

Theory on Rates of Excitation-Energy Transfer between Molecular Aggregates through Distributed Transition Dipoles with Application to the Antenna System in Bacterial Photosynthesis

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It has often been observed in the light-harvesting antenna system of bacterial photosynthesis that excitation-energy transfer (EET) takes place very rapidly to or from a nearly (or completely) optically forbidden state. So far, the rate constant of EET has usually been calculated by Förster's formula, which regards EET as arising from the overlap integral between the luminescence spectrum of the excitation donor and the absorption spectrum of its acceptor. The observed EETs are much faster than expected from this formula, since the transition dipole as a whole nearly (or completely) vanishes in this state, giving a very small (or completely vanishing) Förster's overlap integral. We note in these EETs that at least one of the donor and acceptor is an aggregate of chromophores. Individual chromophores comprising the aggregate retain nonvanishing transition dipoles, even if their sum nearly (or completely) vanishes at an exciton state which is nearly (or completely) optically forbidden therein. EET to (or from) the exciton state can arise due to interactions to (or from) individual transition dipoles in the aggregate when the distance between the donor and the acceptor is not much larger than the physical size of the aggregate. A new formula is proposed for calculating the rate constant of such an EET. It fills well the gap between theory and experiment mentioned above.

I. Introduction

Recent clarification of the three-dimensional structure of pigment-protein complexes in the photosynthetic antenna system of purple bacteria has aroused a surprise due to its beautiful nanoscale ring structure of bacteriochlorophyll molecules (BChls).^{1,2} Energy of solar radiation is harvested as an electronic excitation of BChls therein. The energy of the excitation is transferred within the antenna system and finally to a reaction center where it is converted to the electrostatic energy of an electron pumped against the cross-membrane electric potential.³ The antenna system is composed of two kinds of rings called LH1 and LH2. The former works as a core antenna, which is believed to encircle the reaction center, and the latter is an element in a peripheral antenna system around the core antenna. LH1 is a ring composed of 16 dimeric units of BChls.⁴ On the other hand, LH2 constitutes a double ring where the inner and the outer ring are composed of circularly arranged dimeric and monomeric units of BChls, respectively. The total number of these units in each ring is 8 or 9, depending on species.^{1,2}

We can regard the circular arrangement of dimeric units of BChls in LH1 and the inner ring of LH2 as having, respectively, C_{16} and C_8 or C_9 symmetry, neglecting a small amount of structural disorder. The distance between BChls is similar between a dimeric unit and an adjacent pair from different units, for example, with the Mg-to-Mg distance of ~ 8.9 and ~ 9.6 Å, respectively, in the inner ring of LH2 from *Rhodospseudomonas acidophila*. The lowest, optically allowed, electronic excited state of a BChl is called the Q_y state. Its transition dipole moment is arranged approximately in parallel to the ring tangent in both LH1 and the inner ring of LH2. In this situation, these rings possess a special character in the exciton states that are given

by a linear combination of excited states of individual BChls therein:^{5–11} The lowest exciton state is optically forbidden, belonging to the (totally symmetric) A irreducible representation, since the vectorial sum of the transition dipoles vanishes in their arrangement of head-to-tail order. The second lowest exciton state, which is doubly degenerate, is optically allowed, belonging to the E_1 irreducible representation, where the direction of the head-to-tail order is reversed at two nodes. All other higher exciton states are optically forbidden, where in the highest state the transition dipoles are arranged in the head-to-head order. In the outer ring of LH2, on the other hand, BChls are so apart from each other (for example, with the Mg-to-Mg distance of ~ 21 Å in *Rps. acidophila*) that they are regarded as monomeric, with their excited states describable by isolated Q_y states.

The rate constant for transfer of the excitation energy has usually been calculated by Förster's theory,¹² which formulates it as proportional to the overlap integral between the luminescence spectrum of the excitation donor and the absorption spectrum of the excitation acceptor. It has often been observed in the antenna system, however, that excitation-energy transfer (EET) seems to take place very rapidly from or to a nearly (or completely) optically forbidden exciton state in an aggregate of BChls, as shown below by three examples. Such observations are difficult to rationalize on the basis of this theory.

Optical absorption of LH2 is composed of two strong peaks called B850 and B800, well separated at $\sim 11\,765\text{ cm}^{-1}$ (850 nm in wavelength) and $\sim 12\,500\text{ cm}^{-1}$ (800 nm).³ The second lowest optically-allowed exciton state, mentioned above, in the inner ring of LH2 can be ascribed to B850, and the Q_y state of the monomeric BChls in the outer ring can be ascribed to B800. The first one of the three examples mentioned earlier is concerned with an observation that EET from the outer to the inner ring within LH2 takes place very rapidly with a time

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constant of ~ 0.7 ps at 300 K and ~ 1.5 ps at 4.2 K.^{13–23} It has been pointed out that this observation cannot be rationalized on the basis of Förster's theory.^{22,23} The luminescence spectrum associated with B800, Stokes shifted only by ~ 12 cm⁻¹ from 12 500 cm⁻¹,¹⁶ is so apart from the absorption spectrum of B850 that their overlap is negligibly small. The overlap increases rapidly with temperature, but the rate constant of the EET increases only gradually. A possibility has also been argued, affirmatively^{15,24} or negatively,²³ on the basis of Förster's theory that intramolecular-phonon sidebands of B850 might give rise to an appreciable overlap with the luminescence spectrum of B800. The inner ring of LH2 has also exciton states with energies around 12 500 cm⁻¹ of B800, but all of them are optically forbidden when transition dipoles of individual BChls are arranged completely in parallel to the ring tangent. Since the individual transition dipoles are, in reality, a little tilted from the ring plane, these states can be weakly allowed (although nearly forbidden), with a total transition dipole perpendicular to the ring plane.⁷ Taking this fact into account, it has been argued also on the basis of Förster's theory that weak optical absorption by these exciton states might give rise to an overlap with the luminescence spectrum of B800.²⁵

As the second example, EET to LH1 from the inner ring of LH2 is also rapid with a time constant of ~ 3 ps at 300 K and ~ 5 ps at 77 K,²⁰ or ~ 4.6 ps at 300 K,²⁶ with a little variation among investigators. In this case, the EET can be regarded as taking place dominantly from the lowest exciton state in the inner ring of LH2, which is located at ~ 11 500 cm⁻¹ (870 nm in wavelength), determined by hole-burning spectroscopy.⁸ Since this state is optically forbidden, as mentioned earlier, this rapid EET cannot be rationalized on the basis of Förster's theory either. It might be expected on the basis of this theory that the thermal occupancy at the second lowest optically-allowed exciton state in the inner ring at ~ 11 765 cm⁻¹ gives rise to the hot-band luminescence for the EET. The observed rate, however, increases only very gradually with temperature as mentioned above, excluding also this possibility.

As the third example, EET takes place in the reaction center also very rapidly from a monomeric accessory BChl to the special pair of BChls with a time constant of ~ 80 fs at 300 K and ~ 160 fs at 85 K.^{27–30} The luminescence spectrum of the monomeric BChl is Stokes shifted¹⁶ only by ~ 12 cm⁻¹ from its absorption peak at ~ 12 500 cm⁻¹ (~ 803 nm in the reaction center from *Rhodobacter sphaeroides*), while the special pair absorbs light preferentially to its optically allowed exciton state at ~ 11 500 cm⁻¹ (~ 870 nm in this reaction center).^{27–30} There exists practically no overlap between the luminescence and the absorption spectrum, similarly to the first example in this section. In this example, the upper exciton state in the special pair is weakly optically allowed due to deviation from parallelism of the arrangement of BChls in the special pair, and its absorption peak is located at ~ 12 300 cm⁻¹ (~ 815 nm in the reaction center from *Rb. sphaeroides*) just at the shoulder of the absorption peak by the accessory BChl. In this situation, it is possible to get an appreciable value of the rate constant of the EET from Förster's overlap. However, the transition dipole of the upper exciton state is so small that the rate constant calculated with this overlap is about 20–30 times as small as the observed ones.^{27–30}

In these three examples, we note that at least one of the donor and the acceptor of excitation is an aggregate of chromophores (BChls in these examples), in which each chromophore has a nonvanishing transition dipole. Moreover, the donor–acceptor distance is not much larger than the physical size of the

aggregate. In these situations, application of Förster's theory becomes problematic: If the acceptor is an aggregate, a chromophore in the donor sees individual chromophores in the acceptor aggregate at a relatively large range of distances. The aggregate cannot be represented by its total transition dipole, which is obtained only by looking at individual transition dipoles in the aggregate with an equal weight. At such a donor–acceptor distance, therefore, EET can take place effectively even to an optically forbidden exciton state in the acceptor aggregate through the interaction between a transition dipole in the donor and individual transition dipoles in the acceptor, although their vectorial sum vanishes in this state. Similarly, EET can take place effectively even from an optically forbidden exciton state at such a distance when the donor is an aggregate of chromophores. Förster's theory gives erroneous values to the rate constant in these situations. For calculating the rate constant of EET, therefore, we need a new formula that accounts for the observations mentioned in this section and merges into Förster's formula when the donor–acceptor distance is much larger than the size of the aggregate.

The aim of the present work is to present such a formula. It is formulated in section II. It is shown in section III that spectral functions appearing in the new formula are related to Green's functions for an exciton in the donor or the acceptor. Since methods of calculation of Green's functions have well been developed in theoretical physics,³¹ we can calculate these spectral functions by standard techniques. Section IV is devoted to showing the applicability of the new formula. The third example mentioned in this section is taken as an example, since it is the simplest case where the donor is a single chromophore and the acceptor is a dimer of chromophores. In this example, the new formula describes correctly that EET takes place in the reaction center from an accessory BChl to the upper weakly allowed (nearly forbidden) exciton state in the special pair with the rate constant 20–30 times as large as that obtained by Förster's formula. The first example, mentioned earlier, of the EET from the outer ring (B800) to the inner ring (B850) within LH2 will be treated in a forthcoming paper.³² There, the new formula describes that the EET takes place, with a rate in agreement with observations, to exciton states in the inner ring with energies around 12 500 cm⁻¹ of B800 although they are optically forbidden. Remaining details are in section V.

II. Formulation Based on a Distributed Transition-Dipole Approximation

Let us consider that the donor and the acceptor are respectively composed of M and N chromophores with $M \geq 1$ and $N \geq 1$. We represent the electronic excited state of the i th chromophore in the donor and the j th one in the acceptor, respectively, by $|\varphi_{\text{D}}^{(i)}\rangle$ and $|\varphi_{\text{A}}^{(j)}\rangle$ with $1 \leq i \leq M$ and $1 \leq j \leq N$. We represent the electrostatic interaction between transition dipoles at the (D) th and the (A) th chromophore as $W_{\text{A}|\text{D}}^{(j|i)}$, as illustrated in Figure 1. In the point-dipole approximation, the magnitude of $W_{\text{A}|\text{D}}^{(j|i)}$ is given by

$$f(\mathbf{d}_j, \mathbf{R}_j; \mathbf{d}_i, \mathbf{R}_i) = \epsilon^{-1} [\mathbf{d}_j \cdot \mathbf{d}_i / |\mathbf{R}_{ji}|^3 - 3(\mathbf{d}_j \cdot \mathbf{R}_{ji})(\mathbf{d}_i \cdot \mathbf{R}_{ji}) / |\mathbf{R}_{ji}|^5] \quad (2.1)$$

as the interaction between transition dipoles (\mathbf{d}_i and \mathbf{d}_j) on these two chromophores (at position vectors \mathbf{R}_i and \mathbf{R}_j , respectively) with $\mathbf{R}_{ji} \equiv \mathbf{R}_j - \mathbf{R}_i$, where ϵ represents an appropriate dielectric constant. This approximation is justified when the distance

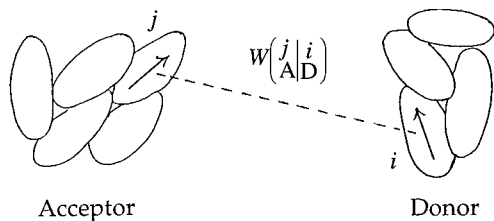


Figure 1. Electrostatic interaction $W_{A,D}^{(j|i)}$ between transition dipoles on the i th chromophore in the excitation donor and the j th one in its acceptor when both of them are aggregates of chromophores.

between these two chromophores is much larger than their physical sizes. Otherwise, the magnitude of $W_{A,D}^{(j|i)}$ can be calculated by the so-called monopole approximation,³³ as the next approximation, in which account is taken of the distribution of positive and negative charges in both the ground and the excited states in a chromophore.^{11,33–35} We introduce an (N,M) matrix $W_{A,D}$ whose (j,i) element is given by $W_{A,D}^{(j|i)}$ on the basis of the electronic excited state $|\varphi_{(D)}^{(i)}\rangle$'s in the donor and $|\varphi_{(A)}^{(j)}\rangle$'s in the acceptor, as

$$W_{A,D} \equiv \sum_{j=1}^N \sum_{i=1}^M |\varphi_{(A)}^{(j)}\rangle W_{A,D}^{(j|i)} \langle \varphi_{(D)}^{(i)}| \quad (2.2)$$

where $\langle \varphi_{(D)}^{(i)}|$ represents the bra vector associated with the ket vector $|\varphi_{(D)}^{(i)}\rangle$.

Since both the donor and the acceptor were assumed to be, in general, aggregates of chromophores, an excitation in them as a whole can be described in terms of excitons. As assumed in Förster's theory, let us assume also here that, depending on whether the excitation resides in the donor or the acceptor, it interacts with different phonon systems, whose Hamiltonians are written as $H_{ph}^{(D)}$ and $H_{ph}^{(A)}$, respectively. Under this assumption, $H_{ph}^{(D)}$ and $H_{ph}^{(A)}$ are commutable with each other. We write the Hamiltonian describing an exciton–phonon system within the donor and the acceptor, respectively, as $H_{e-p}^{(D)}$ and $H_{e-p}^{(A)}$. They are commutable with each other, too. They are composed of an exciton interacting with static disorders within each of the donor and the acceptor, and phonons described respectively by $H_{ph}^{(D)}$ and $H_{ph}^{(A)}$, and the exciton–phonon interaction. $H_{ph}^{(D)}$ and $H_{e-p}^{(A)}$ (and also $H_{ph}^{(A)}$ and $H_{e-p}^{(D)}$) are commutable with each other, but neither $H_{ph}^{(D)}$ and $H_{e-p}^{(D)}$ nor $H_{ph}^{(A)}$ and $H_{e-p}^{(A)}$ are because of the presence of the exciton–phonon interaction in both $H_{e-p}^{(D)}$ and $H_{e-p}^{(A)}$. Since $W_{A,D}$ does not include phonons but electronic excitations, both $H_{ph}^{(A)}$ and $H_{ph}^{(D)}$ commute with $W_{A,D}$, but neither $H_{e-p}^{(D)}$ nor $H_{e-p}^{(A)}$ does.

We introduce

$$I_{ij'}^{(A)}(E) = C \int dF e^{-\beta F} \text{Tr}^{(ph)} \langle \varphi_{(A)}^{(j)} | \delta(H_{e-p}^{(A)} - E - F) | \varphi_{(A)}^{(j')} \rangle \delta(H_{ph}^{(A)} - F) \quad (2.3)$$

with $\beta = (k_B T)^{-1}$, where $\text{Tr}^{(ph)}$ means taking a trace over phonon states and C is a constant independent of j and j' . Since both $|\varphi_{(D)}^{(i)}\rangle$ and $|\varphi_{(A)}^{(j)}\rangle$ are singlet states and hence can be represented by real functions, $I_{ij'}^{(A)}(E)$ can be taken as symmetric in j and j' and real. We define an (N,N) matrix $I_A(E)$ whose (j,j')

element is given by $I_{ij'}^{(A)}(E)$ of eq 2.3 on the basis of the electronic excited state $|\varphi_{(A)}^{(j)}\rangle$'s in the acceptor, as

$$I_A(E) \equiv \sum_{j=1}^N \sum_{j'=1}^N |\varphi_{(A)}^{(j)}\rangle I_{ij'}^{(A)}(E) \langle \varphi_{(A)}^{(j')}| \quad (2.4)$$

The constant C is determined by

$$\int dE \text{Tr}^{(A)} I_A(E) = N \quad (2.5)$$

where $\text{Tr}^{(A)}$ means taking a trace over electronic excited states in the acceptor, for example, over each excited state of individual chromophores therein. Defining $I_{ii'}^{(D)}(E)$ by changing A , j , and j' in eq 2.3, respectively, to D , i , and i' , we introduce

$$L_{ii'}^{(D)}(E) = B e^{-\beta E} I_{ii'}^{(D)}(E) \quad (2.6)$$

where B is a constant independent of i and i' . This function can be taken also as symmetric in i and i' and real. We define an (M,M) matrix $L_D(E)$ whose (i,i') element is given by $L_{ii'}^{(D)}(E)$ of eq 2.6 on the basis of the electronic excited state $|\varphi_{(D)}^{(i)}\rangle$'s in the donor, as

$$L_D(E) \equiv \sum_{i=1}^M \sum_{i'=1}^M |\varphi_{(D)}^{(i)}\rangle L_{ii'}^{(D)}(E) \langle \varphi_{(D)}^{(i')}| \quad (2.7)$$

The constant B is determined here by

$$\int dE \text{Tr}^{(D)} L_D(E) = 1 \quad (2.8)$$

where $\text{Tr}^{(D)}$ means taking a trace over electronic excited states in the donor.

$I_{ij'}^{(A)}(E)$ represents the density of states for excitons that propagate with energy E from the j th to the i th chromophore within the acceptor. It is defined under thermal averaging over phonons therein since $F = H_{ph}^{(A)}$ in eq 2.3. Similarly, $L_{ii'}^{(D)}(E)$ represents that for excitons propagating from the i' th to the i th chromophore within the donor. It is here defined under thermal averaging over exciton–phonon states therein since $E + F = H_{e-p}^{(D)}$ in eq 2.6 with eq 2.3. EET from the donor to the acceptor is induced by the electronic interaction, represented by the (N,M) matrix $W_{A,D}$, between an excitation in the donor and that in the acceptor. It will be proved below that in the lowest order perturbation in $W_{A,D}$, the rate constant for the EET is given by

$$k = \frac{2\pi}{\hbar} \int dE \text{Tr}^{(D)} W_{A,D}^t \cdot I_A(E) \cdot W_{A,D} \cdot L_D(E) \quad (2.9)$$

where $W_{A,D}^t$ represents the transposed matrix of $W_{A,D}$, and \cdot denotes matrix multiplication. Equation 2.9 is the new formula for the rate constant of EET that we propose.

When $M = N = 1$, especially, $I_{1,1}^{(A)}(E)$ in $I_A(E) = |\varphi_{(A)}^{(1)}\rangle I_{1,1}^{(A)}(E) \langle \varphi_{(A)}^{(1)}|$ represents the absorption spectrum of the acceptor whose integrated intensity is normalized to unity, and $L_{1,1}^{(D)}(E)$ in $L_D(E) = |\varphi_{(D)}^{(1)}\rangle L_{1,1}^{(D)}(E) \langle \varphi_{(D)}^{(1)}|$ represents the luminescence spectrum of the donor whose integrated intensity is normalized also to unity. In this case, $\text{Tr}^{(D)}$ reduces to an operation taking an expectation value on the electronic excited state $|\varphi_{(D)}^{(1)}\rangle$ of the unique chromophore in the donor. We see, thus, that eq 2.9 turns out to coincide with Förster's formula in the case of $M = N = 1$.

In general cases, eq 2.9 differs from Förster's formula: It is assumed in Förster's formula that EET takes place only through optically allowed exciton states of both the donor and the acceptor by an electrostatic interaction between their nonvanishing total transition dipoles separated by an average distance. In eq 2.9, on the other hand, all the exciton states, either optically allowed or forbidden, in both the donor and the acceptor are incorporated as components in matrix multiplication mediated by $L_D(E)$ and $I_A(E)$, respectively. When the distance between the donor and the acceptor aggregates is much larger than their physical sizes, eq 2.9 merges into Förster's formula, as shown later in this section. In other words, it does so naturally when all the position vectors of transition dipoles on individual chromophores in the donor and the acceptor are replaced by the average position vectors of the donor and the acceptor as a whole, respectively, in the point-dipole approximation of eq 2.1 for $W_{A,D}^{(j|i)}$. [Readers not interested in the proof of eq 2.9 can skip from here to section IV.]

Before EET, the donor and the acceptor are in one of eigenstates, respectively, in the exciton-phonon system described by the Hamiltonian $H_{e-p}^{(D)}$ and in the phonon system described by the Hamiltonian $H_{ph}^{(A)}$. After EET, they change to one of the eigenstates, respectively, in the phonon system described by $H_{ph}^{(D)}$ and in the exciton-phonon system described by $H_{e-p}^{(A)}$. This EET is induced by $W_{A,D}$. Taking these features into account in the lowest order perturbation in $W_{A,D}$, we get the rate constant of the EET by Fermi's Golden Rule as

$$k = \{2\pi \text{Tr}^{(D)} \text{Tr}^{(ph)} \int dX \int dY e^{-\beta X} \delta(Y - X) W_{A,D}^t \cdot \delta(H_{e-p}^{(A)} + H_{ph}^{(D)} - Y) \cdot W_{A,D} \cdot \delta(H_{e-p}^{(D)} + H_{ph}^{(A)} - X)\} / \{\hbar \text{Tr}^{(D)} \text{Tr}^{(ph)} \times \exp[-\beta(H_{e-p}^{(D)} + H_{ph}^{(A)})]\} \quad (2.10)$$

Since $H_{e-p}^{(D)}$ and $H_{ph}^{(A)}$ (and also $H_{e-p}^{(A)}$ and $H_{ph}^{(D)}$) are commutable with each other, it is possible to define both $\delta(H_{e-p}^{(D)} + H_{ph}^{(A)} - X)$ and $\delta(H_{e-p}^{(A)} + H_{ph}^{(D)} - Y)$ appearing in eq 2.10. The trace operation $\text{Tr}^{(D)}$ over electronic excited states in the donor in eq 2.10 is concerned with thermal averaging over eigenstates in the initial state of the EET in Fermi's Golden Rule. Equation 2.10 can be expressed also in terms of matrix elements of $W_{A,D}$ between eigenstates in the initial and the final state of the EET, as shown in Appendix A. We see, thus, that eq 2.10 is a result of straightforward application of the familiar expression of Fermi's Golden Rule found in textbooks in quantum mechanics.

Now, let us apply, to eq 2.10, identities

$$\delta(H_{e-p}^{(D)} + H_{ph}^{(A)} - X) = \int dE \int dF \delta(H_{ph}^{(A)} - F) \delta(H_{e-p}^{(D)} - E - G) \delta(E + F + G - X)$$

and

$$\delta(H_{e-p}^{(A)} + H_{ph}^{(D)} - Y) = \int dF' \int dG \delta(H_{e-p}^{(A)} - E - F') \delta(H_{ph}^{(D)} - G) \delta(E + F' + G - Y) \quad (2.11)$$

where both G in the first equality and E in the second equality are dummy variables introduced for later convenience. On this procedure, considering that $H_{ph}^{(A)}$ and $H_{ph}^{(D)}$ are commutable with

each other and both also with $W_{A,D}$, the X and Y integration in the numerator in eq 2.10 can be rewritten into

$$\int dE \int dF \int dG e^{-\beta(E+F+G)} W_{A,D}^t \cdot \delta(H_{e-p}^{(A)} - E - F) \delta(H_{ph}^{(A)} - F) \cdot W_{A,D} \cdot \delta(H_{ph}^{(D)} - G) \delta(H_{e-p}^{(D)} - E - G)$$

Since $W_{A,D}$ is concerned only with electronic excitations, not with phonons, and the donor and the acceptor part have been separated in the rewriting shown above, eq 2.10 can be expressed in the form of eq 2.9, with

$$I_A(E) = \int dF e^{-\beta F} \text{Tr}^{(ph)} \delta(H_{e-p}^{(A)} - E - F) \delta(H_{ph}^{(A)} - F) / \text{Tr}^{(ph)} \exp(-\beta H_{ph}^{(A)}) \quad (2.12)$$

and

$$L_D(E) = e^{-\beta E} \int dG e^{-\beta G} \text{Tr}^{(ph)} \delta(H_{ph}^{(D)} - G) \delta(H_{e-p}^{(D)} - E - G) / \text{Tr}^{(D)} \text{Tr}^{(ph)} \exp(-\beta H_{e-p}^{(D)}) \quad (2.13)$$

We should note here that after the trace operation over phonons in eq 2.12, $I_A(E)$ given therein is an (N,N) matrix spanned by electronic excited states in the acceptor, while $L_D(E)$ given by eq 2.13 is an (M,M) matrix spanned by those in the donor. Equivalence of $I_A(E)$ and $L_D(E)$ to those introduced previously will be shown below.

Since the denominator on the right-hand side of eq 2.12 is a constant, the matrix element of the right-hand side between the electronic states $|\varphi_A^{(j)}\rangle$ and $|\varphi_A^{(j')}\rangle$ is proportional to the right-hand side of eq 2.3. The right-hand side of eq 2.12 satisfies eq 2.5. Thus, $I_A(E)$ given by eq 2.12 is the same as that introduced previously. A similar argument can be applied for proving the equality between $L_D(E)$ of eq 2.13 and that obtained by eq 2.6 with eq 2.3.

Let us investigate here a limit that the distance between the donor and the acceptor aggregates is much larger than sizes of themselves. In this limit, the distance is much larger than sizes of individual chromophores comprising the donor and the acceptor. Therefore, the point-dipole approximation in eq 2.1 is applicable for the component of $W_{A,D}$, giving $W_{A,D}^{(j|i)} \approx f(d_j, \mathbf{R}_j; d_i, \mathbf{R}_i)$. In this limit, moreover, the position vectors \mathbf{R}_j and \mathbf{R}_i of the j th and the i th chromophore in the donor and the acceptor, respectively, can be approximated by the average position vectors \mathbf{R}_A and \mathbf{R}_D , obtaining

$$W_{A,D}^{(j|i)} \approx f(d_j, \mathbf{R}_A; d_i, \mathbf{R}_D) \quad (2.14)$$

Since matrix multiplication in $W_{A,D} \cdot L_D(E)$ in eq 2.9 can be performed by any complete set of electronic excited states in the donor, it is performed by a set of exciton states in the donor, which are represented by $|\psi_D^{(\mu)}\rangle$ for $\mu = 1, 2, \dots, M$, as

$$W_{A,D} \cdot L_D(E) = \sum_{\mu=1}^M W_{A,D} |\psi_D^{(\mu)}\rangle \langle \psi_D^{(\mu)}| L_D(E) \quad (2.15)$$

where $\langle \psi_D^{(\mu)}|$ represents the bra vector associated with the ket vector $|\psi_D^{(\mu)}\rangle$. We introduce an M th-order column vector $\langle d|$ whose i th component is given by the transition dipole d_i of the i th chromophore in the donor for $i = 1, 2, \dots, M$. When any

component $W_{A,D}^{(j|i)}$ of $W_{A,D}$ can be approximated as eq 2.14 with eq 2.1, $W_{A,D}|\psi_D^{(\mu)}\rangle$ represents the electrostatic interaction between a transition dipole d_j at the average position vector R_A of the acceptor and a transition dipole $\langle d|\psi_D^{(\mu)}\rangle$ associated with an exciton state $|\psi_D^{(\mu)}\rangle$ at the average position vector R_D of the donor. Let us assume here that only one of $|\psi_D^{(\mu)}\rangle$'s, e.g., $|\psi_D^{(\alpha)}\rangle$, is optically allowed in the donor. Under this assumption, only $\langle d|\psi_D^{(\alpha)}\rangle$ is nonvanishing in all the $\langle d|\psi_D^{(\mu)}\rangle$'s in the donor, and it is written as d_D , which gives the total transition dipole of the donor. Similarly, let us assume that only one exciton state, e.g., $|\psi_A^{(\beta)}\rangle$, is optically allowed in all the exciton state $|\psi_A^{(\nu)}\rangle$'s for $\nu = 1, 2, \dots, N$ in the acceptor, and the nonvanishing transition dipole associated with this state is written as d_A , which gives the total transition dipole of the acceptor. Under these assumptions, we get

$$\langle \psi_A^{(\nu)} | W_{A,D} | \psi_D^{(\mu)} \rangle = \begin{cases} f(d_A, R_A; d_D, R_D), & \text{for } \mu = \alpha \text{ and } \nu = \beta \\ 0, & \text{otherwise} \end{cases} \quad (2.16)$$

Concomitantly, we express matrix multiplication in both $W_{A,D} \cdot I_A(E)$ and $I_A(E) \cdot W_{A,D}$ in eq 2.9 by the exciton state $|\psi_A^{(\nu)}\rangle$'s for $\nu = 1, 2, \dots, N$ in the acceptor, as in eq 2.15. Expressing k of eq 2.9 as k_F in this limit, we see thus that it reduces into

$$k_F = \frac{2\pi}{\hbar} f(d_A, R_A; d_D, R_D)^2 \int I_A(E) L_D(E) dE \quad (2.17)$$

with

$$L_D(E) \equiv \langle \psi_D^{(\alpha)} | L_D(E) | \psi_D^{(\alpha)} \rangle \quad (2.18)$$

and

$$I_A(E) \equiv \langle \psi_A^{(\beta)} | I_A(E) | \psi_A^{(\beta)} \rangle \quad (2.19)$$

Here, $L_D(E)$ and $I_A(E)$ represent respectively the luminescence spectrum of the donor and the absorption spectrum of the acceptor. Inserting eqs 2.12 and 2.13 into eqs 2.19 and 2.18, respectively, we can show that they are normalized as

$$\int L_D(E) dE = \frac{\langle \psi_D^{(\alpha)} | \text{Tr}^{(\text{ph})} \exp(-H_{e-p}^{(D)}/k_B T) | \psi_D^{(\alpha)} \rangle}{\text{Tr}^{(D)} \text{Tr}^{(\text{ph})} \exp(-H_{e-p}^{(D)}/k_B T)} \quad (2.20)$$

and

$$\int I_A(E) dE = 1 \quad (2.21)$$

The right-hand side of eq 2.20 represents the thermal occupation probability at the optically allowed exciton state $|\psi_D^{(\alpha)}\rangle$ in all the electronic excited states in the donor. Equation 2.17 is nothing but Förster's formula. We see thus that the new formula (2.9) for the rate constant of EET between molecular aggregates merges into Förster's formula when the

distance between the donor and the acceptor aggregates is much larger than their physical sizes.

III. Relation of $I_{jj'}^{(A)}(E)$ and $L_{ii'}^{(D)}(E)$ to Green's Functions for Excitons

It seems important to note here that both $I_{jj'}^{(A)}(E)$ and $L_{ii'}^{(D)}(E)$ defined by eqs 2.3–2.8 are closely related to Green's functions for an exciton in the donor and the acceptor, respectively. Since the method of calculation of Green's functions by means of Feynman's diagrams has well been developed in theoretical physics,³¹ it is useful to prove the relation here. The relation means that $I_{jj'}^{(A)}(E)$, for example, equals $(-1/\pi)$ times the imaginary part of a Green's function, $G_{jj'}^{(A)}(E)$, which is defined as the Fourier transform of a retarded Green's function

$$\bar{G}_{jj'}^{(A)}(t) = -i\theta(t) \text{Tr}^{(\text{ph})} \langle \varphi_A^{(j)} | \exp(-iH_{e-p}^{(A)}t/\hbar) | \varphi_A^{(j')} \rangle \times \exp[(it/\hbar - \beta)H_{\text{ph}}^{(A)}] / \text{Tr}^{(\text{ph})} \exp(-\beta H_{\text{ph}}^{(A)}) \quad (3.1)$$

where $\theta(t)$ represents the step function equal to unity for $t > 0$ and zero for $t < 0$, with

$$G_{jj'}^{(A)}(E) = \int \bar{G}_{jj'}^{(A)}(t) e^{iEt/\hbar} dt/\hbar \quad (3.2)$$

Although the definition of a retarded Green's function in eq 3.1 might look a little different from that found in textbooks, they are the same, as shown in Appendix B.

First, let us insert, into eq 3.1, identities

$$\exp(-iH_{e-p}^{(A)}t/\hbar) = \int e^{-i(E'+F)t/\hbar} \delta(H_{e-p}^{(A)} - E' - F) dE'$$

and

$$\exp(iH_{\text{ph}}^{(A)}t/\hbar) = \int e^{iFt/\hbar} \delta(H_{\text{ph}}^{(A)} - F) dF \quad (3.3)$$

where F in the first equation is a dummy variable introduced for later convenience. In this case, performing the t integration in eq 3.2 with eq 3.1, we obtain

$$G_{jj'}^{(A)}(E) = \int dE' I_{jj'}^{(A)}(E') / (E - E' + i\epsilon) \quad (3.4)$$

by using $I_{jj'}^{(A)}(E)$ given by eq 2.12, where ϵ represents a positive infinitesimal. Such an equation as (3.4) is called the spectral representation of the Green's function $G_{jj'}^{(A)}(E)$.³¹ Thus, we see that $I_{jj'}^{(A)}(E)$ corresponds to the spectral function of $G_{jj'}^{(A)}(E)$. Since the imaginary part of $(E - E' + i\epsilon)^{-1}$ is $-\pi\delta(E - E')$, that of $G_{jj'}^{(A)}(E)$ equals $-\pi I_{jj'}^{(A)}(E)$ in eq 3.4, and we have proved the relation mentioned earlier. Using eq 2.6, we can relate also $L_{ii'}^{(D)}(E)$ to a retarded Green function for an exciton in the donor. Thus, both $I_{jj'}^{(A)}(E)$ and $L_{ii'}^{(D)}(E)$, whose matrix representations are respectively $I_A(E)$ and $L_D(E)$ appearing in eq 2.9, turn out to be quantities whose calculation has well been developed in theoretical physics.

IV. EET in the Reaction Center of Bacterial Photosynthesis

The simplest case in which the present formula for the rate constant of EET differs from Förster's one is when at least one of M and N is unity and the other is two. It is realized just as the third example in section I, where $M = 1$ and $N = 2$, since EET takes place from an accessory monomeric BChl to the special pair of BChls in the photosynthetic reaction center of purple bacteria. This example is briefly discussed here.

When $M = 1$ in eq 2.9, $L_D(E)$ is spanned only by the electronic excited state $|\varphi(\frac{1}{D})\rangle$ of the unique chromophore in the donor. Accordingly, it can be expressed by

$$L_D(E) = |\varphi(\frac{1}{D})\rangle L_D(E) \langle \varphi(\frac{1}{D})| \quad (4.1)$$

with

$$L_D(E) \equiv \langle \varphi(\frac{1}{D}) | L_D(E) | \varphi(\frac{1}{D}) \rangle \quad (4.2)$$

where $L_D(E)$ represents the luminescence spectrum of the donor, whose integration intensity is normalized to unity. Since $N = 2$, the acceptor has two exciton states. Since two BChls comprising the special pair are not completely parallel to each other, both exciton states are optically allowed. However, the lower exciton state, represented by $|\psi(\frac{-}{A})\rangle$, carries almost all of the total oscillator strength of the special pair, and the upper exciton state, represented by $|\psi(\frac{+}{A})\rangle$, is only weakly allowed (i.e., nearly forbidden). In fact, the lower exciton state in the special pair is given by a linear combination of Q_y states of the two BChls with nearly head-to-tail arrangement of their transition dipoles, and the upper one is given by that with nearly head-to-head arrangement. As noted in section I, $L_D(E)$ shows a peak at $\sim 12\,500\text{ cm}^{-1}$ in the reaction center from *Rb. sphaeroides*, while the absorption spectrum by the lower exciton state in the acceptor shows a peak at $\sim 11\,500\text{ cm}^{-1}$, and there exists practically no overlap between them. The absorption spectrum by the upper exciton state in the acceptor, on the other hand, shows a peak at $\sim 12\,300\text{ cm}^{-1}$, and it fully overlaps with $L_D(E)$, although its absorption intensity is very small compared with that by the lower exciton state.

In the situation mentioned above, the matrix $I_A(E)$ in eq 2.9 can be approximated as

$$I_A(E) \approx |\psi(\frac{+}{A})\rangle I_A^+(E) \langle \psi(\frac{+}{A})| \quad (4.3)$$

with

$$I_A^+(E) \equiv \langle \psi(\frac{+}{A}) | I_A(E) | \psi(\frac{+}{A}) \rangle \quad (4.4)$$

[This approximation corresponds to neglecting $|\psi(\frac{-}{A})\rangle \langle \psi(\frac{-}{A})|$ in the sum of $|\psi(\frac{+}{A})\rangle \langle \psi(\frac{+}{A})| + |\psi(\frac{-}{A})\rangle \langle \psi(\frac{-}{A})|$, which equals the unit matrix in the space spanned by electronic excited states in the acceptor.] We should note here that $I_A^+(E)$ of eq 4.4 represents the absorption spectrum by the upper exciton state in the acceptor and that its integration intensity is normalized to unity, similarly to eq 2.21 for $I_A(E)$ of eq 2.19.

Two BChls comprising the special pair are nearly in the antiparallel card-packing arrangement. In this situation, under a simplification that they are equivalent, $|\psi(\frac{+}{A})\rangle$ with nearly head-to-head arrangement of their transition dipoles is given by

$$|\psi(\frac{+}{A})\rangle = \frac{1}{\sqrt{2}} [|\varphi(\frac{1}{A})\rangle + |\varphi(\frac{2}{A})\rangle] \quad (4.5)$$

where $|\varphi(\frac{j}{A})\rangle$ for $j = 1$ or 2 represents the electronic excited state of the j th BChl in the special pair. Inserting eqs 4.1 and

4.3 into eq 2.9, we get

$$k = \frac{2\pi}{\hbar} |W^{(+)}|^2 \int I_A^+(E) L_D(E) dE \quad (4.6)$$

with

$$W^{(+)} \equiv \langle \psi(\frac{+}{A}) | W_{A,D} | \varphi(\frac{1}{D}) \rangle = \frac{1}{\sqrt{2}} [W(\frac{1}{A} | \frac{1}{D}) + W(\frac{2}{A} | \frac{1}{D})] \quad (4.7)$$

Adopting the point-dipole approximation of eq 2.1 for $W(\frac{j}{A} | \frac{1}{D})$, we get

$$W^{(+)} \approx \frac{1}{\sqrt{2}} \{ f[d(\frac{1}{A}), \mathbf{R}(\frac{1}{A}); \mathbf{d}_D, \mathbf{R}_D] + f[d(\frac{2}{A}), \mathbf{R}(\frac{2}{A}); \mathbf{d}_D, \mathbf{R}_D] \} \quad (4.7')$$

where \mathbf{d}_D and \mathbf{R}_D represent respectively the transition dipole and the position vector of the donor BChl, while $\mathbf{d}(\frac{j}{A})$ and $\mathbf{R}(\frac{j}{A})$ represent those of the j th BChl in the acceptor.

The rate constant of EET given by Förster's formula was written as k_F . In the present situation that $L_D(E)$ overlaps practically only with the absorption spectrum by the upper exciton state in the acceptor, k_F is given by the same expression as eq 4.6 except that $W^{(+)}$ therein becomes different, as

$$k_F = \frac{2\pi}{\hbar} |W_F^{(+)}|^2 \int I_A^+(E) L_D(E) dE \quad (4.8)$$

As shown in eq 2.17, $W_F^{(+)}$ is given by

$$W_F^{(+)} = f[d(\frac{+}{A}), \mathbf{R}_A; \mathbf{d}_D, \mathbf{R}_D] \quad (4.9)$$

where $\mathbf{d}(\frac{+}{A})$ represents the transition dipole associated with the upper exciton state in the acceptor, and \mathbf{R}_A represents the mean position vector of the acceptor as a whole, given by $[\mathbf{R}(\frac{1}{A}) + \mathbf{R}(\frac{2}{A})]/2$. As shown in the discussion below eq 2.15, $\mathbf{d}(\frac{+}{A})$ is given by $[d(\frac{1}{A}) + d(\frac{2}{A})]/\sqrt{2}$. We remember here that $\mathbf{d}(\frac{1}{A})$ and $\mathbf{d}(\frac{2}{A})$ are nearly antiparallel to each other, as mentioned earlier. If they were completely antiparallel to each other, $\mathbf{d}(\frac{+}{A})$ and hence $W_F^{(+)}$ would vanish and so would k_F . [Even in this case, $W^{(+)}$ in eq 4.6 retains an appreciable value since $f[d(\frac{1}{A}), \mathbf{R}(\frac{1}{A}); \mathbf{d}_D, \mathbf{R}_D]$ and $f[d(\frac{2}{A}), \mathbf{R}(\frac{2}{A}); \mathbf{d}_D, \mathbf{R}_D]$ do not cancel each other in eq 4.7' because of the difference between $\mathbf{R}(\frac{1}{A})$ and $\mathbf{R}(\frac{2}{A})$.] In reality, $\mathbf{d}(\frac{+}{A})$ does not vanish, but the deviation from antiparallelism between $\mathbf{d}(\frac{1}{A})$ and $\mathbf{d}(\frac{2}{A})$ is so small that $|\mathbf{d}(\frac{+}{A})|$ is much smaller than $|\mathbf{d}(\frac{1}{A})|$ [= $|\mathbf{d}(\frac{2}{A})|$] in agreement with the observation that the optical absorption of the acceptor is much weaker by the upper exciton state than by the lower one.

The ratio between the rate constant k of eq 4.6 obtained by the new formula (2.9) and k_F of eq 4.8 obtained by Förster's formula is given by

$$k/k_F = |W^{(+)}|/|W_F^{(+)}|^2 \quad (4.10)$$

Since $|\mathbf{d}(\frac{1}{A})| = |\mathbf{d}(\frac{2}{A})|$, this ratio does not depend on the magnitude of transition dipoles but is determined only by the geometrical arrangement of BChls in the reaction center.

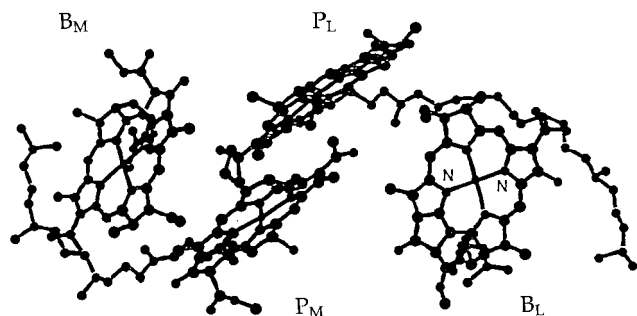


Figure 2. Arrangement of BChls for EET in the photosynthetic reaction center from *Rhodospirillum rubrum*.³⁶ BChls labeled by P_L and B_L are immersed in the L protein subunit and those labeled by P_M and B_M are in the M subunit. BChls labeled by P_L and P_M comprise the special pair.

This EET occurs through two strands of BChls immersed in the L and M protein subunits in the reaction center. The arrangement of BChls, relevant to the EET, in these strands is shown in Figure 2 for *Rb. sphaeroides*,³⁶ where BChls labeled by letters with subscript M and L are immersed in the M and the L subunit, respectively, and the central two BChls labeled by P_M and P_L comprise the special pair. The direction of a transition dipole in each BChl is regarded as that connecting the two nitrogen atoms (N's in Figure 2) on the pyrrole rings I and III of the chlorin macroring, and its position is regarded as the midpoint between these two N's.²⁷ This enables us to calculate the ratio of eq 4.10, and to obtain

$$k/k_F \approx 21.3 \text{ and } 31.4 \quad (4.11)$$

respectively, for the M and L strand of *Rb. sphaeroides*. Similarly, for *Rhodopseudomonas viridis*³⁷ we obtain

$$k/k_F \approx 20.8 \text{ and } 18.1 \quad (4.12)$$

respectively, for the M and L strand. These values fill up well the gap between k_F and observations noted in section I.

V. Discussion

The Mg-to-Mg distances between an accessory BChl and the special pair are ~ 10.5 Å within the same protein subunits and ~ 13 Å between the different subunits in photosynthetic purple bacteria.^{36,37} At these distances, it might be more appropriate to calculate the electrostatic interaction between transition dipoles on the basis of the so-called monopole approximation^{11,33–35} than by the point-dipole approximation adopted in the estimate of eqs 4.11 and 4.12. It is known that at the distance of 10 Å, the square of the electrostatic dipole–dipole interaction calculated by the monopole approximation varies from about 0.5 to about 2 times as large as that of $f(d_j, \mathbf{R}_j; d_i, \mathbf{R}_i)$ of eq 2.1 calculated by the point-dipole approximation, depending on the mutual orientation of BChls.³³ It seems, therefore, meaningful that we calculate $W_{AD}^{(j|i)}$ in eq 2.9 by a more appropriate approximation such as the monopole one or, more rigorously, by original Coulomb integrals from which both the point-dipole and the monopole approximations are derived. For the EET in the photosynthetic reaction center in section IV, however, results thus obtained will not differ so much from those of eqs 4.11 and 4.12, as noted in the next paragraph. Anyhow, this subject should be left for future works, since the aim of the present work is to present the new formula (2.9) for the rate constant of EET applicable also to such cases that the

distance between the donor and the acceptor aggregates is not much larger than their physical sizes. EETs in the photosynthetic antenna system of purple bacteria are good examples of such cases. In such cases, Förster's formula becomes unrealistic, but the new formula gives quantitatively acceptable values for their rate constants, even if the point-dipole approximation is adopted for W_{AD} therein, although it is not limited by this approximation.

It has often been mentioned that when Förster's formula based on the dipole–dipole interaction is inapplicable, EET might be caused by short-range interactions such as electron exchange and/or multipole effects.^{22–30} It was shown in the present work, however, that even in this case EET can be rationalized within this interaction when at least one of the donor and acceptor is an aggregate of chromophores on which transition dipoles are distributed. This interaction depends on both the mutual distance and orientation between two transition dipoles. When the distance between the donor and the acceptor aggregates is not much larger than their physical sizes, the image of individual chromophores in the acceptor seen by a chromophore in the donor, through this interaction, significantly varies depending on their location and orientation within the acceptor, and vice versa. In this situation, the interaction between the donor and the acceptor cannot be approximated by that between their total transition dipoles, only which is regarded as causing EET in Förster's theory. In the example treated in section IV, the interaction is composed of the two terms in $W^{(+)}$ of eq 4.7'. They do not cancel each other. Interestingly, moreover, the term for a BChl at a longer distance from \mathbf{R}_D in the special pair is much larger than that for the other BChl at a shorter distance from \mathbf{R}_D , about 10 and 5 times as large, respectively, in *Rb. sphaeroides* and *Rps. viridis*. [We note here as a byproduct that since $W^{(+)}$ is dominated almost only by the longer-distance term at ~ 13 Å in this situation, the monopole correction on the point-dipole approximation for $W^{(+)}$ is not so indispensable for this EET.] The differences between these two terms are correctly taken into account in $W^{(+)}$ in the rate constant k of eq 4.6 obtained by the new formula (2.9) for the rate constant of EET. In Förster's formula giving the rate constant k_F of eq 4.8 with $W_F^{(+)}$ of eq 4.9, on the other hand, these terms are estimated by an approximation of $\mathbf{R}_{AD}^{(2)} \approx \mathbf{R}_{AD}^{(2)} \approx \mathbf{R}_A$. Thus, they are approximately summed up into $W_F^{(+)}$ of eq 4.9, and they are erroneously regarded as nearly canceling each other because of near cancellation between $d_A^{(1)}$ and $d_A^{(2)}$ in $d_A^{(+)}$ given by $[d_A^{(1)} + d_A^{(2)}]/\sqrt{2}$.

Since both Hamiltonians $H_{e-p}^{(D)}$ and $H_{e-p}^{(A)}$ include the exciton–phonon interaction, both spectral functions $I_A(E)$ and $L_D(E)$ defined respectively by eqs 2.4 with eq 2.3 and eqs 2.7 with eq 2.6 should be composed of main peaks and phonon sidebands. Therefore, the new formula (2.9) describes also that EET can take place from main peaks in $L_D(E)$ to phonon sidebands in $I_A(E)$ at the same energy E between them. Such features have already been discussed for the EET from B800 to B850 within LH2 in the photosynthetic antenna system of purple bacteria, but in the framework of Förster's formula.^{16,23,24} The new formula describes also that EET can take place from sidebands in $L_D(E)$ to main peaks in $I_A(E)$ at the same energy E between them.

Matrix multiplication in eq 2.9 can be performed by any complete set of electronic excited states in the donor or the acceptor. An example can be found in eq 2.15 where matrix multiplication in $W_{AD} \cdot L_D(E)$ was performed by a set of exciton

states $|\psi_{\text{D}}^{(\mu)}\rangle$ for $\mu = 1, 2, \dots, M$ in the donor, not by a set of electronic excited states $|\varphi_{\text{D}}^{(i)}\rangle$ for $i = 1, 2, \dots, M$ localized at each chromophore in the donor. Which set of electronic excited states is most convenient depends on the physical situation in the donor or the acceptor. When the aggregate of the donor or the acceptor has a symmetric ring structure, as found in both LH1 and the inner ring of LH2, the most convenient seems a set of exciton states specified by wavenumbers (i.e., angular momenta) with respect to rotations around the ring axis. In this set, each exciton state has the same symmetry as a basis function of each irreducible representation for the rotation group composed of symmetry operations in the ring. Spectral functions $I_{\text{A}}(E)$ or $L_{\text{D}}(E)$ for the ring become diagonal with respect to wavenumbers, when they are represented on this set of exciton states. This property is very convenient in calculating the right-hand side of eq 2.9 since the total number of nonvanishing matrix elements in $I_{\text{A}}(E)$ and $L_{\text{D}}(E)$ is greatly reduced. This property was highly utilized in calculating the rate constant of EET from B800 to B850 within LH2 (the first example in section I) on the basis of the new formula (2.9), and acceptable values were obtained.³² It is expected that this property will be also effective in calculating the rate constant for the second example in section I.

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Appendix A. Fermi's Golden Rule

$H_{\text{e-p}}^{(\text{D})} + H_{\text{ph}}^{(\text{A})}$ constitutes the total Hamiltonian for the exciton-phonon system in the initial state of EET where the donor is electronically excited while the acceptor is electronically in the ground state. On the other hand, $H_{\text{ph}}^{(\text{D})} + H_{\text{e-p}}^{(\text{A})}$ constitutes that in the final state where the donor is electronically in the ground state while the acceptor is electronically excited. Let us write eigenstates and eigenenergies of $H_{\text{e-p}}^{(\text{D})} + H_{\text{ph}}^{(\text{A})}$ as $|\Psi_m\rangle$ and E_m , respectively, for $m = 1, 2, 3, \dots$. With these notations, $H_{\text{e-p}}^{(\text{D})} + H_{\text{ph}}^{(\text{A})}$ can be expressed as

$$H_{\text{e-p}}^{(\text{D})} + H_{\text{ph}}^{(\text{A})} = \sum_m |\Psi_m\rangle E_m \langle \Psi_m| \quad (\text{A.1})$$

Similarly, $H_{\text{ph}}^{(\text{D})} + H_{\text{e-p}}^{(\text{A})}$ be expressed by using its eigenstates $|\Phi_n\rangle$ and eigenenergies F_n for $n = 1, 2, 3, \dots$ as

$$H_{\text{ph}}^{(\text{D})} + H_{\text{e-p}}^{(\text{A})} = \sum_n |\Phi_n\rangle F_n \langle \Phi_n| \quad (\text{A.2})$$

Inserting eqs A.1 and A.2 into eq 2.10, and performing integrations in variables X and Y therein, we get

$$k = \frac{2\pi}{\hbar} \sum_m \sum_n |\langle \Phi_n | \mathbf{W}_{\text{A,D}} | \Psi_m \rangle|^2 \delta(F_n - E_m) e^{-\beta E_m} / \sum_{m'} e^{-\beta E_{m'}} \quad (\text{A.3})$$

This is nothing but the usual expression of the rate constant by Fermi's Golden Rule found in textbooks in quantum mechanics.

Appendix B. Green's Functions

An operator that creates an electronic excitation at the j th chromophore in the acceptor can be expressed as

$$a_j^\dagger = |\varphi_{\text{A}}^{(j)}\rangle \langle 0| \quad (\text{B.1})$$

where $\langle 0|$ represents the bra vector associated with the ket vector $|0\rangle$, which represents the vacuum state of electronic excitations. Accordingly, the annihilation operator for the electronic excitation can be expressed as

$$a_j = |0\rangle \langle \varphi_{\text{A}}^{(j)}| \quad (\text{B.2})$$

The electronic excitation created evolves in time under the influence of the Hamiltonian $H_{\text{e-p}}^{(\text{A})}$ for the exciton-phonon system in the acceptor. Therefore, the Heisenberg operator for describing the time (t) evolution of a_j is given by

$$a_j(t) = \exp(iH_{\text{e-p}}^{(\text{A})}t/\hbar) a_j \exp(-iH_{\text{e-p}}^{(\text{A})}t/\hbar) \quad (\text{B.3})$$

with $a_j(0) = a_j$. Since there exists no electronic excitation in $|0\rangle$, we have $H_{\text{e-p}}^{(\text{A})}|0\rangle = H_{\text{ph}}^{(\text{A})}|0\rangle$, where $H_{\text{ph}}^{(\text{A})}$ represents the Hamiltonian for phonons in the acceptor. This enables us to rewrite eq B.3 into

$$a_j(t) = \exp(iH_{\text{ph}}^{(\text{A})}t/\hbar) |0\rangle \langle \varphi_{\text{A}}^{(j)}| \exp(-iH_{\text{e-p}}^{(\text{A})}t/\hbar) \quad (\text{B.3}')$$

where $\exp(iH_{\text{ph}}^{(\text{A})}t/\hbar)|0\rangle = |0\rangle \exp(iH_{\text{ph}}^{(\text{A})}t/\hbar)$.

Usually, in text books,³¹ a retarded Green's function for transfer of an exciton from the j' th chromophore to the j th one in the acceptor is expressed as

$$\bar{G}_{jj'}^{(\text{A})}(t) = -i\theta(t)\text{Tr}^{(\text{ph})}\langle 0|a_j(t)a_{j'}^\dagger|0\rangle \exp(-\beta H_{\text{ph}}^{(\text{A})})/\text{Tr}^{(\text{ph})} \times \exp(-\beta H_{\text{ph}}^{(\text{A})}) \quad (\text{B.4})$$

Inserting eqs B.2 and B.3' into eq B.4, we see that the right-hand side of eq B.4 is the same as that of eq 3.1.

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