Electronic excitation transfer in clustered chromophore systems: Calculation of time-resolved observables for intercluster transfer

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A theoretical description is given for electronic excitation transport among interacting clusters of chromophores. Each cluster is a finite volume system with a limited number of chromophores. At high cluster concentration, intercluster transfer will become significant. The theory is based on a first-order cumulant approximation of the solution to the transport master equation. $G^s(t)$ the probability of finding the excitation on the initially excited chromophore is calculated. The problem is first solved for two clusters at fixed separations. This result is extended to many clusters and then to the thermodynamic limit of an infinite number of clusters in an infinite volume. An example calculation is performed of excitation transport among chromophores on the surfaces of interacting micelles. For realistic parameters characterizing the system octadecylrhodamine B (chromophores) in Triton X-100 micelles, it is found that intermicelle excitation transfer can compete with intramicelle transfer. For an isolated micelle–chromophore system (chromophores on the surface of a sphere), a new time domain expression for $G^s(t)$ is obtained.

I. INTRODUCTION

During the past ten years, electronic excitation transport among molecules distributed in finite volumes has been an area of active study, both theoretically[1-9] and experimentally.[5,10-12] Since the transfer rate of an excitation from one molecule to another depends on distance and orientation,[13] the limitations on system size introduce considerable complexity into the transfer dynamics. Molecules near the boundaries of a distribution experience a different environment than those near the center. Examples of such systems include chromophores distributed randomly throughout a micelle, chromophores on the surface of a micelle, and isolated polymer coils which are tagged with chromophores. The surface micelle system can be constructed with octadecylrhodamine B in Triton X-100 micelles;[5] the tagged polymer system by a copolymer consisting of methyl methacrylate and vinyl naphthalene subunits.[10]

Previous research has focused on excitation transport within single finite volumes. Geometries such as molecules randomly distributed in spheres,[1] infinite cylinders, and fractal pores,[4] as well as on the surface of spheres[5] and infinite planes[2] have been studied. These systems all share the common characteristic of being isolated; i.e., the micelles or tagged polymers are separated by a large enough distance that there is no intersystem interaction.

There are situations, however, where excitation transport from one clustered system to another can become important. For example, at very low concentrations of tagged polymer chains in a solid polymer blend, the tagged chains are isolated and only intrachain transport occurs.[12] Observation of intrachain transport has provided detailed information on chain structure.[10,12] At higher concentrations, particularly in an incompatible blend, microphase separation will occur, i.e., the tagged chains will aggregate.[14] Microphase separation results in interchain excitation transfer which causes the overall rate of transfer to increase.[12] Analysis of the time and concentration dependence of the interchain transfer should provide detailed information on the nature of microphase separated domains.[14,15] Another example, which is discussed in detail below, is a concentrated solution of micelles having chromophores on their surfaces.

Here we develop a generalized model for incoherent donor–donor transport among chromophores distributed in many finite volumes. Each finite system is a cluster of chromophores and thus has internal transport dynamics unique to its configuration. The centers of mass of the clusters are taken to be separated by small enough distances so that transport between clusters is significant. By this we mean that intercluster transfer dynamics occur on a time scale comparable to the excited state lifetime.

The time-dependent motion of an excitation within an ensemble of interacting chromophores can be characterized by the function $G^s(t)$.[16,17] $G^s(t)$ represents the self part of the Green's function solution to the transport master equation.[16] Its physical meaning is the probability that an initially excited molecule is still excited at time t. $G^s(t)$ does not contain the excited state lifetime decay. It does include transfer events in which the excitation leaves the initial site and later returns.

The usefulness of $G^s(t)$ lies in its relationship to the observables measured in time-resolved depolarization experiments. A polarized excitation of an ensemble of randomly oriented chromophores results in a photoselective excited state. Only chromophores with the appropriate transition dipole vectors can be excited. Transfer to surrounding molecules, which are randomly oriented, and subsequent relaxation of the excited state lead to depolarization of the observed fluorescence.[18,19] $G^s(t)$ can be studied in this way provided that other depolarization processes (such as molecular rotation) occur on a slower time scale.

In the following development, it is necessary to work with complicated molecular distribution functions. We employ a cumulant expansion method developed by Huber[20]

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for infinite three-dimensional isotropic systems which was later extended to finite volume systems by Petersen and Fayer.[1] The interaction between a donor (initially excited molecule) and its identical neighbors can be approximated by performing a pairwise configurational average over acceptors (initially unexcited, but otherwise identical molecules). This leads to a power series in the density of acceptor molecules which is truncated to first order. The major advantage of the cumulant method is that it provides a mathematically tractable form for systems with complicated distributions.

We separate $G^s(t)$ into two contributions $G^s_{on}(t)$ and $G^s_{off}(t)$. $G^s_{on}(t)$ describes transport "on" the cluster which contains the initial excitation. This problem has been treated in detail previously.[1] $G^s_{off}(t)$ describes forward and back transfer among the initially excited cluster and other clusters. First, transfer between a pair of clusters and a fixed distance is analyzed. $G^s_{off}(t)$ is obtained as an average over all possible configurations of chromophores on the two clusters. The result is then averaged over the intercluster separation and the thermodynamic limit is obtained for the interaction of the initially excited cluster with neighboring clusters. We refer to this approach as the "effective chromophore method." The details of the cluster structure and possible chromophore locations are contained in the cluster–cluster pair $G^s_{off}(t)$. Once $G^s_{off}(t)$ for the pair of clusters has been obtained, the problem appears like transfer between a pair of "effective chromophores" as long as cluster excluded volume is properly incorporated when necessary. $\langle G^s_{off}(t)\rangle$ is then calculated as an average over the ensemble of effective chromophores.

This paper is organized in the following manner: In Sec. II, we briefly review the cumulant method and discuss its applications to finite volumes. In Sec. III, a general technique to model multiple cluster systems is developed; this is then applied in Sec. IV to the specific problem of chromophores randomly distributed on the surfaces of spheres (a model of micelles in concentrated solutions). Section V concludes with a discussion of the relationship between these calculations and measurements in real systems.

II. THE FIRST-ORDER TRUNCATED CUMULANT APPROXIMATION

In this section, we follow the methods of Huber[20] and of Blumen[8] to derive the ensemble averaged decay of excitation probability of a donor molecule surrounded by a random distribution of acceptors. (Here "donor" means the initially excited molecule. The "acceptors" are the unexcited, but otherwise identical molecules. The donor–acceptor transfer rate constant is equal to the acceptor–donor rate constant.) In order to establish the notation and to show the logical extension of infinite volume systems to finite volume systems, we repeat the initial steps of Blumen in Ref. 8. The donor is placed at the origin of a lattice. The probability that a nearby lattice site is occupied by an acceptor is p. Assuming that there is no cooperativity involved in site occupation, the probability of obtaining a particular configuration $K_{n,m}$ of n acceptors distributed in N lattice sites is

$$P(K_{n,m}) = p^n(1-p)^{N-n}. \tag{2.1}$$

The index m counts the number of ways of obtaining the configuration $K_{n,m}$:

$$1 \leqslant m \leqslant \binom{N}{n}.$$

We next introduce the two-particle approximation. The excitation decay of the donor molecule due to an acceptor at site j, $E_j(t)$, is assumed to be unaffected by the presence of an acceptor at some other site. This allows us to reduce the n-particle problem of the donor decay to a superposition of two-particle problems. The total decay function, therefore, is a product of the independent two-particle decays

$$Gs(K_{n,m};t) = \prod_{j \in K_{n,m}} E_j(t). \tag{2.2}$$

For the case of Förster dipole–dipole interactions, the transfer rate is given by[13]

$$E_j(t) = 1/2\{1 + \exp[(-2t/\tau)(R_0/r_j)^6]\}. \tag{2.3}$$

In Eq. (2.3), τ is the excited state fluorescence lifetime and R_0 is the Förster critical transfer radius. This radius depends on the magnitudes on the electronic transition dipoles of the donor and acceptor chromophores. It is defined as the separation between the acceptor and donor when the excitation probability decays to 0.5 in one lifetime. The quantity of interest is the ensemble average of $G^s(t)$:

$$\langle G^s(t)\rangle = \sum_{n,m} G^s(K_{n,m};t)P(K_{n,m}). \tag{2.4}$$

After substituting Eq. (2.1) and (2.2) into Eq. (2.4), we obtain the expression

$$\langle G^s(t)\rangle = \sum_{n=0}^{N} \sum_{m=1}^{\binom{N}{n}} \prod_{i \in K_{n,m}} E_i p \prod_{i \in \bar{K}_{n,m}} (1-p). \tag{2.5}$$

It can be shown that the above equation is equivalent to

$$\langle G^s(t)\rangle = \prod_{i=1}^{N} [1 - p + pE_i(t)]. \tag{2.6}$$

A Taylor expansion of the logarithm yields a power series in the site occupancy

$$\ln\langle G^s(t)\rangle = \sum_{i=1}^{N} \ln\{1 - p[1 - E_i(t)]\}$$
$$= -\sum_{i=1}^{N} \sum_{k=1}^{\infty} (p^k/k)[1 - E_i(t)]^k. \tag{2.7}$$

Equation (2.7) is an exact expression for the two-particle model proposed above. The advantage of the binomial distribution of acceptors (2.1) is that the number of acceptors in any local region is not strictly fixed. That is, the configurational average done in Eq. (2.4) accounts for all possible local distributions about any given donor position. The density of acceptors may thus vary from one region to another. This is a necessary requirement when dealing with restricted geometries.

At low acceptor concentrations, the lattice site occupancy is small. In this case, only the first-order term of the k summation in Eq. (2.7) is retained and the summation over lattice points can be replaced by an integration over space.

The discrete lattice positions are modeled by a continuous distribution function $u(\mathbf{r})$. Thus,

$$\ln\langle G^s(t)\rangle = -\rho/2 \int_{\text{space}} \{1-\exp[(-2t/\tau)(R_0/r)^6]\} \times u(\mathbf{r})d\mathbf{r}. \quad (2.8)$$

Here a local number density of acceptors ρ replaces the site occupancy p. For a random distribution of chromophores in an infinite volume, Eq. (2.8) yields an analytical expression which has been shown to be a very accurate approximation.[1,2,16]

The vector distribution $u(\mathbf{r})$ is defined such that $\rho u(\mathbf{r})d\mathbf{r}$ is the fraction of acceptors in the region between $\mathbf{r}$ and $\mathbf{r}+d\mathbf{r}$. For finite volume systems, this distribution will generally be significant near the location of the donor, but will approach zero for distances far away. In addition, restricted distributions could have discontinuities in the angular or radial components of $\mathbf{r}$. The normalization condition is

$$\rho\int_{\text{space}} u(\mathbf{r})d\mathbf{r} = (N-1), \quad (2.9)$$

where N is the total number of chromophores (donor and acceptors) within the finite volume.

Equation (2.8) describes the excitation decay of a single donor molecule interacting with a distribution of acceptors. In general, for a finite volume or nonrandom system, there is a distribution of nonequivalent donor sites $\sigma(\mathbf{r}_d)d\mathbf{r}_d$ and the acceptor distribution is a parametric function of the donor position. Thus, $u(\mathbf{r})d\mathbf{r} = u(\mathbf{r}_a;\mathbf{r}_d)d\mathbf{r}_a$ and the left-hand side of Eq. (2.8) should read $\ln\langle G^s(t;\mathbf{r}_d)\rangle$. Any experimental observable must therefore be related to the average of Eq. (2.8) over the ensemble of donor positions[1,2]

$$\langle G^s(t)\rangle = 1/V_d \int_{\text{space}} \langle G^s(t;\mathbf{r}_d)\rangle\sigma(\mathbf{r}_d)d\mathbf{r}_d,$$

$$\langle G^s(t;\mathbf{r}_d)\rangle = \exp\Big(-[(N-1)/2V_a] \times\int_{\text{space}} \{1-\exp[(-2t/\tau)(R_0/\mathbf{r}_a)^6]\} \times u(\mathbf{r}_a)d\mathbf{r}_a\Big). \quad (2.10)$$

In Eq. (2.10), the constants V_a and V_d are the volumes occupied by the acceptor and donor distributions, respectively.

Examination of Eq. (2.10) reveals that the long time limit of $\langle G^s(t)\rangle$ approaches $\exp[-(N-1)/2]$. This is contrary to the physically correct answer $1/N$. For an N particle system at infinite time, the excitation probability is equalized among the particles. The problem of correcting the asymptotic behavior ($t\to\infty$) of $\langle G^s(t)\rangle$, thereby improving the long time accuracy ($t\approx 2$ lifetimes), will be dealt with in Sec. V.

III. MULTIPLE CLUSTER SYSTEMS

Consider a system of n chromophore clusters, labeled $i = 1,2,3,\ldots,n$. We identify two components responsible for the decay of excitation probability of a single excited donor molecule in one of the i clusters, $G^s_{\text{off}}(t)$ and $G^s_{\text{on}}(t)$. $G^s_{\text{on}}(t)$ is the decay due to transport within the cluster containing the donor chromophore, while $G^s_{\text{off}}(t)$ is the decay due to transfer to chromophores on other clusters. In Appendix A, we show that within the context of the first-order cumulant approximation $G^s(t) = G^s_{\text{on}}(t)G^s_{\text{off}}(t)$. Hence, the calculation of a multiple cluster problem is reduced to the calculation of $G^s_{\text{off}}(t)$; the single cluster behavior can be factored out and calculated separately.

The factorization of $G^s(t)$ into G^s_{off} and G^s_{on} is a consequence of the two particle approximation inherent in the first-order cumulant expansion. In other contexts, the two particle approximation has been found to be accurate, e.g., for infinite random systems, the first-order cumulant treatment of Huber[20] gives the same results as the Gochanour–Andersen–Fayer (GAF) theory,[16] in spite of the fact that the GAF theory includes an infinite number of pathways among an infinite number of particles. This has been verified experimentally as has the accuracy of the first-order cumulant treatment of excitation transport on finite polymer chains lightly tagged with chromophores. Under the appropriate physical situations, G^s_{on} will decay on a faster time scale than G^s_{off}. The excitation probability will become delocalized within the donor cluster prior to excitation transport to other clusters. In this case, the separation of G^s into G^s_{on} and G^s_{off} is strictly valid.

A. Calculation of $G^s_{\text{off}}(t)$ for a pair of clusters

The cumulant method employs the averaging of two-molecule interactions between a donor located at position $\mathbf{r}_1$ and a distribution of acceptors which we now define as $P_a(\mathbf{r}_2)$. We construct a multiple frame coordinate system (see Fig. 1). The origin of frame 1 is placed at the center of mass of the cluster containing the donor, while the origin of frame 2 coincides with the center of mass of an acceptor cluster. The separation vector $\mathbf{R}$ joins the origins of the two frames. A third coordinate system (frame 12) has its origin at the position of the donor molecule. For a specified donor position $\mathbf{r}_1$, and cluster separation $\mathbf{R}$, a linear transformation of coordinates ($\mathbf{r}_2 = A\mathbf{r}_{12} = \mathbf{r}'_{12}$) leads to an expression for the acceptor distribution in terms of the donor position. Thus, $P_a(\mathbf{r}_2) = P_a(\mathbf{r}'_{12})$. In Appendix B, we show in detail

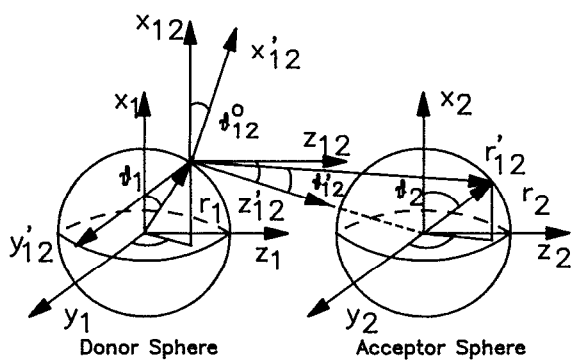

FIG. 1. Multiframe coordinate system showing the transformations necessary to express $P(\mathbf{r}_2)$ in terms of the vectors $\mathbf{r}_1$ and $\mathbf{r}_{12}$ for a given separation $\mathbf{R}$. For spherical shell distributions $|\mathbf{r}_2|$ is a function of only the angles θ'_{12} and θ_1.

how this is done for the general case of asymmetric clusters and the simplified cases of spherically symmetric clusters. The configurational average over acceptors is then performed with respect to the position of the donor molecule

$$\ln\langle G^s_{\text{off}}(t,\mathbf{R};\mathbf{r}_1)\rangle = [(N-1)/2V_a] \times \int_{\text{space}} \{\exp[(-2t/\tau)(R_0/r'_{12})^6] - 1\} \times P_a(\mathbf{r}'_{12})d\mathbf{r}_2, \tag{3.1}$$

where N is the number of interacting molecules under consideration (single donor on the donor cluster and $N-1$ acceptors on the acceptor cluster), V_a is the volume occupied by the acceptor cluster, and τ and R_0 are parameters defined in Eq. (2.8). The vector integral in Eq. (3.1) is converted into a triple integral over the spherical components of $\mathbf{r}_2$ according to

$$\int_{\text{space}} d\mathbf{r}_2 = \int\int\int r_2^2 \sin(\theta_2) dr_2\, d\theta_2\, d\phi_2.$$

Since Eq. (3.1) is an explicit function of $\mathbf{r}_1$, an additional average over the donor position must be performed

$$\langle G^s(t,R)\rangle = 1/V_d \int\int\int \langle G^s(t,R;r_1,\theta_1,\phi_1)\rangle \times P_d(r_1,\theta_1,\phi_1) dr_1\, d\theta_1\, d\phi_1. \tag{3.2}$$

B. $G^s_{\text{off}}(t)$ in the thermodynamic limit

Equation (3.2) is the probability of finding a molecule in the donor distribution excited at time t in the presence of an acceptor distribution centered at $\mathbf{R}_i$. We, however, are interested in the decay function due to many acceptor clusters. For a distribution of n clusters defined by the set of coordinates $\{\mathbf{R}_i\}$,

$$G^s_{\text{off}}(t,n) = G^s(t,\mathbf{R}_1)G^s(t,\mathbf{R}_2)G^s(t,\mathbf{R}_3)\cdots G^s(t,\mathbf{R}_n) = \prod_{i=1}^{n} G^s(t,\mathbf{R}_i). \tag{3.3}$$

In a macroscopic sample, the number of clusters is large. Any measured observable would correspond to a statistical average of Eq. (3.2) over an infinitely large number of clusters. Assuming all clusters are identical in geometry (but not in the locations of the chromophores in the clusters), the finite distribution $\{\mathbf{R}_i\}$ is replaced by a weighted average over the continuous separation variable R. Given a radial distribution function $g(R)$ describing the spatial proximity of donor–acceptor cluster pairs, the expression in the thermodynamic limit for excitation transport between clusters in a solution with cluster concentration c is[21]

$$G^s_{\text{off}}(t,c) = \lim_{\substack{n\to\infty \\ V\to\infty \\ N/V\to c}} \left[\int_0^{R_v} g(R)G^s(t,R)dR \quad \int_0^{R_v} g(R)dr\right]^n, \tag{3.4}$$

where $R_v = (3n/4\pi c)^{1/3}$ and $V = \int_0^{R_v} g(R)dR$.

The integration in Eq. (3.4) is carried out over a large enough volume to contain a macroscopic number of clusters. For a random distribution of clusters $g(R)dR = 4\pi R^2 dR$. Equation (3.4) becomes

$$G^s_{\text{off}}(t,c) = \exp\left\{-4\pi c\int_0^{R_v} [1 - G^s_{\text{off}}(t,R)]R^2 dR\right\}. \tag{3.5}$$

Equation (3.5) is the decay of a solution of clusters with concentration c. In deriving Eq. (3.5), it was assumed that all clusters have the same shape so that the functions $G^s_{\text{off}}(t,R_i)$ can be explicitly written only as a function of cluster separation R and orientation Ω. In this way, a cluster to cluster $G^s_{\text{off}}(t)$ can be obtained by performing a radial and an angular configurational average. For clusters with a distribution of shapes, an explicit average over shapes could be performed, or the average shape could be used as a reasonable approximation. Once a functional form for $G^s(t,R,\Omega)$ has been found for two clusters, a basis for treating a solution of interacting clusters is established. The concentrations in Eq. (3.5) are in units of (number of clusters)/(cluster diameter).[3] For the micelle system discussed below, the meaning of the diameter is clear. For an ensemble of polymer coils, e.g., the diameter would be twice the root-mean-square radius of gyration.[15]

IV. CALCULATIONS FOR CHROMOPHORES DISTRIBUTED ON SPHERICAL SURFACES

In this section, the theory developed above is applied to the specific example of chromophores randomly distributed on the surfaces of spheres. This system lends itself to the above formulation for the following reasons: spherical distributions are relatively simple. The symmetry properties of spheres allow the transformations described in Appendix B to be carried out such that the resulting expressions for $G^s_{\text{off}}(t)$ are computationally straightforward. Most important, this model mimics a particularly useful experimental system. As mentioned previously, energy transport among dye molecules distributed on the surfaces of noninteracting micelles has been successfully studied by other workers.[5] The surfactant molecules used in these studies, Triton X-100 are known to form essentially monodispersive, approximately spherical shaped micelles in water.[22] In addition, these homogeneous, isotropic solutions remain in the mesotropic phase, even at high concentrations.[23]

A. The two sphere problem

In deriving $G^s(t;R)$ from Eqs. (3.1) and (3.2), we model both the donor and acceptor distributions as radially dependent delta functions

$$P_d(\mathbf{r}_1)=\delta(r_1-\rho)=\begin{cases}0, & \text{if } r_1\neq\rho\\ \infty, & \text{if } r_1=\rho,\end{cases}\quad\int_0^\infty\delta(r_1-\rho)dr_1=1/4\pi\rho^2=1/V_d,$$
$$P_a(\mathbf{r}_2)=\delta(r_2-\rho)=\begin{cases}0, & \text{if } r_2\neq\rho\\ \infty, & \text{if } r_2=\rho,\end{cases}\quad\int_0^\infty\delta(r_2-\rho)dr_2=1/4\pi\rho^2=1/V_a. \tag{4.1}$$

In Eq. (4.1), the "volumes" of the distributions are the surface areas of spheres with radius ρ. Substitution of Eq. (4.1) into Eqs. (3.1) and (3.2) and omission of the brackets indicating a configurational average results in

$$G^s(t;R)=\frac{1}{V_d}\int_{r_1}\int_{\theta_1}\int_{\phi_1} r_1^2\sin\theta_1\delta(r_1-\rho)dr_1\,d\theta_1\,d\phi_1$$
$$\times\exp\left[\frac{(N-1)}{2V_a}\int_{r_2}\int_{\theta_2}\int_{\phi_2}\{\exp\{-2[R_0/r'_{12}(\theta'_{12},\theta_1)]^6t/\tau\}-1\}\delta(r_2-\rho)r_2^2\sin\theta_2\,dr_2\,d\theta_2\,d\phi_2\right]. \tag{4.2}$$

The function $r'_{12}(\theta'_{12},\theta_1)$ is obtained by performing the coordinate transformation $\mathbf{r}_2\rightarrow\mathbf{r}'_{12}$ (see Appendix B) and then finding the subsequent roots of the argument of the δ function in r_2. In this way, the radial dimension of Eq. (4.2) can be eliminated. In addition, it is necessary to express the angle θ_2 in terms of the integration variable θ'_{12}:

$$G^s(t;R)=\frac{1}{2}\int_{\theta_1}\sin\theta_1\,d\theta_1\exp\left[\frac{(N-1)}{4}\right.$$
$$\times\int_{\theta_2}(\exp\{-2[R_0/r'_{12}(\theta'_{12},\theta_1)]^6t/\tau\}-1)$$
$$\left.\times\sin\theta_2\,d\theta_2\right], \tag{4.3a}$$
$$\theta_2=\theta'_{12}+\arcsin(r^0_{12}\sin\theta'_{12}/\rho)$$
$$-\arcsin(\rho\sin\theta_1/r^0_{12}), \tag{4.3b}$$
$$d\theta_2=\left\{1+\frac{r^0_{12}\cos\theta'_{12}}{\rho[1-(r_{12}\sin\theta_{12}/\rho)^2]^{1/2}}\right\}, \tag{4.3c}$$

where

$$r^0_{12}=(\rho^2+R^2-2R\rho\cos\theta_1)^{1/2}, \tag{4.3d}$$
$$r'_{12}(\theta'_{12},\theta_1)=\cos\theta'_{12}(\rho^2+R^2-2R\rho\cos\theta_1)^{1/2}$$
$$\pm[\cos\theta'_{12}(\rho^2+R^2-2R\rho\cos\theta_1)$$
$$-(R^2+2R\rho\cos\theta_1])^{1/2}. \tag{4.4}$$

Equation (4.4) exhibits the correct limiting behavior as a function of sphere separation R. For large separations, the linear dependence of r'_{12} on R leads to behavior of the decay (4.3a) consistent with that of a single donor molecule interacting with a single effective acceptor. Under these circumstances, there is little decay on the time scale of fluorescence. As $R\rightarrow 0$, however, the nontrivial solution of Eq. (4.4) approaches $\cos\theta'_{12}$. In this case, the inner integral of Eq. (4.3) is not a function of the donor position θ_1 and the outer integral can be performed independently. The result is the decay expected from transport among chromophores distributed on the surface of a single sphere

$$G^s(t;0)=\exp\Big((N-1)$$
$$\times\int_0^{\pi/2}\{\exp[-2(R_0/2\rho\cos\theta'_{12})^6t/\tau]-1\}$$
$$\times\cos^2\theta'_{12}\sin\theta'_{12}d\theta'_{12}\Big). \tag{4.5}$$

Equation (4.5) has an analytical solution

$$G^s(t;0)=\exp\left\{\frac{(N-1)}{2}[\mu^{1/3}\gamma(2/3,\mu)-\mu^{1/3}\Gamma(2/3)\right.$$
$$\left.+\exp(-\mu)-1]\right\}, \tag{4.6}$$

where $\mu=2Q^6t/\tau$, $Q=(R_0)2\rho$, and $\Gamma(2/3)=1.354\,117\,94$. $\Gamma(x)$ and $\gamma(a,x)$ are the complete and incomplete Euler gamma functions, respectively, defined by

$$\Gamma(a)=\int_0^\infty e^{-t}t^{a-1}dt\quad\text{and}\quad\gamma(a,x)=\int_0^x e^{-t}t^{a-1}dt.$$

It is interesting to examine the limiting behavior of Eq. (4.6) as a function of sphere radius. When the sphere radius is large in comparison to R_0, energy transport only occurs between chromophores within a local section of the sphere surface. In the limit of infinite sphere radius, the transport behavior should look like that of an infinite planar surface with a chromophore density δ equal to the total number of chromophores on the sphere divided by the total surface area of the sphere. The equation describing energy transport on an infinite two-dimensional surface is given by[2]

$$G^s_{2\text{dim}}=\exp[-\delta\pi R_0^2 2^{-2/3}\Gamma(2/3)(t/\tau)^{1/3}]. \tag{4.6a}$$

After rewriting the density in terms of the sphere radius contained in μ and the total number of chromophores on the sphere,

$$G^s_{2\text{dim}}(t)=\exp\left\{\frac{(N-1)}{2}[-\mu^{1/3}\Gamma(2/3)]\right\}. \tag{4.6b}$$

As the sphere radius grows large, μ becomes very small and the following approximations can be made in Eq. (4.6)[24]:

$$\exp(-\mu)-1\approx-\mu+\mu^2/2-\mu^3/6+\cdots,$$
$$\mu^{1/3}\gamma(2/3,\mu)\approx 3\mu/2-3\mu^2/5+3\mu^3/16-\cdots.$$

In the large sphere limit, μ is a number much less than 1. Therefore the lowest order term $\mu^{1/3}\Gamma(2/3)$ dominates the behavior of Eq. (4.6) in this range. Equation (4.6) then, is identical to the infinite two-dimensional system (4.6a) in the large sphere limit.

B. The two sphere problem in the thermodynamic limit

To extend Eq. (4.3) to a realistic description of the micelle solution as a function of micelle concentration, the effect of volume excluded by the micelles must be considered. The thermodynamic limit given by Eq. (3.5) must be modified to allow for volume exclusion.[8,25] This is essentially the same problem developed in Sec. II for the interactions of particles which are binomially distributed over the points of a lattice. In this case, however, the lattice spacing is set equal to the micelle diameter. Replacing the particle–particle interaction term $E_i(t)$ with the intercluster term $G^s_{\text{off}}(t,R_i)$ in Eq. (2.7),

$$\ln\langle G^s_{\text{off}}(t)\rangle = -\sum_{k=1}^{\infty}\sum_{i=1}^{N}(p^k/k)\left[1-G^s_{\text{off}}(t;R_i)\right]^k. \tag{4.7}$$

In converting the sum over the discrete lattice points R_i to an integration over the continuous variable R, we do not consider distances smaller than the micelle diameter d_m. The site occupancy p is the probability that a lattice cell contains a micelle and is related to the micelle concentration by $p = c(d_m)^3$. The analog to Eq. (3.5) with a random distribution of micelles in solution is[8,25]

$$\ln\langle G^s_{\text{off}}(t,c)\rangle = -4\pi\sum_{k=1}^{\infty}\frac{(d_m)^{(3k-3)}ck}{k} \times\int_{d_m}^{\infty}\left[-G^s_{\text{off}}(t;R)\right]^k R^2 dR. \tag{4.8}$$

The donor–acceptor micelle excluded volume is taken care of by the lower limit of the integral in Eq. (4.8). The acceptor–acceptor excluded volume is related to the lattice site occupancy. Notice that acceptor–acceptor excluded volume only becomes important for terms in k higher than 1.

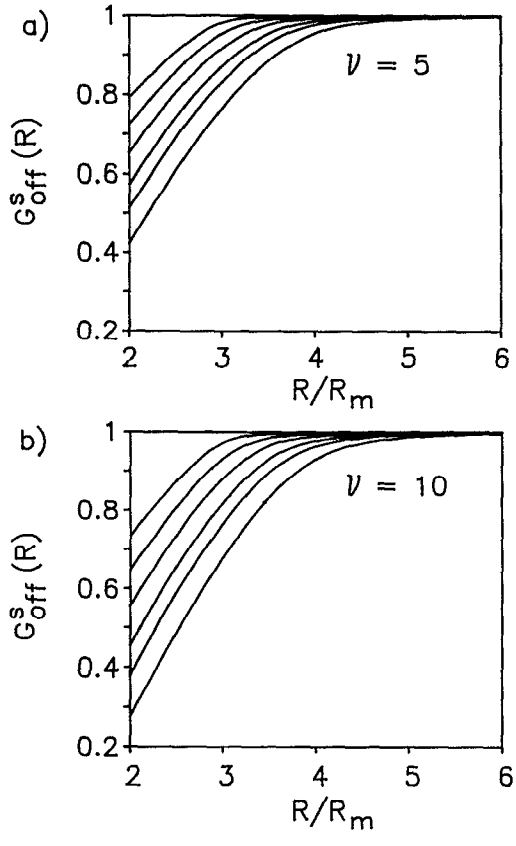

FIG. 2. G^s_{off} for chromophores distributed on the surfaces of two spheres [Eqs. (4.3) and (4.4)] is plotted as a function of sphere separation. Curves are shown for different times ranging from 0 to 2.0 lifetimes. The $t = 0$ curve is a horizontal line with a value at 1.0. Subsequently decreasing curves are for $t = 0.04$, 0.12, 0.28, 0.6, 1.0, and 2.0. ν is the Poisson averaged number of chromophores per sphere. For octadecylrhodamine B, $R_0 = 51.5$ Å. For Triton X-100 micelles, the micelle radius is $R_m = 37$ Å.

V. RESULTS AND DISCUSSION

Calculations were performed to obtain $G^s_{\text{off}}(t)$ for the Triton X-100 micelle/octadecylrhodamine B (ODRB) system as a function of micelle concentration. Previous excitation transport studies have determined the radius of the chromophore distribution (approximately the micelle radius) $R_m \approx 37$ Å and the Förster transfer distance for static ODRB molecules $R_0 \approx 51.5$ Å.[5] Equation (4.3) was numerically integrated using a Gaussian quadrature method for values of micelle separation ranging from zero to six R_m. Since the number of ODRB molecules per micelle are known to follow a Poisson distribution,[5] it is further necessary to weight $G^s(t;R)$ with respect to N:

$$G^s(N,R,t) = \sum_{N=0}^{\infty}\frac{N}{\nu}\left(\frac{e^{-\nu}\nu^N}{N!}\right)G^s(N,R,t), \tag{5.1}$$

where ν is the average number of chromophores per micelle. This was done for $\nu = 5$ and 10.

Figure 2 shows spline-fitted plots of G^s_{off} for a pair of micelles at several different values of t as a function of micelle separation. At all times greater than zero, the curves smoothly increase with the intermicelle separation. This is the same behavior one observes when increasing the distance between a pair of chromophores, i.e., the intermicelle excitation probability decay looks like the decay between two effective chromophores. It can be seen that no significant decay occurs for separations greater than $5.0R_m$ ($3.9R_0 = 200$ Å) during the time scale of interest (two excited state lifetimes). The effect of doubling the average number of chromophores per micelle is small at distances greater than $4.0R_m$ ($3.1R_0 = 160$ Å), but more pronounced at shorter distances. This is because all the chromophores on the acceptor sphere, regardless of how many are present, are outside the transfer range to all the chromophore positions on the donor sphere.

The intermicelle decays (Fig. 2) were numerically integrated with respect to the micelle separation according to Eq. (4.8), which accounts for excluded volume effects. The resulting functions represent the time decay of G^s_{off} due to intermicelle interactions for a micelle solution of concentration c. Figure 3 shows plots of these functions for several micelle concentrations ranging from 0.1% to 50.0%. The time dependence of $G^s_{\text{off}}(t)$ is strikingly different for different ranges of concentration. At low concentrations ($c = 0.1$–1.0%), $G^s_{\text{off}}(t)$ decays approximately linearly with time and only to a very small extent ($\sim 10\%$ at two lifetimes for the 1% solution). Here, chromophores on the acceptor spheres are mainly out of range of the excited chro-

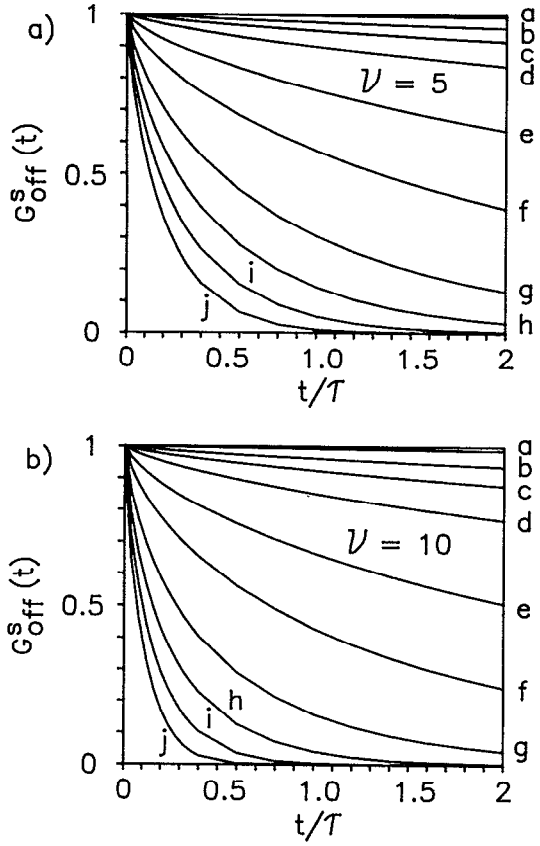

FIG. 3. $G^s_{off}(t)$ for a solution of interacting micelles [Eq. (4.8)] is plotted for several different concentrations: (a) 0.1%; (b) 0.5%; (c) 1.0%; (d) 2.0%; (e) 5.0%; (f) 10.0%; (g) 20.0%; (h) 30.0%; (i) 40.0%; (j) 50.0%. ν is the Poisson averaged number of chromophores per sphere. For octadecylrhodamine B, $R_0 = 51.5$ Å. For Triton X-100 micelles, the micelle radius is $R_m = 37$ Å.

mophores on the donor spheres. At intermediate concentrations ($c = 1.0\%$–5.0%), the short time decay is more pronounced and the long time decay can be as much as 40%. In these solutions, the average distance between micelles is on the order of a few R_0 and intermicelle transport is significant. At high concentrations ($c = 10\%$–50%), the average micelle center to center separation is between two and three R_0. Chromophores on acceptor spheres can interact with donor chromophores. The decay of G^s_{off} is steep at short times, while the long time decay can range from 50% to 100%. Comparison of the $\nu = 5$ and $\nu = 10$ plots shows that $G^s_{off}(t)$ scales approximately linearly with ν. That is, when ν is doubled, $G^s_{off}(t)$ has a similar functional form, but decays twice as fast.

The solution for an isolated micelle [Eq. (4.6)] was plotted for several values of N and compared to results obtained by Ediger and Fayer.[5] In this study, the authors used a second-order truncated density expansion of chromophores with a Padé approximant to solve the problem of chromophores distributed on the surface of a single sphere. Although the two theories agree well for short times, at longer times they can differ by as much as 20%. The Padé approximant used in the aforementioned theory has the effect of correcting the long time behavior of G^s within the limitations of the function's accuracy. The long time limits are forced to approach $1/N$. To correct the asymptotic behavior of the first-order cumulant theory, a (2/2) Pade approximant of Eq. (4.6) was constructed[26]

$$\ln G^s(t) = \frac{-(N-1)/2[\Gamma(2/3)]x}{1+(N-1)/2[1/2\Gamma(2/3]x^2}, \qquad (5.2)$$

where $x = \{2(R_0/2\rho)t\}^{1/3}$. Figure 4 shows a comparison of Eq. (5.2) with the results obtained by Ediger. The agreement is excellent, within 4%. Thus the first-order cumulant with a Padé gives an accuracy equivalent to a second-order density expansion with a Padé. The density expansion was checked against a numerical simulation and found to be accurate. Since the density expansion result is in Laplace space, a numerical inverse transform must be performed to obtain time–dependent decays. Therefore, the simple time domain expression (5.2) provides a considerable advantage.

As discussed in Sec. III, $G^s(t) = G^s_{on}(t)G^s_{off}(t)$. Since a fluorescence depolarization experiment will contain contributions from both intra- and intermicelle transport, detection of G^s_{off} is limited by the behavior of G^s_{on}. The situation can be analyzed in the limit of low, intermediate, and high micelle concentrations.

For low concentrations ($c = 0.1\%$–1.0%), chromophores within a single micelle are closer to one another than chromophores on neighboring micelles. G^s_{off} decays only slightly and follows an approximately linear form. This leads to a fluorescence depolarization indistinguishable from the single micelle decay at short times and deviating between 1.0% and 10% at long times. Since the single micelle decay reaches its asymptotic limit (between 0.5 and 0.07 in Fig. 4) at long times, the deviations at best border on the edge of detectability.

For intermediate concentrations ($c = 1.0\%$–5.0%), the micelle separations are on the order of a few R_0. Intramicelle randomization still occurs faster than intermicelle transfer, but the long time decay will deviate by as much as 40%.

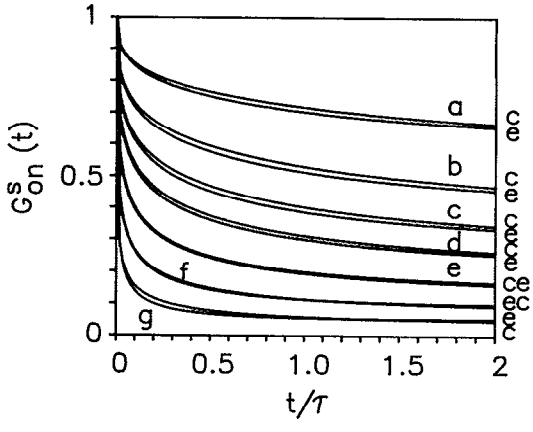

FIG. 4. A comparison of the cumulant solution of G^s_{on} [Eq. (5.2)] with the results obtained by Ediger and Fayer. Curves were generated for the following number of chromophores per micelle: (a) 2; (b) 3; (c) 4; (d) 5; (e) 7; (f) 10; (g) 15. For octadecylrhodamine B, $R_0 = 51.5$ Å. For Triton X-100 micelles, the micelle radius is $R_m = 37$ Å.

In the high concentration limit ($c = 10\%$–30%), the center to center separation is down to two or three R_0. G^s_{off} becomes a steeply decaying function at short times and asymptotically approaches zero at long times. This should be readily detectable. For example, in a 20% solution of micelles containing an average of five chromophores each, G^s_{off} will decay to 0.5 in 0.5 lifetimes. G^s_{on} will decay to 0.37 during this time and the decay of polarization will be 0.185. It is reasonable to expect to see this difference. On the other hand, for a 20% solution of micelles containing ten chromophores each, at 0.5 lifetimes the product of G^s_{off} (0.36) and G^s_{on} (0.14) will approach zero. Only the short time behavior can then be used to study the off-micelle transfer. A readily observable experimental situation would then be a concentrated solution of micelles ($5 < c < 20\%$), each containing an intermediate number of chromophores ($4 < N < 6$). Such solutions should be possible to prepare.[17,18]

The use of a Padé approximant to correct the asymptotic behavior of G^s_{on} could be extended to a correction of G^s_{off} [Eq. (4.3)] as well. However, since most of the useful information of G^s_{off} is contained in the short time region where the cumulant is most accurate, Eq. (4.3) can be considered a good approximation. The validity of this approximation, and the method in general, can be tested experimentally.

VI. CONCLUDING REMARKS

A method has been presented which makes use of the truncated cumulant approximation, introduced by Huber[20] and extended to finite volume systems by Peterson and Fayer,[1] to model the incoherent energy transport of molecules distributed among many interacting finite volumes. This is made possible by the mathematical tractability of the cumulant approximation.

The method was applied to the problem of Triton X-100 micelle solutions with octadecylrhodamine B probe molecules. The energy transport was taken to be donor donor (no traps). The extension to the donor-trap problem is straightforward.[2] An analytical result in the time domain was obtained for the excitation transfer dynamics of an isolated micelle. This was corrected with a Pade approximant which was found to agree with previous accurate calculations. Numerical calculations showed that the range of interaction between micelles is independent of the number of probe molecules and is approximately six times the micelle radius of $4.7R_0$ for this system. This corresponds to the average distance between micelles in a 3% solution. The concentration dependence of the interaction was calculated for the cases of five and ten chromophores on average per micelle. For randomly distributed Triton X-100 micelles with ODRB chromophores, intermicelle excitation transfer can have a significant influence on experimental observables at concentrations above a few percent.

The method could be useful in obtaining structural information from restricted systems such as energy transport of tagged copolymers in multicomponent polymer blends. In the calculations presented here, the micelles were taken to be randomly distributed. Nonrandom distributions will result in deviations from the predicted concentration dependence. If the micelles tend to aggregate, the onset of intermicelle transfer will occur at lower concentrations. In a polymer system or other systems in which there is aggregation of clusters, it should be possible to obtain information on the spatial distribution and the number of clusters in the aggregates.

ACKNOWLEDGMENTS

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APPENDIX A

We want to show for a multiple cluster system that the approximation

$$\langle G^s(t)\rangle = \langle G^s_{on}(t)\rangle\langle G^s_{off}(t)\rangle \tag{A1}$$

is consistent with the first-order cumulant approximation which includes only pairwise interactions. From Eq. (2.10),

$$\ln\langle G_s(t;\mathbf{r}_d)\rangle = -[(N-1)/2V_a] \times \int_{space}\{1-\exp[(-2t/\tau)(R_0/\mathbf{r}_a)^6]\} \times u(\mathbf{r}_a)d\mathbf{r}_a. \tag{A2}$$

The distribution of acceptor molecules can be written as

$$u(\mathbf{r}_a) = u_{on}(\mathbf{r}_a) + u_{off}(\mathbf{r}_a), \tag{A3}$$

so that

$$G^s(t;\mathbf{r}_d) = G^s_{on}(t;\mathbf{r}_d)G^s_{off}(t;\mathbf{r}_d). \tag{A4}$$

It remains to show that Eq. (A1) follows from Eq. (A4). We follow standard methods of probability theory.[27] Let α represent those events which lead to on-micelle transfer and β represent ones that lead to transfer off. Also, suppose $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$ are independent random vectors with distributions $P(\mathbf{r}_\alpha)$ and $P(\mathbf{r}_\beta)$, respectively. Then the real valued functions $G^s_\alpha(t;\mathbf{r}_\alpha)$ and $G^s_\beta(t;\mathbf{r}_\beta)$ are independent random variables. This means that there exists a function $G^s(t;\mathbf{r}_\alpha,\mathbf{r}_\beta) = G^s_\alpha(t;\mathbf{r}_\alpha)G^s_\beta(t;\mathbf{r}_\beta)$ and a joint distribution $P(\mathbf{r}_\alpha,\mathbf{r}_\beta) = P(\mathbf{r}_\alpha)P(\mathbf{r}_\beta)$. Thus,

$$\begin{aligned}\langle G^s_\alpha(t)\rangle\langle G^s_\beta(t)\rangle &= \int G^s_\alpha(t;\mathbf{r}_\alpha)P(\mathbf{r}_\alpha)d\mathbf{r}_\alpha \int G^s_\beta(t;\mathbf{r}_\beta)P(\mathbf{r}_\beta)d\mathbf{r}_\beta \\ &= \int\int G^s_\alpha(t;\mathbf{r}_\alpha)G^s_\beta(t;\mathbf{r}_\beta)P(\mathbf{r}_\alpha)P(\mathbf{r}_\beta)d\mathbf{r}_\alpha d\mathbf{r}_\beta \\ &= \int\int G^s(t;\mathbf{r}_\alpha,\mathbf{r}_\beta)P(\mathbf{r}_\alpha,\mathbf{r}_\beta)d\mathbf{r}_\alpha d\mathbf{r}_\beta = \langle G^s(t)\rangle.\end{aligned}$$

APPENDIX B

Here we show how the acceptor coordinate $\mathbf{r}_2$ is expressed as a function of the cluster separation $\mathbf{R}$ and the donor position $\mathbf{r}_1$. We choose reference frames 1, 2, and 12

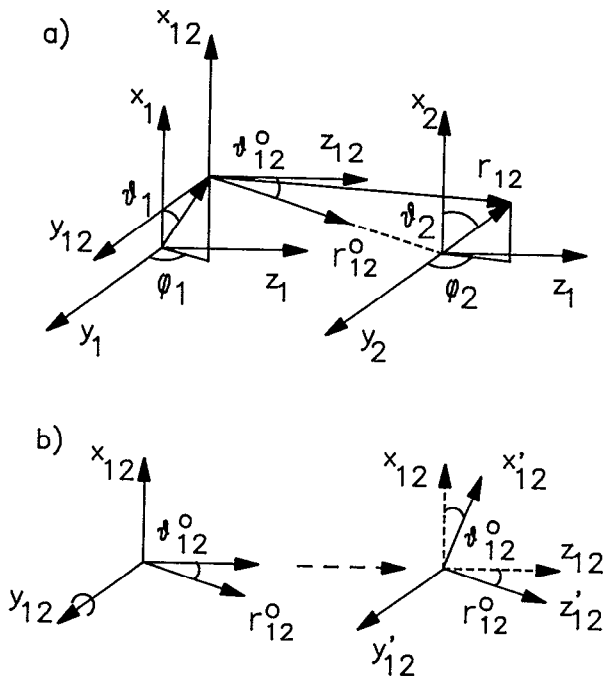

FIG. 5. A multiframe coordinate system showing the general relationship between the donor position $\mathbf{r}_1$, the acceptor position $\mathbf{r}_2$, and the donor–acceptor distribution separation $\mathbf{R}$. The vector $\mathbf{r}^0_{12}$ points from the origin of frame 12 to the origin of frame 2. (b) Frame 12′ is obtained by rotating frame 12 an angle θ^0_{12} about the y_{12} axis.

with the additional vectors $\mathbf{r}_2$, $\mathbf{r}_{12}$, and $\mathbf{r}^0_{12}$ as in Fig. 5. Apparently, $\mathbf{r}_2 = \mathbf{r}_{12} + \mathbf{r}_1 - \mathbf{R}$ and $\mathbf{R} = \langle 0, 0, R \rangle$. Breaking $\mathbf{r}_2$ into its components,

$$r_2 = r_{12x} + r_{1x}, \quad r_{2y} = r_{12y} + r_{1y}, \quad r_{2z} = r_{12z} + r_{1z} - R. \tag{B1}$$

The relationship between polar and cartesian coordinates is

$$r_x = r \sin\theta \cos\phi, \quad r_y = r \sin\theta \sin\phi, \quad r_z = r \cos\theta. \tag{B2}$$

Now assume the vectors $\mathbf{r}_1$ and $\mathbf{r}^0_{12}$ are both in the x–z plane.

Then $r_{1y} = 0$, $r^0_{12y} = 0$, and $r_{2y} = r_{12y}$. We next rotate frame 12 about the y_{12} axis so that the z_{12} axis is parallel to the vector $\mathbf{r}^0_{12}$ (Fig. 5). The rotation is given by

$$\mathbf{r}_{12} = B^{-1}\mathbf{r}'_{12}, \tag{B3a}$$

where B^{-1} is the matrix of direction cosines:

$$B^{-1} = \begin{pmatrix} B_{11} & B_{12} & B_{13} \\ B_{21} & B_{22} & B_{23} \\ B_{31} & B_{32} & B_{33} \end{pmatrix} = \begin{pmatrix} \cos\theta^0_{12} & 0 & -\sin\theta^0_{12} \\ 0 & 1 & 0 \\ \sin\theta^0_{12} & 0 & \cos\theta^0_{12} \end{pmatrix}, \tag{B3b}$$

where $\theta^0_{12} = \arctan(r_{1x}/r_{1z} - R)$.

Substitution of Eq. (B3) into (B1) gives

$$r_{2x} = B_{11}r'_{12x} + B_{31}r'_{12z} + r_{1x}, \tag{B4a}$$

$$r_{2y} = B_{22}r'_{12y}, \tag{B4b}$$

$$r_{2z} = B_{13}r'_{12x} + B_{33}r'_{12z} + r_{1z} - R. \tag{B4c}$$

Equations (B4) are the general relationship between the coordinates of an acceptor position and those of a specified donor position. The acceptor distribution $P_a(\mathbf{r}_2)$ can be written $P_a(r'_{12})$ and the integration over $\mathbf{r}_2$ is replaced with an integration over $\mathbf{r}'_{12}$. For the special case of spherically symmetric distributions, $P_a(\mathbf{r}'_{12})$ is independent of ϕ'_{12}. Then ϕ'_{12} can be set to zero and Eq. (B2) becomes

$$r'_{12x} = r'_{12}\sin\theta'_{12}, \quad r'_{12y} = 0, \quad r'_{12z} = r'_{12}\cos\theta'_{12} \tag{B5}$$

which in turn allows us to write Eq. (B4) as

$$r_{2x} = B_{11}r'_{12}\sin\theta'_{12} + B_{31}r'_{12}\cos\theta'_{12} + r_{1x}, \tag{B6a}$$

$$r_{2y} = 0, \tag{B6b}$$

$$r_{2z} = B_{13}r'_{12}\sin\theta'_{12} + B_{33}r'_{12}\cos\theta'_{12} + r_{1z} - R. \tag{B6c}$$

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