{n,m} \bar{\mu}_n \cdot \bar{\mu}_m \text{tr}_{\text{env}}\{ U^n(t)U^m_{\pi}(t) \rho_{\text{env}} \}. \] (A5)

In our description the ground state Hamiltonian \( H^g \) is just a constant denoting the absolute energy of \( |g_{el}\rangle \), which we choose to be \( E_0 \) = 0, leaving

\[ c^{\text{Abs}}(t) = \sum_{nm} \bar{\mu}_n \cdot \bar{\mu}_m C_{nm}(t) \] (A6)

with

\[ C_{nm} = \langle \pi_n | \bar{U}^c(t) | \pi_m \rangle \] (A7)

\[ \bar{U}^c(t) = \text{tr}\{ U^c(t) \rho_{\text{env}} \} \] (A8)

If the propagation of the ground state is more than just a constant phase factor, equation (A5) is the final expression.

For calculating circular dichroism one needs to include the polarization and relative phases of the electric field

\[ \frac{\bar{E}(t, \vec{R})}{\langle \bar{E}(t, \vec{R}) \rangle} = \bar{\varepsilon} e^{-i\vec{k} \cdot \vec{R}} e^{i\omega t} \] (A9)

with \( \bar{\varepsilon} \) the complex valued polarization vector (\(|\bar{\varepsilon}| = 1\)) and \( \vec{k} \) the wave vector.

Following the above derivation the final expression now reads

\[ c^{\text{CD}}(t) = \sum_{nm} (\bar{\mu}_n \cdot \bar{\varepsilon} \cdot e^{-i\vec{k} \cdot \vec{R}_m}) (\bar{\mu}_m \cdot \bar{\varepsilon} e^{-i\vec{k} \cdot \vec{R}_n}) C_{nm}(t). \] (A10)

The CD signal is obtained by taking the difference of left and right polarized light.

In the often used Rosenfeld formalism \[33\], which essentially corresponds to the approximation \( e^{i\vec{k} \cdot \vec{R}} \approx 1 + i\vec{\varepsilon} \cdot \vec{R} \) the expression for circular dichroism is

\[ c^{\text{CD}}(t) = \sum_{nm} \vec{R}_{nm} \cdot (\bar{\mu}_n \times \bar{\mu}_m) C_{nm}(t), \] (A11)

with \( \vec{R}_{nm} = \vec{R}_m - \vec{R}_n \) and \( C_{nm}(t) \) as defined above. Here again an orientational averaging was done to get the final expression (A11).

Note that applying the long wavelength approximation and performing an orientational averaging of (A10) yields again (A6).
Appendix B: General equations of motion

In this appendix we will first present an evolution equation for the general propagator $G(t, \zeta^*, \xi^*)$ defined in Eq. (39). Then we treat the special case of Hermitian system-bath coupling operators and derive Eq. (42).

We start by differentiating Eq. (39) with respect to time and obtain the evolution equation

$$\partial_t G(t, \zeta^*, \xi^*) = \{\xi|\lambda^t|\xi\}D (-i\hat{H}^*\hat{U}(t))|0(\beta)\} \quad (B1)$$

with $\hat{H}^*$ given in Eq. (32). (Note: Unlike the full excited state propagator $\hat{U}(t)$ the reduced propagator $G(t, \zeta, \xi)$ obtained by projecting on the environmental degrees of freedom is no longer unitary.)

After a transformation to the interaction picture and using the properties of the Bargmann representation one obtains the equation of motion

$$\partial_t G(t, \zeta^*, \xi^*) = -i H_{syst} G(t, \zeta^*, \xi^*)$$

$$-i \sum_n L_n \sum_\lambda (g_{n,\lambda}^+ e^{i\omega_{n,\lambda} t} - s_{n,\lambda} G(t, \zeta^*, \xi^*)$$

$$-i \sum_n L_n \sum_\lambda (g_{n,\lambda}^- e^{-i\omega_{n,\lambda} t} \partial_{\xi_{n,\lambda}} G(t, \zeta^*, \xi^*)$$

$$-i \sum_n L_n \sum_\lambda (g_{n,\lambda}^+ e^{-i\omega_{n,\lambda} t} \partial_{\zeta_{n,\lambda}} G(t, \zeta^*, \xi^*)$$

$$(B2)$$

where we have defined

$$g_{n,\lambda}^+ = \sqrt{n_{n,\lambda} + 1} \kappa_{n,\lambda} \quad \omega_{n,\lambda} = \omega_{n,\lambda}$$

$$(B3)$$

$$g_{n,\lambda}^- = \sqrt{n_{n,\lambda}} \kappa_{n,\lambda} \quad \omega_{n,\lambda} = -\omega_{n,\lambda}$$

$$(B4)$$

As shown in Ref. 21 22 one can pave the way to an efficient stochastic treatment by rewriting this equation according to

$$\partial_t G(t, \zeta^*, \xi^*) = -i H_{syst} G(t, \zeta^*, \xi^*)$$

$$+ \sum_n L_n \xi_{n,1}^* G(t, \zeta^*, \xi^*) + \sum_n L_n \xi_{n,2}^* G(t, \zeta^*, \xi^*)$$

$$- \sum_n L_n \int_0^t ds \alpha_{n,1}(t-s) \frac{\delta}{\delta \xi_{n,s}} G(t, \zeta^*, \xi^*)$$

$$- \sum_n L_n \int_0^t ds \alpha_{n,2}(t-s) \frac{\delta}{\delta \xi_{n,s}} G(t, \zeta^*, \xi^*)$$

$$(B5)$$

with initial condition $G(0, \zeta^*, \xi^*) = 1$. In Eq. (B5) $\xi_{t,n}$ and $\zeta_{t,n}$ are time-dependent complex numbers given by

$$\zeta_{t,n} = -i \sum_\lambda \sqrt{n_{n,\lambda} + 1} \kappa_{n,\lambda} \zeta_{n,\lambda} e^{i\omega_{n,\lambda} t}$$

$$\xi_{t,n} = -i \sum_\lambda \sqrt{n_{n,\lambda}} \kappa_{n,\lambda} \xi_{n,\lambda} e^{-i\omega_{n,\lambda} t}$$

$$(B6)$$

and $\alpha_{1,n}$, $\alpha_{2,n}$ are defined as

$$\alpha_{1,n}(t-s) = \sum_\lambda (\bar{n}_{n,\lambda} + 1)|\kappa_{n,\lambda}|^2 e^{-i\omega_{n,\lambda} (t-s)}$$

$$\alpha_{2,n}(t-s) = \sum_\lambda (\bar{n}_{n,\lambda})|\kappa_{n,\lambda}|^2 e^{i\omega_{n,\lambda} (t-s)}$$

$$(B7)$$

1. Hermitian coupling

For Hermitian coupling operators $L_n = L^*_n$ the above equations simplify considerably, since one can now combine the $\xi$ and $\zeta$ terms in the summation. Introducing the convention that $\lambda$ summation runs over the positive integers (i.e. 1, 2, 3, ...) and introducing new quantities labeled by $\mu = ..., -3, -2, -1, +1, +2, +3, ...$ which are defined as

$$z_{n,\mu} = \begin{cases} (\zeta_{n,\mu} ; g_{n,\mu} = \begin{cases} g_{n,\mu}^+ ; & \omega_{n,\mu} = \begin{cases} \omega_{n,\mu}^+ \end{cases} & \end{cases} \end{cases}$$

$$(B8)$$

where the upper row holds for $\mu > 0$ and the lower row for $\mu < 0$.

Equation (B2) can then be written as

$$\partial_t G(t, z^*) = -i H_{syst} G(t, z^*)$$

$$- i \sum_n L_n \sum_\mu g_{n,\mu} e^{i\omega_{n,\mu} t} z_{n,\mu}^* G(t, z^*)$$

$$(B9)$$

To obtain Eq. (42) we follow the procedure of Ref. 21 and introduce

$$z_{t,n} = -i \sum_\mu g_{n,\mu} e^{i\omega_{n,\mu} t} z_{n,\mu}^*$$

$$(B10)$$

Note that $z_{t,n} = z_{n,\mu}^*(t) = \xi_{t,n}^* + \zeta_{t,n}$. Using that $\partial / \partial z_{n,\mu}^* = \int ds (\partial z_{n,s}^* / \partial z_{n,\mu}) (\partial / \partial z_{s,n}^*)$ one obtains Eq. (42) with the definition

$$\alpha_n(\tau) = \sum_\mu |g_{n,\mu}|^2 e^{-i\omega_{n,\mu} \tau}.$$  

$$(B11)$$

Noting that $\alpha_n(\tau) = \alpha_{1,n}(\tau) + \alpha_{2,n}(\tau)$ and using $\coth(\omega_{n,\lambda}/2T) = 2\bar{n}_{n,\lambda} + 1$ one finds Eq. (16).

Appendix C: The dimer

We consider a dimer where the transition dipoles of the monomers are perpendicular to the distance vector $R_{12}$ between them and are rotated by an angle $\theta$ with respect to each other (see Fig. 3). Then the expressions for
We obtain
\begin{equation}
(A^{ab})_{11} = (A^{ab})_{22} = \mu^2 \quad (C1)
\end{equation}
\begin{equation}
(A^{ab})_{12} = (A^{ab})_{21} = \mu^2 \cos \theta \quad (C2)
\end{equation}
and
\begin{equation}
(A^{cd})_{11} = (A^{cd})_{22} = 0 \quad (C3)
\end{equation}
\begin{equation}
(A^{cd})_{12} = (A^{cd})_{21} = -|R| \mu^2 \sin \theta. \quad (C4)
\end{equation}
This leads to
\begin{equation}
c^{ab}(t) = \mu^2 \left[ (C_{11}(t) + C_{22}(t)) + \cos \theta (C_{12}(t) + C_{21}(t)) \right] \quad (C5)
\end{equation}
\begin{equation}
c^{cd}(t) = -R \mu^2 \sin \theta [C_{12}(t) + C_{21}(t)] \quad (C6)
\end{equation}
with \( R = |R| \).

Keeping in mind (see subsection III D 3) that the propagation of \( C_{nm}(t) \) is equivalent to propagating the initial state \( |\pi_m \rangle \) until time \( t \) and then projecting on the state \( |\pi_n \rangle \) one can express the above Eqs. (C5) and (C6) in a way which is sometimes more convenient. For the propagation of the wave function one uses the same equations as for \( C_{nm}(t) \) but with the matrix \( C_{nm}(t) \) replaced by a vector \( |\psi^{(m)}(t)\rangle \), where the upper index indicates that the initial condition is \( |\psi^{(m)}(0)\rangle = |\pi_m \rangle \). With this one can write:
\begin{equation}
c^{ab}(t) = \mu^2 \left[ \cos^2(\theta/2) (|\pi_1 \rangle + |\pi_2 \rangle) \langle \psi^+(t) | + |\psi^-(t) \rangle \right] + \sin^2(\theta/2) (|\pi_1 \rangle - |\pi_2 \rangle) \langle \psi^+(t) | - |\psi^-(t) \rangle \right] \quad (C7)
\end{equation}
\begin{equation}
c^{cd}(t) = -R \mu^2 \sin \theta \left[ (|\pi_1 \rangle |\psi^+(t) \rangle + |\pi_2 \rangle |\psi^-(t) \rangle \right] \quad (C8)
\end{equation}
Note that \((|\psi^+(t) \rangle \pm |\psi^-(t) \rangle) / \sqrt{2} = |\psi^\pm(t) \rangle \) is a state which can be obtained by propagating the initial state \( |\phi^\pm \rangle \equiv (|\pi_1 \rangle \pm |\pi_2 \rangle) / \sqrt{2} \).

The above formulas can then be rewritten to
\begin{equation}
c^{ab}(t) = 2 \mu^2 \left[ \cos^2(\theta/2) \langle \phi_+ | \psi^+(t) \rangle + \sin^2(\theta/2) \langle \phi_- | \psi^-(t) \rangle \right] \quad (C9)
\end{equation}
\begin{equation}
c^{cd}(t) = -4R \mu^2 \sin \theta \left[ \langle \phi_+ | \psi^+(t) \rangle - \langle \phi_- | \psi^-(t) \rangle \right]. \quad (C10)
\end{equation}
Thus the absorption spectrum can be calculated from a weighted sum of the ‘symmetric’ and ‘antisymmetric’ contributions. The circular dichroism spectrum is just the difference of these two contributions with equal weight.

[1] G. Scheibe; Kolloid-Zeitschrift 82 1 (1938).
[2] L. D. Bakalis and J. Knoester; J. Lumin. 87-89 66 (2000).
[3] A. Eisfeld; Chem. Phys. Lett. 445 321 (2007).
[4] F. C. Spanso; J. Am. Chem. Soc. 131 4267 (2009).
[5] C. Spitz, S. Dähne, A. Ouart and H.-W. Abraham; J. Phys. Chem. B 104 8664 (2000).
[6] R. F. Fink, J. Seibt, V. Engel, M. Renz, M. Kaupp, S. Lochbrunner, H.-M. Zhao, J. Pfister, F. Würthner and B. Engels; J. Am. Chem. Soc. 130 12858 (2008).
[7] K. Griebenow, A. R. Holzwarth, van Mourik and R. van Grondelle; Biochim. Biophys. Acta Bioenergetics 1058 194 (1991).
[8] H. van Amerongen, L. Valkunas and R. van Grondelle; Photosynthetic Excitons; World Scientific, Singapore (2000).
[9] M. T. W. Milder, B. Brüggemann, R. van Grondelle and J. L. Herek; Photosynth. Res. 104 257 (2010).
[10] J. Adolphs and T. Renger; Biophys. J. 91 2778 (2006).
[11] A. Eisfeld, J. Seibt and V. Engel; Chem. Phys. Lett. 467 186 (2008).
[12] J. Roden, A. Eisfeld, M. Dvořák, O. Bünemann and F. Stienkemeier; J. Chem. Phys. 134 054907 (2011).
[13] W. T. Strunz; Phys. Lett. A 224 25 (1996).
[14] L. Diósi; Quantum Semiconductor. Opt. 8 309 (1996).
[15] L. Diósi and W. T. Strunz; Phys. Lett. A 235 569 (1997).
[16] J. Roden, A. Eisfeld, W. Wolff and W. T. Strunz; Phys. Rev. Lett. 103 058301 (2009).
[17] J. Roden, W. T. Strunz and A. Eisfeld; Int. J. Mod. Phys. B 24 3060 (2010).
[18] J. Roden, W. T. Strunz and A. Eisfeld; J. Chem. Phys. 134 034902 (2011).
[19] G. Ritschel, J. Roden, W. T. Strunz and A. Eisfeld; New J. Phys. 13 113034 (2011).
[20] G. Ritschel, J. Roden, W. T. Strunz, A. Aspuru-Guzik and A. Eisfeld; J. Phys. Chem. Lett. 2 2912 (2011).
[21] L. Diósi, N. Gisin and W. T. Strunz; Phys. Rev. A 58 1699 (1998).
[22] T. Yu; Phys. Rev. A 69 062107 (2004).
[23] A. Witkowski and W. Moffitt; J. Chem. Phys. 33 872 (1960).
[24] R. E. Merrifield; Radiat. Res. 20 154 (1963).
[25] R. L. Fulton and M. Gouterman; J. Chem. Phys. 41 2280 (1964).
[26] A. Witkowski; Coupling of the Molecular Exciton with the Nuclear Vibrations; in Sinanoğlu, editor, Modern Quantum Chemistry III; pages 161–175; Academic Press (1965).
[27] P. O. J. Scherer and S. F. Fischer; Chem. Phys. 86 269 (1984).
[28] A. Eisfeld, L. Braun, W. T. Strunz, J. S. Briggs, J. Beck and V. Engel; J. Chem. Phys. 122 134103 (2005).
[29] J. Seibt, P. Marquetand, V. Engel, Z. Chen, V. Dehm and F. Würthner; Chem. Phys. 328 354 (2006).
[30] P. B. Walczak, A. Eisfeld and J. S. Briggs; J. Chem. Phys. 128 044505 (2008).
[31] V. May and O. Kühl; Charge and Energy Transfer Dynamics in Molecular Systems, 3rd, Revised and Enlarged Edition; WILEY-VCH (2011).
[32] J. Roden, W. T. Strunz, K. B. Whaley and A. Eisfeld; J. Chem. Phys. 137 204110 (2012).
[33] L. Rosenfeld; Z. Phys. 52 161 (1929).
[34] J. G. Kirkwood; J. Chem. Phys. 5 479 (1937).
[35] A. Eisfeld, R. Kniprath and J. S. Briggs; J. Chem. Phys. 126 104904 (2007).
[36] G. W. Semenoff and H. Umezawa; Nucl. Phys. B 220 196 (1983).
[37] V. Bargmann; Commun. Pure Appl. Math. 14 187 (1961).
[38] W. T. Strunz, L. Diósi and N. Gisin; Phys. Rev. Lett. 82 1801 (1999).
[39] W. T. Strunz and T. Yu; Phys. Rev. A 69 052115 (2004).
[40] J. Jing, X. Zhao, J. Q. You and T. Yu; Phys. Rev. A 85 042106 (2012).
[41] T. Yu, L. Diósi, N. Gisin and W. T. Strunz; Phys. Rev. A 60 91 (1999).
[42] D. Süß, A. Eisfeld and W. T. Strunz; arXiv:1402.4647 [quant-ph] (2014).
[43] G. Ritschel, W. T. Strunz and A. Eisfeld; to be published (2014).
[44] C. Meier and D. J. Tannor; J. Chem. Phys. 111 3365 (1999).
[45] G. Ritschel and A. Eisfeld; arXiv:1405.2440 [quant-ph] (2014).
[46] J. Hu, R.-X. Xu and Y. Yan; J. Chem. Phys. 133 101106 (2010).
[47] S. Mukamel; Principles of Nonlinear Optical Spectroscopy; Oxford University Press, Inc. (1995).
[48] If one extends the dipole-auto-correlation function $c(t)$ to negative times such that $c(-t) = c^*(t)$, the transition strength can be calculated as

$$F(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} c(t).$$

[49] The spectra are converged in the sense that by increasing the order of the hierarchy from 9 to 10 the presented plots do not change noticeably on the presented scale. In fact already at smaller order most spectra can be considered to be converged.