Influence of phonons on exciton transfer dynamics: comparison of the Redfield, Förster, and modified Redfield equations

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Abstract

The effect of the reorganization of phonons on exciton transfer dynamics is examined. Starting from a general quantum master equation, we obtain population transfer rates for the Redfield, the Förster, and the modified Redfield equations and compare the predictions of these three models over various ranges of parameters. It is shown that the validity of the traditional Redfield equation is justified by a broad spectrum of phonons rather than a small magnitude of electron–phonon coupling strength as is usually implied. The modified Redfield equation suggested by Zhang et al. [J. Chem. Phys. 108 (1998) 7763] is shown to have a wide range of applicability and to reduce numerically to the traditional Redfield equation and the Förster equation in the respective limiting cases. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Calculation of quantum dynamics in the condensed phase is a major objective of many recent theoretical studies. With the help of advances in computing power, one can extend exact quantum dynamical calculation to systems with a large number of degrees of freedom but still it is extremely difficult to apply an exact quantum calculation to condensed phase dynamics. Many different levels of approximation including classical, semi-classical, and mixed quantum–classical simulation methods as well as the path integral technique have been developed in the field of quantum computing chemistry.

In addition to direct computational approaches, one popular approach to quantum dynamics in the condensed phase is based on a reduced density matrix approach. Traditionally, an equation of motion for the reduced density matrix is obtained by averaging out of the full density matrix irrelevant bath degrees of freedom.
freedom which indirectly appear in observations via coupling to the system variables. Projection operator
技术 for this purpose were developed by Zwanzig [1] (in the Schrödinger picture) and independently
by Mori [2] (in the Heisenberg picture). Clearly, the reduced density matrix is an appropriate language to
describe the complicated dynamics in the condensed phase because our observables are not fully relevant to
a pure quantum state of the system which involves the full quantum dynamics of the system plus bath. In
contrast with the popular mixed quantum–classical computation method, the reduced density matrix ap-
proach can describe the dynamics of the bath quantum mechanically. Miller and coworkers pointed out
that an arbitrary separation of the total system into quantum (for subsystem) and classical (for bath) parts
will not be an appropriate approach in some cases because inherent mixing of the system and bath es-
tentially makes the total system quantum in nature [3].

A famous standard reduced density matrix approach is the Redfield equation [4]. Originally developed for
the study of nuclear magnetic resonance spectroscopy, this equation has been widely used to study con-
densed phase dynamics [5]. With the development of the Redfield equation, a systematic investigation of the
dynamics of the off-diagonal density matrix was achieved. With the help of advances in computing combined
with efficient numerical methods [6–9], it seems plausible to carry out calculations of Redfield equations with
larger dimensionality than has been previously considered. Recently, interesting applications of this equa-
tion to chemical reaction systems [10–19] and to optical experiments [20–23] have been reported.

In particular, as interest in the energy transfer and electron transfer dynamics in biological systems
grows, the utility of the Redfield equation has become apparent. In some biological systems, the electronic
coupling between pigments is comparable to the fluctuation of their excitation energies and in this case
direct application of the alternative Förster energy transfer or Marcus-type theories of electron transfer are
not appropriate. In such systems, an electronic eigenstate representation will be appropriate and the effect
of the fluctuations of the excitation energy of an individual chromophore is described by a Redfield type of
equation. For example, Leegwater et al. [24] applied the Redfield equation (in their “multimer” model) to
calculate the rates of excitation energy transfer within the reaction center of photosystem II. Kühn and
Sundström investigated the dissipative dynamics of excitons in the outer antenna system of photosynthetic
bacteria by employing the Redfield relaxation theory [25] and applied it to explain their pump–probe
spectroscopy [26]. By extending the system variables to include the electronic and a few coherent vibrational
modes, Renger et al. [27] extended the Redfield equation approach to incorporate the coherent vibration
dynamics in a description of a chlorophyll dimer of the light harvesting complex of photosystem II. They
examined the exciton dynamics occurring in various biological systems using a similar framework [28–33].

Although these studies have been successfully applied to particular systems, the basic assumption in-
volved in the Redfield equation is that the system–bath coupling is very small so that a perturbation ex-
ansion over this should be valid. In this case, the decay of and transfer between the elements of the density
matrix of the system variables are described by a set of coupled differential equations with rate constants
expressed in terms of time correlation functions of the perturbation terms. It is certainly desirable to go
beyond the weak system–bath coupling regime. One possible method is a straightforward extension of the
perturbation theory to higher order. Laird et al. [34] examined a higher-order model of population transfer
rates based on a model of two quantum levels coupled off-diagonally and linearly to a bath of harmonic
oscillators. Another approach for non-weakly coupled systems is to reduce strong-coupling systems to
weak-coupling form by a transformation method. When the system–bath coupling is linear in the bath
coordinates, the small-polaron transformation method is one example [35]. In this case, the minimum
position of the bath oscillators is shifted proportionately to the value of the system variable to which it is
coupled. As a result, the system–bath coupling Hamiltonian can be made minimal but the off-diagonal
system Hamiltonian is dressed by the bath coordinates. When the off-diagonal system Hamiltonian is small,
one takes the dressed off-diagonal system Hamiltonian as a perturbation term. This is the approach that
was taken by Soules and Duke [36] to derive the excitation transfer rate. In their paper they showed that
there are corrections to the Förster rate if the donor and acceptor are interacting with the same bath modes.
Rackovsky and Silbey [37] used this approach to derive the Redfield equations for a donor–acceptor pair interacting with a harmonic bath in order to assess the interplay between coherent and incoherent excitation transfer. Another theoretical approach was taken by Kenkre and Knox [38,39], who derived the generalized master equation (GME) for this case. Kenkre [40,41] later went on to discuss the relationship among various theoretical methods.

Recently, Zhang et al. [42] derived expressions of the population relaxation rates of the modified Redfield equation for statically disordered exciton systems and applied them to study the non-linear spectroscopy of molecular aggregates. Even though their derivation is limited to a consideration of the population dynamics only, by taking the off-diagonal Hamiltonian in the exciton representation as a perturbation, they could minimize the perturbation term associated with electron–phonon coupling. By doing this, the diagonal fluctuation of the exciton energy is described non-perturbatively and the off-diagonal Hamiltonian responsible for population transfer is minimized based on the less effective overlap of the exciton wave functions due to static disorder. As a result, the perturbation approach with respect to the off-diagonal Hamiltonian becomes more accurate than the traditional Redfield equation. A drawback of Zhang et al.’s approach is that the fates of the off-diagonal density matrix initially created (the initial condition term in the Nakajima–Zwanzig equation) are not described. In addition, the dynamics of the off-diagonal density matrix does not appear explicitly in the set of equations. This does not mean the dynamics of the off-diagonal density matrix is ignored completely. It may be necessary to remove these limitations in order to complete the description of the exciton dynamics.

However, it will still be interesting to examine the population kinetics predicted by the modified Redfield equation compared to the traditional Redfield equation and/or the Förster kinetics. Following this approach, in this paper, we quantify the limitations of the existing models for energy transfer dynamics utilizing the Redfield equation and the Förster expression. We will show that the numerical predictions of the traditional Redfield equation (strong Coulombic coupling) and the Förster energy transfer rate (weak Coulombic coupling) are reproduced by the modified Redfield equation in the parameter regimes where those approaches should be valid. This result leads us to conclude that the modified Redfield equation can be reasonably applied to the intermediate-coupling case also and has a much wider regime of applicability than the two earlier theories.

This paper is organized as follows. In Section 2, the Hamiltonian of interest is introduced and the general quantum master equation is derived by use of the projection operator technique. Direct applications of the general result to three cases are made in the following subsections. Section 3 compares the predictions of the three models obtained in Section 2.

2. Quantum master equation

The following Frenkel exciton Hamiltonian for molecular aggregate consisting of molecules coupled to each other by Coulombic interaction has been employed to study dynamics of the excited electronic state in various levels of approximations.

\[ H(q) = H^{\text{el}} + A + E^\text{ph} + H^{\text{el-ph}} + H^{\text{Coul}}, \]

\[ H^{\text{el}} = \sum_{n=1}^{N} |e_n\rangle \langle e_n|, \]

\[ A = \sum_{n=1}^{N} |e_n\rangle \lambda_n \langle e_n|, \]
\[E_{\text{ph}}^n = \sum_{n=1}^{N} \epsilon_{\text{ph}}^n,\]  
\[H_{\text{el-ph}}^n = \sum_{n=1}^{N} |\epsilon_n\rangle \langle \epsilon_n|,\]  
\[H_{\text{Coul}}^n = \sum_{n=1}^{N} \sum_{m>n} J_{nm}(\langle |\epsilon_n\rangle |\epsilon_m| + \text{h.c.).}\]  

Here \(|\epsilon_n\rangle\) represents the excited electronic states of the \(n\)th monomer. h.c. is an abbreviation for Hermitian conjugate. Eq. (2) is the electronic Hamiltonian where the Hamiltonian of the ground electronic state is set to be zero by definition. \(\epsilon_{\text{ph}}^n\) is the excited electronic energy of the \(n\)th monomer in the absence of phonon and \(\lambda_n = \frac{1}{2} \sum_i m_i \omega_i^2 d_i^2\) is the reorganization energy of the monomer \(n\) where \(m_i\) and \(\omega_i\) are the mass and frequency of the \(i\)th phonon mode and \(d_i\) is the displacement of the equilibrium configuration of this mode between the ground and excited electronic states of the monomer. \(\epsilon_{\text{ph}}^n = \sum_i (p_i^2/2m_i + \frac{1}{2} m_i \omega_i^2 q_i^2)\) is the phonon Hamiltonian associated with the monomer \(n\) where \(p_i\) is the momentum of the \(i\)th phonon mode. The phonons associated with each monomer are assumed to be independent from those associated with different monomers. \(u_n = \sum_i m_i \omega_i^2 d_i q_i\) is the electron–phonon coupling Hamiltonian. \(J_{nm}\) is the Coulombic interaction Hamiltonian between the \(n\)th and the \(m\)th monomers which is responsible for excitation energy transfer between individual monomers. This is assumed to be homogeneous.

Suppose that the molecular Hamiltonian equation is divided into two parts:
\[H = H^0 + H',\]  
where \(H^0\) and \(H'\) represent a reference and a perturbation Hamiltonian, respectively, and their specific forms will be given depending on the characteristics of the system. We can write the time evolution of molecular density matrix by the Liouville equation
\[\frac{d}{dt} \rho(t) = -iL\rho(t) = -i(L^0 + L')\rho(t),\]  
with \(L^0\rho = [H^0, \rho]\) and \(L'\rho = [H', \rho]\). We set \(\hbar = 1\) throughout the paper. Let \(x\) be an index of the electronic eigenstates of \(H^0\) and \(H'^0\) be the corresponding nuclear Hamiltonian.

Now we introduce the following projection operator: \(PA \equiv \sum_x |x\rangle \langle x|^x_{\text{eq}} \text{Tr}_Q(A_{xx})\) and \(Q = 1 - P\) where \(|x\rangle\) is a reference electronic eigenstate of \(H^0\), \(A_{xx} = \langle x|A|x\rangle\), and \(|x|^x_{\text{eq}} = e^{-\beta \epsilon_x^0}\). Hereafter we drop partition functions in distribution functions for brevity. We can derive a reduced equation of motion for the projected part of a total density matrix. By these projectors, we limit our interest only to the electronic population elements of the density matrix averaged over the phonon degrees of freedom. With the above definition of the projection operator, we can clearly see that \(P^2 = P\) and \(PL^0A = L^0PA = PL'PA = 0\). Applying the well-known projection operator technique, we can derive the exact Nakajima–Zwanzig equation
\[\frac{d}{dt} P\rho(t) = -iPL e^{-iQ^t L'} Q\rho(0) - iPLP\rho(t) - \int_0^t dt' P L Q e^{-iQ(t-t')} LPLP\rho(t_1).\]  
If the phonon is initially in the canonical distribution \(\rho^x_{\text{eq}}\), i.e., \(Q\rho(0) = 0\), Eq. (9) becomes, in the second-order approximation over \(H'\),
\[\frac{d}{dt} P\rho(t) = -\int_0^t dt' PL e^{-iL(t-t')} L'P\rho(t_1).\]
Employing a time scale separation approximation between the projected and the complementary parts, Eq. (10) becomes a Markovian relaxation equation (quantum master equation) for the projected density matrix (population elements of the electronic density matrix):

$$\frac{d}{dt} \rho_{qq}(t) = -\sum_{\beta \neq q} K_{\beta q,qq} \rho_{qq}(t) + \sum_{\beta \neq q} K_{qq,\beta \beta} \rho_{\beta \beta}(t),$$

(11)

where \( \rho \equiv P \rho \) and

$$K_{qq,\beta \beta} \equiv 2\Re \int_0^\infty d\tau \text{Tr}_q(e^{iH_\beta^e \tau} H_\beta^e e^{-iH_\beta^e \tau} H_\beta^e \rho_{\beta \beta}).$$

(12)

Eqs. (11) and (12) comprise of general quantum master equation when the molecular Hamiltonian is arbitrarily split into the reference and perturbation parts. In the following subsections, we apply the general master equation to three types of different cases.

### 2.1. Weak electronic coupling: Förster regime

When the Coulombic coupling strength is small, the Coulombic interaction Hamiltonian is treated as a perturbation Hamiltonian in Eq. (7) and the remaining Hamiltonians comprise the reference Hamiltonian:

$$H^0 = H^{el} + A + E^{ph} + H^{el-ph},$$

(13)

$$H' = H^{Coul}.$$

(14)

In this case, the electronic eigenstate (within the single excitation states) of \( H^0 \), Eq. (13), is given by

$$|n\rangle = |e_n\rangle \prod_{m=1, m\neq n}^N |g_m\rangle \quad \text{for } n = 1, \ldots, N,$$

(15)

which represents a state when only the \( n \)th molecule is in its excited electronic state and the others are in their own ground electronic states. Noting that

$$H_m^0 = s_m^0 + \lambda_m + E^{ph} + u_n,$$

(16)

$$H'_mn = J_mn,$$

(17)

from Eq. (12), we can write down the energy transfer rate between the monomers induced by the Coulombic interaction:

$$K_{mn,mn} = 2|J_{mn}|^2 \Re \int_0^\infty d\tau F_m^{\ast}(\tau) A_n(\tau),$$

(18)

where \( * \) denotes a complex conjugate and

$$F_m(\tau) = e^{-i\lambda_n \tau} \text{Tr}_q \left( e^{-i(\lambda_m + E^{ph} + u_n) \tau} e^{iE^{ph} \tau} e^{-i(\lambda_m + E^{ph} + u_n) \tau} \right),$$

(19)

$$A_n(\tau) = e^{-i\lambda_n \tau} \text{Tr}_q \left( e^{iE^{ph} \tau} e^{-i(\lambda_n + E^{ph} + u_n) \tau} e^{-i(\lambda_m + E^{ph} + u_n) \tau} \right).$$

(20)

The Feynman diagram for the time correlation function in Eq. (18) is presented in Fig. 1(a). Fig. 1(a) describes the evolutions of the phonons starting from the equilibrium distribution in the electronic excited state of the monomer \( m \) and in the ground electronic state of the monomer \( n \). At \( \tau = 0 \), due to the Coulombic interaction between the two monomers, the electronic de-excitation and excitation occur simulta-
neously on the ket sides of the monomer \( m \) and \( n \), respectively. The phonon states right after the impulsive change of electronic states are given by the Franck–Condon factor. After a finite time \( \tau \), the same kind of transitions occur on the bra side of the two monomers.

By looking at the propagators in the time correlation functions, Eqs. (19) and (20), we realize that \( F_m(\tau) \) and \( A_n(\tau) \) are the line shape functions of the fluorescence of the monomer \( m \) (energy donor) and the absorption of the monomer \( n \) (energy acceptor), respectively [43]. Noting that \( \lambda_m + \nu_m^\text{ph} + u_m \) corresponds to the Hamiltonian of a displaced harmonic oscillator in the excited electronic state of the monomer \( m \), we can analyze Eqs. (19) and (20) by use of the cumulant expansion technique and get

\[
F_m(\tau) = \exp \left\{ -i(\nu_m^0 - \lambda_m^0)\tau - g_m^*(\tau) \right\}, \\
A_n(\tau) = \exp \left\{ -i(\nu_n^0 + \lambda_n)\tau - g_n(\tau) \right\},
\]

where the line broadening function is defined by [43]

\[
g_m(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 C_m(t_2)
\]

with the time correlation function of transition energy of the monomer \( m \)

\[
C_m(t) \equiv \text{Tr}_q(e^{i\nu_m^0 t}u_m e^{-i\nu_m^0 t_1}u_m e^{-i\nu_m^0 t_2}).
\]

Using the properties of the Fourier transform, Eq. (18) is rewritten as

\[
K_{m,m} \equiv \frac{|J_{nn}|^2}{2\pi} \int_{-\infty}^{\infty} d\omega \tilde{F}_m(\omega)\tilde{A}_n(\omega),
\]

where the tilde denotes the Fourier transform, \( \tilde{f}(\omega) = \int_{-\infty}^{\infty} d\omega \exp(i\omega t) f(t) \). Eq. (25) is the expression for the Förster energy transfer rate expressed in terms of the experimental observables. The Förster expression is very useful, even if it is applicable only to cases of weak Coulombic coupling, because the energy transfer rate is given in terms of experimental observables rather than in terms of microscopic variables which are usually hard to determine [44].

2.2. Weak electron–phonon coupling: traditional Redfield regime

When the electron–phonon coupling strength \( H_{el-ph}(q) \) is small, \( H_{el-ph}(q) \) is treated as a perturbation Hamiltonian and the remaining Hamiltonians comprise the reference Hamiltonian:

\[
H^0 = H_{el} + \Lambda + E_{ph} + H_{\text{Coul}},
\]

Fig. 1. Feynman diagrams for the kernels of energy transfer given by (a) the Förster model, (b) the traditional Redfield model, and (c) the modified Redfield model. In (b), \( v \) denotes a phonon state which is an eigenstate of \( E_{ph}^v \).
\[ H' = H^{\text{el-ph}}. \]  

The electronic Hamiltonian \( H^{\text{el}} + A + H^{\text{Coul}} \) can be numerically diagonalized to give the complete set of exciton states which is a linear combination of the basis equation (15):

\[ |k\rangle = \sum_{n=1}^{N} \varphi_{kn} |n\rangle \quad \text{for } k = 1, \ldots, N, \]  

where \( \varphi_{kn} \) is a mixing constant describing the contribution of monomer \( n \) to the eigenstate \( k \). The eigenvalue obtained numerically is denoted by \( E_k \). In this exciton basis, the Hamiltonians are written as

\[ H_k^0 = E_k + E_{\text{ph}}^{\text{n}}, \]

\[ H_{k'k}^{\text{el-ph}} = H_{k'k}^{\text{el-ph}}, \]

where the perturbation Hamiltonian is obtained by the basis transformation as

\[ H_{k'k}^{\text{el-ph}} = \sum_{n=1}^{N} a_{kn}(n) u_n, \]

where the overlap function of exciton states \( k \) and \( k' \) at the monomer \( m \) is defined by \( a_{kk'}(n) = \varphi_{kn}^* \varphi_{kn'} \). The electron–phonon coupling Hamiltonian \( H^{\text{el-ph}} \) plays two roles in the time evolution of the exciton system: pure dephasing via the diagonal terms and population transfer of the exciton states via the off-diagonal terms.

Inserting Eqs. (29) and (30) into Eq. (12), we obtain

\[ K_{kk'k'} = 2\text{Re} \int_0^\infty d\tau e^{i\omega_{kk'}\tau} \text{Tr}_{\text{q}} \left( e^{iE_{\text{ph}}\tau} H_{k'k}^{\text{el-ph}} e^{-iE_{\text{ph}}\tau} H_{k'k}^{\text{el-ph}} e^{-\beta_{\text{ph}}} \right), \]  

where \( \omega_{kk'} = E_{k'} - E_k. \) As we can see in Eq. (32), the dynamics of the phonon in the correlation function is governed by the phonon Hamiltonian \( E_{\text{ph}}^{\text{n}} \) and is thus independent of the electronic state in which the phonon evolves (system-independent bath dynamics). In this traditional Redfield picture, both the diagonal and off-diagonal electron–phonon couplings are treated as a perturbation whose dynamics is described by the fluctuation dynamics in the reference (ground electronic state) Hamiltonian. However, in the second-order treatment, the diagonal electron–phonon coupling Hamiltonian does not contribute to the population relaxation rate and only the off-diagonal electron–phonon coupling appears as a perturbation.

When the phonon modes of each monomer are independent, Eq. (32) can be given as a sum of contributions from individual monomers:

\[ K_{kk'k'} = \sum_{n=1}^{N} |a_{kk'}(n)|^2 2\text{Re} \int_0^\infty d\tau e^{i\omega_{kk'}\tau} \text{Tr}_{\text{q}} \left( e^{iE_{\text{ph}}\tau} u_n e^{-iE_{\text{ph}}\tau} u_n e^{-\beta_{\text{ph}}} \right) = \sum_{n=1}^{N} |a_{kk'}(n)|^2 \tilde{C}_n(\omega_{kk'}), \]  

where \( \tilde{C}_n(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} C_n(t) \) is the spectral density of the phonon modes of the monomer \( n \). As is well known, Eq. (33) satisfies the detailed balance condition due to the symmetry of the spectral density [43]: \( C_n(-\omega) = e^{-\beta_{\text{ph}}} C_n(\omega) \), which guarantees the detailed balance relation between a pair of exciton relaxation rates.

The Feynman diagram for the time correlation function in Eq. (33) is shown in Fig. 1(b). Since the electron–phonon coupling term \( u_n \) is assumed to be a linear function of the phonon coordinate, only single quantum transitions of the phonon state are allowed by the perturbation \( u_n \) in a harmonic phonon bath. Thus, in order to get a nonzero exciton relaxation rate from Eq. (33), the energy gap of the two exciton states must be exactly matched with the frequency of a phonon mode and exciton relaxation between two states with an energy gap larger than exists in the phonon spectrum is not allowed by this equation. This may
be an acceptable approximation for uphill energy transfer. However, a downhill energy transfer between two exciton states with a large energy gap can occur through hot phonon states in the acceptor exciton state. Clearly this kind of downhill energy transfer process is not captured by the traditional Redfield equation unless a high-frequency vibrational mode is invoked to compensate the exciton energy gap. Eq. (33) has been derived from the traditional Redfield equation and widely used to study exciton relaxation dynamics in many biological aggregate systems based on the observation the electron–phonon coupling strength in those systems is quite weak.

2.3. Intermediate: modified Redfield regime

Recently, Zhang et al. [42] introduced another version of the Redfield equation for the purpose of a study of non-linear spectroscopy. Instead of taking the whole electron–phonon coupling Hamiltonian (27) as a perturbation, they divide the molecular Hamiltonian as follows:

\[
H_0 = \sum_k |k\rangle (E_k + H_{kk}^{el-ph}) \langle k| + E^{ph}, \tag{34}
\]

\[
H' = \sum_{k,k', k \neq k'} |k\rangle H_{kk'}^{el-ph} \langle k'|. \tag{35}
\]

Now a part of electron–phonon coupling, which is contained in \( H_{kk}^{el-ph} \), is described in a non-perturbative way. The diagonal electron–phonon coupling term is included in the intermediate propagator within the rate kernel expression. As we can see in Eq. (31), the magnitude of the \( H_{kk}^{el-ph} \) (for \( k \neq k' \)) is controlled by two factors; the spatial overlap of the two exciton wavefunctions \( (a_{kk}(n) = \phi^*_{n} q_{n} \phi_{n}) \) and the magnitude of electron–phonon coupling strength \( (u_n) \). Consequently, even if the electron–phonon coupling strength is not so weak, a perturbative approach with respect to the off-diagonal Hamiltonian will be valid when the overlap between exciton wave functions is small. This is true when the static disorder of molecular aggregates is significant or energy spectra of the monomers are well separated. In these cases, the exciton wave functions are localized on a small region of the whole aggregate system and exciton states with similar energies (between which exciton transfer is favorable) are more or less spatially distinct.

With the separation of the Hamiltonian by Eqs. (34) and (35), we have

\[
H_0^k = E_k + E^{ph} + H_{kk}^{el-ph}, \tag{36}
\]

\[
H_{kk'}^{el-ph} = H_{kk'}^{el-ph}. \tag{37}
\]

If we define the reorganization energy of the exciton state \( k \) as

\[
\lambda_k = \sum_{n=1}^{N} a_{kk}^2(n) \lambda_n \tag{38}
\]

and consequently the 0–0 transition energy as \( E_k^0 \equiv E_k - \lambda_k \), Eq. (36) can be rewritten as

\[
H_0^k = E_k^0 + E_k^{ph}, \tag{39}
\]

where the phonon Hamiltonian in the exciton state \( k \) is

\[
E_k^{ph} = \lambda_k + E^{ph} + H_{kk}^{el-ph} = \sum_{n=1}^{N} (a_{kk}^2(n) \lambda_n + \tilde{\varepsilon}_n^{ph} + a_{kk}(n) u_n) \equiv \sum_{n=1}^{N} \tilde{\varepsilon}_n^{ph}(k). \tag{40}
\]
We note that \( \hat{\varepsilon}_n^{ph}(k) \) defined in Eq. (40),

\[
\hat{\varepsilon}_n^{ph}(k) = \sum_i \left( \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 (q_i + a_{kk}(n)d_i)^2 \right),
\]

is the Hamiltonian of the phonons associated with the monomer \( n \) and the potential minimum of the \( i \)th phonon mode is displaced by \( a_{kk}(n)d_i \) from the potential minimum of the ground electronic state. Inserting Eqs. (37) and (39) into Eq. (12), we get

\[
K_{kk',kk'} \equiv 2 \text{Re} \int_0^\infty \text{d} \tau \text{e}^{i(E_n^{ph} - E_{n'}^{ph})\tau} \text{Tr}_q \left( e^{iE_n^{ph}} H_{kk}^{el} \text{e}^{-iE_{n'}^{ph}} H_{kk'}^{el} \text{e}^{-\beta E_{n'}^{ph}} \right).
\]

The Feynman diagram for the time correlation function in Eq. (42) is shown in Fig. 1(c), which describes the evolutions of the phonons starting from the equilibrium distribution in the exciton state \( k' \). At \( \tau = 0 \), the off-diagonal electron–phonon coupling induces a transition from exciton state \( k' \) to \( k \). Since the perturbation term is an operator of the phonon variables, in addition to the change of electronic state, a non-Condon transition of phonon states between two exciton states should also occur. In order to emphasize a non-Condon transition, we added a wiggly line on the both sides of the diagram in Fig. 1(c). In contrast with Eq. (32), the diagonal electron–phonon coupling Hamiltonian affects the time evolution of the correlation function as well as the initial distribution (system-dependent bath dynamics). During the time period \( \tau \), the phonon on the ket side evolves under the potential energy of the exciton state \( k' \), while on the bra side it evolves under the state \( k \). Since in Eq. (42) the phonon is transferred to a different exciton state, the limitation of a single quantum transition of the phonon (depicted in Fig. 1(b)) which exists in the traditional Redfield equation is no longer present in the modified Redfield equation. The removal of this limitation is a reflection of a shifted potential energy surface of the acceptor exciton state from that of the donor exciton state due to reorganization of the phonons. Thus the exciton transfer will occur if a non-Condon transition of the phonon is achievable and the extra energy is temporarily stored in the hot phonon state as a reference state, we can use the cumulant expansion technique to obtain the expression of Eq. (46). Defining a new coordinate \( q_i' = q_i + a_{kk'}(n)d_i \), which represents the fluctuation of the \( i \)th mode of phonon in the exciton state \( k' \), we can write
\[
u_n = \sum_i m_i \omega_i^2 d_i q_i = u_n^{k^\prime} - 2a_{kk'}(n) \lambda_n \tag{47}\]

and
\[
\varepsilon_n^{th}(k) - \varepsilon_n^{th}(k') = (a_{kk}(n) - a_{kk'}(n))^2 \lambda_n + (a_{kk}(n) - a_{kk'}(n))u_n^{k^\prime} \tag{48}\]

where \(u_n^{k^\prime} = \sum_i m_i \omega_i^2 d_i q_i^{k^\prime}\). Inserting these into Eq. (46) and using the cumulant expansion method over the new coordinate in the exciton state \(k^\prime\), we finally obtain the expression of the exciton transfer rate:
\[
K_{kk',k''} = 2Re \int_0^\infty d\tau F_{k'}(\tau) A_k(\tau) N_{kk'}(\tau) \tag{49}\]

where the three functions in it are defined by
\[
F_{k'}(\tau) = \exp\{-i(E_{k'}^0 - \lambda_{k'})\tau - g_{k'k,k-k}^s(\tau)\},
\]
\[
A_k(\tau) = \exp\{-i(E_k^0 + \lambda_k)\tau - g_{kk,k-k}^s(\tau)\},
\]
\[
N_{kk'}(\tau) \equiv \left[ \tilde{g}_{k'k,k-k}^s(\tau) - \{ \tilde{g}_{k'k,k-k}^s(\tau) - \tilde{g}_{k'k,k-k'}^s(\tau) - 2i\lambda_{kk',k'k'} \} \times \{ \tilde{g}_{kk,k-k}^s(\tau) - \tilde{g}_{k'k,k-k'}^s(\tau) - 2i\lambda_{kk',k'k'} \} \right] e^{i\lambda_{kk',k'k'}(\tau) + i\lambda_{kk',k'k'}\tau},
\]

with \(g_{\alpha\beta,\gamma\delta}(t) = \sum_{n=1}^N a_{\alpha\beta}(n) a_{\gamma\delta}(n) g_n(t)\) and \(\lambda_{\alpha\beta,\gamma\delta} = \sum_{n=1}^N a_{\alpha\beta}(n) a_{\gamma\delta}(n) \lambda_n\). The dot and double dot on \(g(t)\) denote the first and second time derivative, respectively. \(F_{k'}\) and \(A_k\) functions correspond to the line shapes of the fluorescence from the \(k'\) state and the absorption to the \(k\) state, respectively, in the absence of exciton transfer process. \(N_{kk'}\) describes the dynamics of mixing between the two exciton states resulting from the dynamics of the phonons. Based on the similarity of the structure, Eq. (49) can be regarded as a generalization of the Förster expression, Eq. (18), to the exciton systems while the Coulombic coupling term is replaced by the function \(N_{kk'}\). Using the properties of the Fourier transform, we can have an analog of Eq. (25) for this case:
\[
K_{kk',k''} = (2\pi)^{-2} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \tilde{F}_{k'}(\omega) \tilde{A}_k(\omega') \tilde{N}_{kk'}(\omega - \omega'). \tag{50}\]

In contrast with the traditional Redfield rate, it is difficult to show that the population relaxation rates given by Eq. (49) satisfy the detailed balance condition analytically. However, we will show below that it does numerically. Eq. (49) has been derived by Zhang et al. [42]. Instead of the canonical distribution function in an exciton state, they introduced a distribution function attained at long time after the canonical distribution function of the ground state evolves under the exciton Hamiltonian, i.e., \(\rho_{eq} = \lim_{\tau \to \infty} e^{-\lambda_{kk'} \tau} e^{-\mu_{kk'} \tau} e^{-\beta g_{\alpha\beta,\gamma\delta}(\tau) + i\lambda_{kk',k'k'} \tau}\). They assumed that this distribution function should be essentially equivalent to the canonical distribution function in a reduced description even though, in principle, a canonical distribution function of a total system cannot be obtained by evolution of the closed total system. The re-derivation of Zhang et al.'s result in this paper starting from the canonical distribution function in an exciton state illustrates the validity of the assumption that mechanical evolution of many degrees of freedom well mimics irreversible dissipative dynamics of a reduced observable as Zhang et al. assumed.

3. Discussion

The influence of the phonons on energy transfer in the three cases considered above appears through the line shape function (spectral density) associated with the electronic transition of a monomer, Eq. (23), which can be rewritten in another form [43],
\[
g(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \{ 1 - \cos(\omega t) \} \coth(\beta \omega) \rho(\omega) + \frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega \{ \sin(\omega t) - \omega t \} \rho(\omega), \tag{52}\]
where the spectral density is defined by $\rho(\omega) = i \int_{-\infty}^{\infty} dt e^{i\omega t} \text{Im} C(t)$. For convenience we assume that the phonon spectral density for all monomers is equivalent. To ensure detailed balance in the population transfer rates, we will not introduce an approximation for high temperature in the expression of the line shape function. An accurate form for the spectral density in the condensed phase will be very complicated. For simplicity, we employ the following Gaussian spectral density for our model calculations:

$$\rho(\omega) = \lambda \tau_{\text{g}} \frac{\sqrt{\pi}}{\tau_{\text{g}}} \exp\left\{-\left(\frac{\omega \tau_{\text{g}}}{2}\right)^2\right\},$$

where $\lambda$ is the reorganization energy associated with the excited electronic state of the monomers which is a measure of electron–phonon coupling strength. In the high-temperature limit, this spectral density gives

$$M(t) \equiv \text{Re} \left[C(t)/C(0)\right] = e^{-t/(\tau_{\text{g}})^2}$$

which represents classical inertial motion of the phonon with a time scale $\tau_{\text{g}}$ [45]. This is why we employ the Gaussian spectral density. Because of the rapid decay of our model spectral density with frequency, high-frequency phonons are not included in our model and the present discussion is limited to showing the effect of the coupling of the exciton population transfer to low-frequency phonons only. For more realistic systems, it will be necessary to include details of phonon modes with higher frequencies. In order to calculate the population transfer rates with the modified Redfield equation, we need the first and the second time derivatives of the line shape function as well as the line shape function itself. They are obtained directly by taking the time derivatives of Eq. (52).

We discuss the simplest exciton system, a dimer consisting of heterogeneous molecules whose excited electronic states are denoted by $|1\rangle$ and $|2\rangle$, respectively. We compare the excitation relaxation rates predicted by the traditional Redfield equation and by the modified Redfield equation. In this case, the exciton wavefunction Eq. (28) can be obtained analytically as

$$|k\rangle = \cos \theta |1\rangle + \sin \theta |2\rangle, \quad |k'\rangle = -\sin \theta |1\rangle + \cos \theta |2\rangle,$$

where $\tan 2\theta = 2|J_{12}|/(\varepsilon_1 - \varepsilon_2)$, $0 \leq \theta < \pi/2$. The energy gap between two exciton states is $E_k - E_{k'} = \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4|J|^2}$. Then, the diagonal and off-diagonal electron–phonon coupling Hamiltonian are given by

$$H_{kk}^{\text{el-ph}}(q) = u_1(q) \cos^2 \theta + u_2(q) \sin^2 \theta, \quad H_{kk'}^{\text{el-ph}}(q) = u_1(q) \sin^2 \theta + u_2(q) \cos^2 \theta,$$

$$H_{kk'}^{\text{el-ph}}(q) = H_{kk'}^{\text{el-ph}}(q) = -(u_1(q) - u_2(q)) \cos \theta \sin \theta.$$

As one can see in Eq. (56), the diagonal electron–phonon coupling Hamiltonians of the two exciton states are different from each other unless $2|J_{12}|/(\varepsilon_1 - \varepsilon_2) \rightarrow \infty$. This means that the harmonic potential surfaces of the two exciton states are, in general, displaced from each other as well as from the ground electronic state and the energy transfer rates between those exciton states is influenced by the details of the displacement.

### 3.1. Comparison of the two Redfield equations

When $2|J_{12}|/(\varepsilon_1 - \varepsilon_2) \rightarrow \infty$ the potential energy surfaces of the two exciton states are identically displaced from that of the ground electronic state. Thus in this case exciton transfer occurs between two exciton states whose potential energy surface is identical. Noting that the traditional Redfield equation (in which all exciton states including the ground electronic state have the same potential energy surface) describes such a case, we expect that the traditional and the modified Redfield equations should predict identical population transfer rates. We compare the downhill exciton transfer rates predicted by the traditional and the modified Redfield equations in Fig. 2 [for $|J_{12}| = 100$ cm$^{-1}$ (a) and $|J_{12}| = 20$ cm$^{-1}$ (b)]. As expected, the two different Redfield equations yield the same population transfer rate when the energy gap between two monomers is zero. Other than the numerical illustration, one can easily see that

\[\text{energy gap between two monomers is zero.}\]
Eq. (49) becomes identical to Eq. (33) in this limiting case. We note that the coincidence of the traditional Redfield equation with the modified Redfield equation in this case is not caused by weak electron–phonon coupling (implied by the traditional Redfield equation) but by the degeneracy in the potential energy surface as a special case which can be achieved even for strong electron–phonon coupling (in which the potential energy surfaces of the excited exciton states are substantially displaced). In this region the static exciton states are completely delocalized over the two monomers and the population kinetics in this basis is completely different from the population kinetics in the monomer basis. Thus it will not be useful to compare the population transfer rates of the Redfield equations and the Förster kinetics in these cases.

As the energy gap between two monomers increases, the potential minima of the two exciton states are displaced from each other and the phonons reorganize to the new potential as the energy transfer occurs. The energy transfer rates as a function of the energy gap between the two monomers is illustrated in Fig. 2. The traditional Redfield equation (requiring the exciton transition energy to be matched with a phonon frequency) predicts the energy transfer rate to be monotonically decaying with the energy gap between two monomers. This is because we employed a Gaussian spectral density for the phonons (i.e., the phonon distribution falls off rapidly with increasing energy). In contrast, in Fig. 2(a), the modified Redfield equation first predicts a rise in the energy transfer rate and then a decrease as the energy gap increases between the two monomers. The existence of an optimized energy transfer rate for the modified Redfield equation as the energy gap is varied shows the role of the reorganization of the phonons on the exciton transfer process. After passing the optimum energy gap, further increase of the energy gap between the monomers makes the role of energy gap dominant over the reorganization and consequently the energy transfer rate decreases. After the maximum, the rates predicted by the modified Redfield equation are less sensitive to change in the energy gap than those predicted by the traditional Redfield equation.

Fig. 2(b) shows the energy transfer rates with the same parameters except with weaker Coulombic coupling between the monomers. Since the exciton energy gap in Fig. 2(b) is smaller than in Fig. 2(a) for a given monomer energy gap, the energy transfer rates predicted by the traditional Redfield equation in Fig. 2(b) are simply shifted up compared to Fig. 2(a). However, the behavior of the energy transfer rates of the modified Redfield equation changes greatly from Fig. 2(a) to Fig. 2(b). For example, the exciton wave...
functions for $\varepsilon_1 - \varepsilon_2 = 100$ cm$^{-1}$ in Fig. 2(a) and for $\varepsilon_1 - \varepsilon_2 = 20$ cm$^{-1}$ in Fig. 2(b) are identical to each other, as we can see in Eq. (55), even though the exciton energy gap is smaller in Fig. 2(b). In spite of the reduced energy gap in Fig. 2(b), the modified Redfield equation predicts slower population transfer rate than in Fig. 2(a). This is in contrast with the traditional Redfield equation which captures only the exciton energy gap without taking into account the reorganization energy associated with the energy transfer process.

The role of the reorganization energy in this model calculation is significant because the spectral range of the phonons is relatively narrow as a result of the long time scale of the Gaussian correlation function ($\tau_g = 100$ fs). If the time scale is shorter then the phonon spectrum becomes wider and we expect the role of the reorganization energy should be reduced. Fig. 3 shows such a case. All the other parameters are the same as in Fig. 2(a) other than the time scale of the Gaussian $M(t)$ which is set to 40 fs. Now except for the case of a large energy gap between two monomers, the two Redfield equations predict almost the same behavior. From these calculations, we can see that it is important to know the correct time scale (spectral density) of the phonons for an interpretation of the exciton relaxation dynamics. The rapid decrease of the rates from the traditional Redfield equation at large exciton energy gap appears because the phonon spectrum does not cover such a large energy gap.

3.2. Förster regime

When the energy gap of the monomers is very large, the exciton states are mostly localized on each monomer site and the exciton relaxation rate reduces to the hopping rate between two monomers. In this case the electronic bases for all the three models are almost identical and thus we can directly compare the energy transfer rates predicted by the three models. As we can see in Figs. 2 and 3, the modified Redfield equation predicts energy transfer rates very close to the Förster rates denoted by the open triangles in the figures. Noting that the parameters we used for these calculations in Fig. 2(a) are $|J_{12}| = 100$ cm$^{-1}$, $\lambda = 100$ cm$^{-1}$ (yielding an electron–phonon coupling strength for the monomers of $\Delta_{\text{hom}} = 205$ cm$^{-1}$ at 300 K), the electron–phonon coupling strength of the fast phonon modes is greater than the Coulombic coupling strength. In this case, we expect that the dephasing rate of the localized exciton states should be faster than the energy transfer rates and the Förster rate, which is a second-order perturbation with respect to the Coulombic coupling, should be reasonable.

![Fig. 3. The same as Fig. 2(a) except that a faster time scale ($\tau_g = 40$ fs) is introduced for the dynamics of the phonon.](image-url)
In the modified Redfield equation, a small perturbation parameter is the overlap function between the two exciton states. Since the overlap function is small because of the large energy gap between two monomers, the modified Redfield equation also should be a reasonable approach and be numerically similar to the Förster equation. However, while the Förster equation includes all orders of the electron–phonon coupling, the modified Redfield equation includes all orders of the partial (diagonal) electron–phonon coupling, so the two approaches must not be exactly equivalent. In other words, the influence of the higher-order terms in the off-diagonal electron–phonon coupling and the Coulombic coupling are neglected in the modified Redfield equation and in the Förster kinetics, respectively, and thus they should never become completely identical. In the special case of a large static energy gap and large electron–phonon coupling strength compared with the Coulombic coupling, however, both of these approximations become reasonable (due to very small overlap function resulting from the large static energy gap in the modified Redfield equation and the smaller Coulombic coupling than the electron–phonon coupling in the Förster equation) and both approaches are applicable. This illustrates the wide applicability of the modified Redfield equation in covering the Förster regime as well as the traditional Redfield regime.

Fig. 2(b) shows this aspect more clearly. Here we set $|J_{12}| = 20 \text{ cm}^{-1}$ while the other parameters are the same as in Fig. 2(a). With this coupling strength we expect that the Förster expression should be more accurate. The modified Redfield equation almost completely follows the Förster expression except when the energy gap of the monomers is small. The difference in this region comes from the different definition of energy donor and acceptor in the two approaches. In contrast, the traditional Redfield equation is a perturbation approach over the whole electron–phonon coupling strength and thus in Fig. 2 this approach should not be a good approximation and give a large difference from the other two approaches (up to several order of magnitude) except when the energy gap between the monomers is small.

There is a small difference between the Förster model and the modified Redfield equation when the energy gap is large. In Figs. 2(a) and 3, the rates of the modified Redfield equation are slightly lower than the Förster rates in the localized regime. At $\epsilon_1 - \epsilon_2 = 1000 \text{ cm}^{-1}$ in both figures, the exciton state is completely localized (99%) and thus there is no difference in the definition of the electronic states. Thus the small difference between the two approaches is not believed to come from any difference in the definition of electronic state. Since the Coulombic coupling strength ($|J_{12}| = 100 \text{ cm}^{-1}$) is not much smaller than electron–phonon coupling strength $\Lambda_{\text{hom}} \approx 200 \text{ cm}^{-1}$, we do not expect for the Förster kinetics to be perfect. In this case the Förster kinetics misses repeated forward and backward transfer due to the strong Coulombic coupling during the dephasing time and as a result should give higher values of the rate than the true value. Noting that the modified Redfield equation incorporates all orders of the Coulombic coupling, we can see that the difference between the rates of the Förster and the modified Redfield equation reflects the repeated forward and backward transfer during the electronic dephasing time.

3.3. Weak electron–phonon coupling

Since the traditional Redfield equation is based on the assumption that the electron–phonon coupling strength is smaller than the Coulombic coupling strength, we examine such a case in Fig. 4. While the other parameters ($|J_{12}| = 100 \text{ cm}^{-1}$) are the same as in Fig. 2(a), the reorganization energy of monomer is reduced to $\lambda = 10 \text{ cm}^{-1}$ (yielding an electron–phonon coupling strength for the monomers of $\Lambda_{\text{hom}} = 65 \text{ cm}^{-1}$ at 300 K), which may correspond to the traditional Redfield regime. Overall, the exciton relaxation rates predicted by both Redfield approaches are significantly reduced from the case shown in Fig. 2(a) because the electron–phonon coupling strength determining the exciton relaxation rate is reduced. The rising behavior in the modified Redfield equation in the small energy gap region is much weaker than in Fig. 2(a), which reflects the reduced role of the phonon response. Furthermore, in the decay phase, both the Redfield
equations predict more rapid decay than in Fig. 2(a). This change of behavior can also be understood in terms of the reduced role of the phonons. On the other hand, the energy gap dependence of the transfer rates of the traditional Redfield equation does not change aside from the overall decrease when the reorganization energy is reduced because the reorganization energy has nothing to do with the energy spectrum of the phonons.

As we can see in Fig. 4, the reduced electron–phonon coupling strength does not justify the validity of the population transfer rate predicted by the traditional Redfield equation when the energy gap between monomers is large. Even in the case of weak electron–phonon coupling, the traditional and the modified Redfield equations predict population transfer rates different by several orders of magnitude. Noting this fact is important because, in many biological systems, significant static disorder seems to be naturally present and in this case the traditional Redfield equation seems to break down regardless of the relative strengths of the electron–phonon coupling and the Coulombic coupling. In spite of this, many previous studies on biological systems have been analyzed based on the traditional Redfield equation. We note that even the coincidence between the traditional and modified Redfield equation when \( \epsilon_1 - \epsilon_2 \approx 0 \) does not come from any validity of the perturbation expansion over the electron–phonon coupling in the traditional Redfield equation but from the degeneracy of the potential shape of the two exciton states. An important point to be addressed is the following. By comparing Figs. 3 and 4, we can see that the validity of the traditional Redfield equation is guaranteed not by weak electron–phonon coupling strength (Fig. 4) but by a very wide spectrum of the phonons (Fig. 3).

In contrast with the results in Fig. 2(a), the modified Redfield equation in Fig. 4 yields quite different results from the Förster rate even when the exciton states are localized (\( \epsilon_1 - \epsilon_2 \gg 1 \)). Since the Coulombic coupling strength (\( |J_{12}| = 100 \text{ cm}^{-1} \)) is greater than the electron–phonon coupling strength (\( A_{\text{hom}} = 65 \text{ cm}^{-1} \)) in this case, it is expected that the Förster rate, being based on a perturbation over the Coulombic coupling, will break down. On the other hand, the small perturbation parameter in the modified Redfield equation is not the bare Coulombic coupling strength but the overlap function which is controlled by the ratio of the Coulombic coupling to the static energy gap. Thus we expect that the modified Redfield equation should be valid, only if the overlap function is small, in all cases including those when the Coulombic coupling and electron–phonon coupling are comparable to each other. Many static disordered systems including many biological systems should correspond to the case. One interesting point is that, even in the case in which the traditional Redfield equation is usually considered to be valid (Fig. 4) based on the weak electron–phonon coupling strength, the Förster rate is
closer to the modified Redfield result than to the traditional Redfield equation when the static energy gap is large.

3.4. Intermediate case

As we discussed above, the modified Redfield equation is valid if the exciton states are quite localized on each monomer. When the two monomers are separated by a large static energy gap (such as in a heterodimer), this is the case. In this situation, the Förster expression and the modified Redfield equation describe the energy transfer dynamics in the same basis and direct comparison of the two approaches as a function of the electron–phonon coupling strength should be interesting. We fix $\varepsilon_1 - \varepsilon_2 = 800$ cm$^{-1}$, and $|J_{12}| = 200$ cm$^{-1}$. With these parameters, the exciton states are almost localized on the monomers.

Fig. 5. Comparison of downhill exciton relaxation rates predicted by the Förster model (open triangles) and the modified Redfield model (solid circles) as a function of the electron–phonon coupling strength (reorganization energy, $\lambda$) while the other parameters are fixed to $\tau_e = 100$ fs, $\varepsilon_1 - \varepsilon_2 = 800$ cm$^{-1}$, and $|J_{12}| = 200$ cm$^{-1}$. With these parameters, the exciton states are almost localized on the monomers.

Finally we show that the modified Redfield equation satisfies the detailed balance condition. This relation is analytically proved only in the traditional Redfield equation. The Förster rate and the modified Redfield equation are calculated numerically. In Fig. 6, we plot the detailed balance relation between the downhill and uphill energy transfer rates $\ln(k(\omega)/k(-\omega)) = \beta\omega$. The data set is taken from Fig. 2(a) and the corresponding reverse transfer rates and we plot $\ln(k(\omega)/k(-\omega))$. One can see that all of the three models satisfy the detailed balance condition. To calculate rates with the modified Redfield equation, a
careful numerical analysis is required and in all the calculations above we checked that the numerical values we obtained satisfied the detailed balance condition.

4. Conclusion

The modified Redfield equation (Eq. (49)) is capable of describing both the limiting cases given by the Förster and the traditional Redfield equations. In particular, in contrast with the traditional Redfield equation, the effect of the reorganization of the delocalized exciton states is incorporated into the modified Redfield equation and it is shown that this significantly affects the exciton relaxation kinetics. As a result, the modified Redfield equation can be applied even for the intermediate case where the Coulombic coupling strength is comparable to electron–phonon coupling strength. In particular, when the spectral regions of two monomers are well separated, the exciton wave function should be more or less localized on each monomer and in this case the modified Redfield equation is valid regardless of the magnitudes of the electron–phonon coupling and the Coulombic coupling strengths. We showed that weak electron–phonon coupling strength is not a sufficient condition for the validity of the traditional Redfield equation but rather a broad spectrum of the phonon modes is required.

In many biological systems in which static disorder in the transition energies of the monomers is believed to exist inherently, overlap between partially delocalized exciton wave functions is expected to be small and thus we expect that a master equation based on the modified Redfield equation will be a better description of the dynamics than the traditional Redfield equation.

In this paper we calculated only the exciton population transfer rates. In order for the description of the exciton dynamics to be complete, explicit consideration of the dynamics of the off-diagonal density matrix elements should be taken into account. Although the coupling of the dynamics of the off-diagonal density matrix to the population dynamics is implicitly taken into account within the expressions for the population transfer rates (of the Förster and modified Redfield equations), this is not enough for the description of optical experiments. Inclusion of the dynamics of the off-diagonal density matrix itself becomes very important when one tries to combine a model based on microscopic dynamics with an analysis of an optical experiment. For this, in our definition of the projection operator, we need the off-diagonal elements of the exciton density matrix to be kept in the projected part. We will investigate this point in future work.
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