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Resonance energy transfer: The unified theory *via* vector spherical harmonics

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In this work, we derive the well-established expression for the quantum amplitude associated with the resonance energy transfer (RET) process between a pair of molecules that are beyond wavefunction overlap. The novelty of this work is that the field of the mediating photon is described in terms of a spherical wave rather than a plane wave. The angular components of the field are constructed in terms of vector spherical harmonics while Hankel functions are used to define the radial component. This approach alleviates the problem of having to select physically correct solution from non-physical solutions, which seems to be inherent in plane wave derivations. The spherical coordinate system allows one to easily decompose the photon's fields into longitudinal and transverse components and offers a natural way to analyse near-, intermediate-, and far-zone RET within the context of the relative orientation of the transition dipole moments for the two molecules. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4960732]

I. INTRODUCTION

Resonance energy transfer (RET) is the quantum mechanical process that involves an electronic excitation being exchanged between chromophores[1–3] and is a well known process in photosynthesis.[4] The key feature of RET is that the chromophores, which may be atoms, ions, molecules, or even engineered devices such as quantum wells,[5,6] are separated by distances that exceed any significant wavefunction overlap. Consequently, the process of RET is a specific case of the more general umbrella term "*electronic energy transfer*" (EET), which implicitly includes other forms of electronic energy migration, such as Dexter energy transfer, occurring through chemical bonds *via* a *super-exchange* mechanism,[7,8] and inelastic collisional processes that can involve changes of electronic states.[9]

Resonance energy transfer was discovered in 1923, by the spectroscopic observation of an excitation being transferred from mercury to thallium atoms in the gas phase.[10] Shortly after, early pioneers of the theory were able to describe the RET process adequately over a limited range of distances, both classically[11] and semi-classically.[12,13] However, a complete quantum mechanical description is necessary to describe the process. This is because the transfer of electronic energy between species occurs through the exchange of a photon, its properties being virtual at short distances and becoming real as the chromophore separation increases. Fundamentally, the RET process involves two field-matter interactions; emission of the photon at the exciton donor and absorption at the exciton acceptor and *vice versa* (as described by the two allowed Feynman diagrams).[14] Consequently the minimum level of theory required to describe the process is the *second order perturbation theory*. The theory includes the effect of

retardation, which is typically neglected in a semi-classical description. The mediating photon is *real* if the chromophore separation exceeds its reduced wavelength (i.e., $R \gg \lambda/2\pi$, where R is the distance of separation). If R is significantly less than the reduced wavelength, the photon is said to be *virtual*; emphasising the fact that it does not have well defined physical characteristics, limits of which are fundamentally imposed by the quantum uncertainty. The two limiting cases of RET are therefore sometimes referred to as *radiative* and *non-radiative*, respectively. In the case of the former (called *long-range* or *far-zone* energy transfer), there is a characteristic (Coulombic) R^{-2} dependence on the rate. On the other hand, *near-zone* RET has an R^{-6} dependence, originally identified with the Förster theory.[13] There is also a critical distance, called the intermediate-zone, where the distance separating the chromophores is of the order of the reduced wavelength of the mediating photon. The intermediate-zone has an R^{-4} dependence on the rate of RET.[2] Note that the rate of RET depends quadratically on the electronic coupling.

The most rigorous theory for describing light-matter interactions is *quantum electrodynamics* (QED). Because RET involves slowly moving electrons bound within valence states of the molecules, the *Coulomb gauge* is typically employed whenever the electromagnetic fields associated with the photon are considered explicitly. This variant of QED (as opposed to relativistic or Lorentz gauge QED) is sometimes referred to as molecular QED.[14,15] Central to all previous studies, which consider RET from a QED perspective, is that the description of fields associated with the mediating photon is cast in terms of a mode expansion based on

$$e^{i\vec{k}\cdot\vec{r}} = \sum_l \frac{\left(i\vec{k}\cdot\vec{r}\right)}{l!} = 1 + i\left(\vec{k}\cdot\vec{r}\right) - \frac{\left(\vec{k}\cdot\vec{r}\right)^2}{2} - \frac{i\left(\vec{k}\cdot\vec{r}\right)^3}{6} + \cdots$$

(1.1)

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The focus of the current work is to derive quantum amplitudes by considering the photon mode considered as a spherical wave centred on the emitter,

$$e^{i\vec{k}\cdot\vec{r}} = \sum_l i^l (2l+1) j_l(kr) P_l(\cos\vartheta). \qquad (1.2)$$

This is done using *vector spherical harmonics* and *Hankel functions*. Hankel functions are complex functions that are formed by the linear combinations of Bessel functions. As will be shown in this paper, describing the fields in this way enables us to avoid difficult contour integrations thereby alleviating the problem of having to choose the physically correct solutions from the non-physical solutions that arise in established plane wave approaches. The spherical wave approach leads to interesting physical insights regarding the nature of the photon, where it is inherently described as an outgoing wave when it is emitted from the donor and incoming as it approaches the exciton acceptor. The distinction emerges very clearly in the spherical wave approach but is less obvious in existing plane wave descriptions.

This work may have particular application in the development of materials that can facilitate energy transfer up to distances over several nanometers.[16,17] The approach has the potential to lead to new physical insights related to the role of relative orientation of chromophores in the energy transfer process, and may also be applicable to the field of near-field quantum optics where emerging technologies such as nanoantennas are currently of interest.[18–22]

II. BACKGROUND THEORY

A. Resonance energy transfer derived from QED

The fundamental theory behind the quantum mechanical description of RET is the Power-Zienau-Woolley formalism of molecular QED, which utilizes the Coulomb gauge, $\nabla \cdot \vec{A} = 0$, where fields of the mediating photons can be naturally deconstructed into longitudinal and transverse components.[23–25] The longitudinal components, with respect to the displacement vector $\vec{R}$, are associated with the scalar potential and have a particular affinity for coupling molecular transition moments in the near-zone. In regions far from sources (i.e., away from the donor chromophore), the wavevector $\vec{k}$ and $\vec{R}$ become co-linear and the scalar potential becomes zero. In this case only the transverse parts of the field couple transition dipole moments of individual electronic species.[26,27] This has important implications for the spatial and temporal dynamics of excitons within molecular aggregates.[28,29]

Although the theory of RET can be linked to very early quantum mechanical studies (for example, see Ref. 30), it was in the 1960s that theoretical ideas became firmly established through the work of researchers such as Simpson,[31] McLone and Power,[32] and Avery.[33] Since then there have been numerous studies on the fundamental aspects of RET by a number of authors including Power, Craig, Thirunamachandran, Andrews and Salam, among others.[34–42]

A key result concerning the derivation described in this paper is that of Daniels *et al.*, published in 2003. They calculated the quantum amplitude by solving a Green's function using judicious substitutions within the integrals.[41] The quantum amplitude for RET between a donor and acceptor molecule, in the gas phase is given by

$$V_{ij}^{\pm}(k,\vec{R}) = \sigma_{ij}(k,\vec{R}) + i\tau_{ij}(k,\vec{R}), \qquad (2.1)$$

$$\sigma_{ij}(k,\vec{R})$$
$$= \frac{1}{4\pi\varepsilon_0 R^3} \{ (\cos kR + kR\sin kR)[\delta_{ij} - 3\hat{R}_i\hat{R}_j]$$
$$- k^2 R^2 \cos kR [\delta_{ij} - \hat{R}_i\hat{R}_j] \}, \qquad (2.1a)$$

$$\tau_{ij}^{\pm}(k,\vec{R})$$
$$= \frac{1}{4\pi\varepsilon_0 R^3} \{ \mp (\sin kR - kR\cos kR)[\delta_{ij} - 3\hat{R}_i\hat{R}_j]$$
$$\pm k^2 R^2 \sin kR [\delta_{ij} - \hat{R}_i\hat{R}_j] \}. \qquad (2.1b)$$

What is especially notable here is the fact that there is a choice of sign for the imaginary term. They suggested that the ambiguity of sign for this term signifies that $V_{ij}^{\pm}(k,\vec{R})$ describes both incoming and outgoing waves, accommodating thereby both time-ordered diagrams, as a correct quantum description should. However, the authors stress that it is unimportant which sign to ascribe to a particular process (photon absorption or emission), as only quantum amplitudes are physically relevant, and hence both terms contribute equally to the calculation.

B. Vector spherical harmonics and Hankel functions

In the subsequent derivation of the electronic coupling *via* a spherical wave description of the mediating photons, we make explicit use of both *vector spherical harmonics* and *Hankel functions*. The scalar spherical harmonics (SSHs) $Y_{JM}(\vartheta,\varphi)$ $(M = -J \ldots + J)$ are well-known functions utilised in numerous applications in the physical sciences. The arguments ϑ and φ represent latitude and longitude angles, respectively. The notation $Y_{JM}(\vartheta,\varphi)$ is common, but the Dirac's bra-ket formalism, $|J, M\rangle \equiv Y_{JM}(\vartheta,\varphi)$, is more convenient for our present purposes and we shall use it throughout this paper. SSHs form a complete orthonormal set and are eigenfunctions of the total orbital angular momentum operator, $\hat{J}$ and of its z-component. Each group of $2J+1$ functions having the same value of J and the different values of M form a basis for a $(2J+1)$-dimensional irreducible representation of the symmetry point group of all rotations, SO_3.

In the present context, where the quantized fields of the mediating photon are described by spherical waves, the set of spherical harmonics formed by the three functions, $|J, M\rangle$ with $J = 1$ and $M = 0, \pm 1$, are important. These are the unit spherical vectors often denoted by $\vec{e}_{JM}$ and written explicitly as $\vec{e}_{1\,-1}$, $\vec{e}_{1\,0}$ and $\vec{e}_{1\,+1}$. These are related to the unit Cartesian vectors by the following transformations:

$$|1, x\rangle = -\frac{1}{\sqrt{2}} \{|1, +1\rangle - |1, -1\rangle\}, \qquad (2.2a)$$

$$|1, y\rangle = \frac{i}{\sqrt{2}} \{|1, +1\rangle + |1, -1\rangle\}, \qquad (2.2b)$$

$$|1, z\rangle = |1, 0\rangle. \qquad (2.2c)$$

SSHs may be added according to the well-known rules for the coupling of quantum-mechanical angular momenta, and by coupling $|1, n\rangle$ with any other $|J, M\rangle$ we obtain functions called *vector spherical harmonics* (VSHs), $|J, l, M\rangle$. Methods for constructing these functions are described in many texts.[43,44] For convenience, the most direct method is concisely sketched here.

The VSH can be compactly written as

$$|J, l, M\rangle = \sum_m \sum_n \langle l1mn|JM\rangle \cdot |l, m\rangle |1, n\rangle, \quad (2.3)$$

where $\langle l1mn|JM\rangle$ are Clebsch-Gordan coefficients or Wigner $3j$ symbols. In accordance with the laws of addition of angular momenta in quantum mechanics, for $l \neq 0$, J can take only three values $l + 1$, l and $l - 1$. Consequently, for any SSH $|J, M\rangle$, three VSHs are obtained: $|l + 1, l, M\rangle$, $|l, l, M\rangle$ and $|l - 1, l, M\rangle$. An alternative and more common practice is to denote these three functions by $|J, J - 1, M\rangle$, $|J, J, M\rangle$ and $|J, J + 1, M\rangle$. When $l = 0$ we have only $|1, 0, M\rangle$ and when $J = 0$ just $|0, 1, 0\rangle$.

The $|J, l, M\rangle$ are also eigenfunctions $\hat{J}$ and $\hat{J}_z$,

$$\hat{J}|J, l, M\rangle = [J(J + 1)]^{1/2}\hbar|J, l, M\rangle, \quad (2.4)$$

$$\hat{J}_z|J, l, M\rangle = M\hbar|J, l, M\rangle. \quad (2.5)$$

They also form a complete orthonormal set,

$$\langle J, l, M|J', l', M'\rangle = \delta_{J,J'}\delta_{l,l'}\delta_{M,M'}, \quad (2.6)$$

with

$$\langle J, l, M| = |J, l, M\rangle^* = (-1)^{l+J+M+1}|J, l, -M\rangle. \quad (2.7)$$

When employing VSHs to describe electromagnetic radiation, the functions $|J, l, M\rangle$ may be divided into two classes:[43]

1. $|J, J, M\rangle$ with parity $(-1)^J$ describe the *magnetic* field of *electric* multipole radiation and the *electric* field of *magnetic* multipole radiation.
2. $|J, J \pm 1, M\rangle$ with parity $(-1)^{J+1}$ describe the *electric* field of *electric* multipole radiation and the *magnetic* field of *magnetic* multipole radiation.

The VSHs, like the SSHs, provide a value of the function at particular values of ϑ and φ, but in addition they also provide a direction; they are thus ideally suited to the description of vector fields. In the case of RET, the emitter of the photon makes a natural origin of the coordinate. In the application to electromagnetic radiation the unit vectors, $|1, -1\rangle$, $|1, 0\rangle$ and $|1, 1\rangle$ carry the polarization information.

The VSHs depend upon only two (ϑ and φ) of the three spatial dimensions. Thus, for a complete description of the electromagnetic wave we must combine them with a radial function. Bessel functions are conveniently used for radial functions. Bessel functions of the first kind and of half-integer order, j_n, are called spherical Bessel functions and are solutions to the Helmholtz equation solved in spherical coordinates. They can be combined with Bessel functions of the second kind (i.e., Neumann functions) and of half-integral order, n_n, to produce Bessel functions of third kind (Hankel functions), $h_n^{(1)}$ and $h_n^{(2)}$. Hankel functions are solutions to the Maxwell's equations outside the source of the wave. Since they are solutions of Maxwell's equations they give the fully

retarded fields automatically. A penetrating account on the application of VSHs and Bessel functions, to electromagnetic radiation, has been given by Rose.[45]

Bessel functions, j_n, describe standing waves but the Hankel functions,

$$h_n^{(1)} = j_n + in_n \text{ and } h_n^{(2)} = j_n - in_n, \quad (2.8)$$

describe running waves. $h_n^{(1)}$ is called a Hankel function of the first kind, while $h_n^{(2)}$ is of the second kind. For a time dependence of the form $\exp(-i\omega t)$, $h_n^{(1)}$ describes an outgoing wave and $h_n^{(2)}$ an incoming wave. For a time dependence of the form $\exp(+i\omega t)$ this is reversed. It is therefore Hankel functions that are used, in combination with VSHs to describe the electromagnetic fields of the mediating photon in the RET process, in this work. The extension of the VSH-Hankel function description of electromagnetic radiation into the region of the source has been described by Blatt and Weisskopf.[46] It is interesting to note that Avery employed spherical Hankel functions of the first kind in his 1966 paper.[33] They were not employed again, within the context of RET studies, until Scholes and Andrews used them within a multipolar framework.[47] It appears that they were used, in both studies, primarily for mathematical convenience and the authors did not allude to their physical significance. The derivation reported here allows one to interpret the RET process physically in terms of outgoing and incoming waves, within the context of Hankel functions.

III. DERIVATION OF THE QUANTUM AMPLITUDE

A. The specific case: The emitter dipole aligned along the z-axis

We now re-derive Equation (2.1) starting from the point-of-view of the photon being described by a spherical wave, employing VSHs and Hankel functions. The analysis starts by considering interacting point-dipoles, and then extending the description to include retardation effects.

The well-known expression for the interaction of a transition dipole moment with an electric field is

$$W = -\vec{\mu} \cdot \vec{E}. \quad (3.1)$$

The transition dipole moment, $\vec{\mu}$, is an operator in both the semi-classical and QED pictures. On the other hand, the electric field is a vector quantity within the semi-classical picture and is a quantum mechanical operator within the QED framework. In a classical sense, the expression can be thought of as one of the dipoles being dressed by the time-independent field produced by the other. The scalar product embodies all angular factors that arise as a consequence of the relative orientations of the dipole and the field. The dependence of the energy upon these factors is not changed when we move from the classical to the QED formulation. However, the QED description must account for the fact that the interactions must be fully retarded. That is, there is a finite speed of propagation for the mediating photon, and therefore a time lag in the interaction.

In the case of an electric 2^J-multipole, two values of l, namely, $l = J - 1$ and $l = J + 1$, are combined to give the overall electric field in terms of VSH,

$$\vec{E} = A_J^E e^{iM\varphi} \left\{ a_{J-1} h_{J-1}^{(1)}(kr) \left[\Theta_{J,\,J-1,\,M}\hat{\Theta} + \Phi_{J,\,J-1,\,M}\hat{\Phi} + R_{J,\,J-1,\,M}\hat{R} \right] \right.$$
$$\left. + a_{J+1} h_{J+1}^{(1)}(kr) \left[\Theta_{J,\,J+1,\,M}\hat{\Theta} + \Phi_{J,\,J+1,\,M}\hat{\Phi} + R_{J,\,J+1,\,M}\hat{R} \right] \right\}, \tag{3.2}$$

where the coefficients A_J^E, a_{J-1} and a_{J+1} determine the field amplitude and the exponent is the phase factor common to all VSH coefficients. The coefficients, $\Theta_{J,\,J\pm1,\,M}$, $\Phi_{J,\,J\pm1,\,M}$ and $R_{J,\,J\pm1,\,M}$ of the individual VSH basis functions, $\hat{\Theta}$, $\hat{\Phi}$ and $\hat{R}$ are determined by the angular momentum quantum numbers, which themselves depend on the nature of the electronic transitions involved in the RET process. Table I of Ref. 48 lists all coefficients up to $J = 3$, as well as formulas to calculate them for higher values of J.

One may envisage a transition dipole, $\vec{\mu}$, at the common origin of a Cartesian and a polar co-ordinate system. Since it is the *relative* orientation of two dipoles that is important we can, without loss of generality, choose a particular orientation for $\vec{\mu}$. It is chosen to be co-linear with the z-axis of the Cartesian system, corresponding to $\vartheta = 0$ in the polar system. This restriction will be removed later. But this special case provides a good illustration of our method and clarifies the subsequent generalisation to all orientations of $\vec{\mu}$. The second dipole, $\vec{\mu}'$, at distance R from $\vec{\mu}$ interacts with the electric field, $\vec{E}$, of $\vec{\mu}$. The energy of interaction is given by the negative scalar product $-\vec{\mu} \cdot \vec{E}$. In order to form the scalar product we need to derive the fully retarded components of $\vec{E}$ at $\vec{\mu}'$ in terms of the local basis functions $\hat{\Theta}$, $\hat{\Phi}$ and $\hat{R}$.

For the chosen orientation of $\vec{\mu}$, the fully retarded field may be expressed as follows:[48,49]

$$\vec{E} = E_R\hat{R} + E_\Theta\hat{\Theta}, \tag{3.3}$$

where the longitudinal, E_R, and transverse, E_Θ, components of the field of $\vec{\mu}$ are

$$E_R \equiv E_\parallel = \frac{2\vec{\mu}k^3}{4\pi\varepsilon_0}\exp(ikR)\left[-\frac{i}{(kR)^2} + \frac{1}{(kR)^3}\right]\cos\vartheta, \tag{3.4a}$$

$$E_\Theta \equiv E_\perp = \frac{\vec{\mu}k^3}{4\pi\varepsilon_0}\exp(ikR)\left[-\frac{1}{kR} - \frac{i}{(kR)^2} + \frac{1}{(kR)^3}\right]\sin\vartheta. \tag{3.4b}$$

The identities, $E_\parallel = E_R$ and $E_\perp = E_\Theta$ follow immediately because the four vectors $\vec{\mu}$, $\hat{R}$, $E_\perp$ and $E_\parallel$ all lie in the same plane. There is no Φ component. Equations (3.4a)–(3.14b) reflect the fact that only transverse field components contribute to the far-zone (i.e., far from the source, $kR \gg 1$), whereas both transverse and longitudinal components contribute close to the source. We note that the only difference between the classical and QED formulation of the field lies in the changed dependence upon R, a result of retardation.

We now place a second transition dipole, $\vec{\mu}'$, at distance R from $\vec{\mu}$ and orientated such that its components in the local axis system are $\vec{\mu}'_\Theta$, $\vec{\mu}'_\Phi$ and $\vec{\mu}'_R$. The mutual energy, W, of the two dipoles splits naturally into longitudinal, $W_\parallel$, and transverse, $W_\perp$, components,

$$W_\parallel = -\frac{\mu'_R\mu}{4\pi\varepsilon_0 R^3}\left[2\left(\cos kR + kR\sin kR\right) + 2i\left(\sin kR - kR\cos kR\right)\right]\cos\vartheta, \tag{3.5a}$$

$$W_\perp = -\frac{\mu'_\Theta\mu}{4\pi\varepsilon_0 R^3}\left[\left(\cos kR + kR\sin kR - k^2R^2\cos kR\right) + i\left(\sin kR - kR\cos kR - k^2R^2\sin kR\right)\right]\sin\vartheta. \tag{3.5b}$$

In order to more easily compare these with the previous results, we convert them to Cartesian co-ordinates and tensor notation, and consider the fields associated with outgoing and incoming photons, in turn. The outgoing wave represents the field created by the transition dipole of the photon donor.

For the creation of the photon at the donor, we need the form of an outgoing wave, which can be written as follows:

$$\hat{R} = \sin\vartheta\cos\varphi\hat{x} + \sin\vartheta\sin\varphi\hat{y} + \cos\vartheta\hat{z} \tag{3.6a}$$

and

$$\hat{\Theta} = \cos\vartheta\cos\varphi\hat{x} + \cos\vartheta\sin\varphi\hat{y} - \sin\vartheta\hat{z}. \tag{3.6b}$$

Motivated by Equations (3.6), we can write the relations,

$$\mu_R\cos\vartheta = \mu_x\cos\vartheta\sin\vartheta\cos\varphi + \mu_y\cos\vartheta\sin\vartheta\sin\varphi$$
$$+ \mu_z\cos^2\vartheta, \tag{3.7a}$$
$$\mu_\Theta\sin\vartheta = \mu_x\sin\vartheta\cos\vartheta\cos\varphi + \mu_y\sin\vartheta\cos\vartheta\sin\varphi$$
$$- \mu_z\sin^2\vartheta, \tag{3.7b}$$

to give

$$2\mu_R\cos\vartheta + \mu_\Theta\sin\vartheta = 3\mu_x\cos\vartheta\sin\vartheta\cos\varphi$$
$$+ 3\mu_y\cos\vartheta\sin\vartheta\sin\varphi$$
$$+ \mu_z\left(3\cos^2\vartheta - 1\right). \tag{3.8}$$

Transforming from polar to Cartesian co-ordinates,

$$\cos\vartheta\sin\vartheta\cos\varphi = \frac{xz}{R^2} \text{ and } \cos\vartheta\sin\vartheta\sin\varphi = \frac{yz}{R^2},$$

where

$$\cos^2 \vartheta = \frac{z^2}{R^2} \text{ and } \sin^2 \vartheta = 1 - \frac{z^2}{R^2},$$

we obtain

$$\mu_\Theta \sin \vartheta = \mu_x \frac{xz}{R^2} + \mu_y \frac{yz}{R^2} + \mu_z \left\{ \frac{z^2}{R^2} - 1 \right\}$$

$$= \mu_x \hat{R}_x \hat{R}_z + \mu_y \hat{R}_y \hat{R}_z + \mu_z \left(\hat{R}_z \hat{R}_z - 1 \right). \quad (3.9)$$

Introducing the tensor notation of summing over repeated suffixes, we may write,

$$\mu_\Theta \sin \vartheta = \mu_i \left(\hat{R}_i \hat{R}_z - \delta_{iz} \right), \quad (3.10)$$

which is the orientational factor in the far-zone, as seen in Eq. (2.1).

Similarly the orientational factor associated with the near- and intermediate-zones can be found from

$$2\mu_R \cos \vartheta + \mu_\Theta \sin \vartheta = 3\mu_x \hat{R}_x \hat{R}_z + 3\mu_y \hat{R}_y \hat{R}_z$$
$$+ \mu_z \left(3\hat{R}_z \hat{R}_z - 1 \right)$$
$$= \mu_i \left(3\hat{R}_i \hat{R}_z - \delta_{iz} \right). \quad (3.11)$$

In order to help comparison with Eq. (2.1) we write W as real and imaginary parts,

$$\mathrm{Re}\,(W) = -\frac{\mu}{4\pi\varepsilon_0 R^3} \left[2\mu'_R (\cos kR + kR \sin kR) \cos \vartheta \right.$$
$$\left. + \mu'_\Theta (\cos kR + kR \sin kR - k^2 R^2 \cos kR) \sin \vartheta \right]$$
$$(3.12a)$$

$$= -\frac{\mu}{4\pi\varepsilon_0 R^3} \left[(\cos kR + kR \sin kR)(2\mu'_R \cos \vartheta + \mu'_\Theta \sin \vartheta) \right.$$
$$\left. - k^2 R^2 \mu'_\Theta \cos kR \sin \vartheta \right]. \quad (3.12b)$$

The final form of the *real part* of the interaction energy is, therefore,

$$\mathrm{Re}\,(W) = \frac{\mu \mu'_i}{4\pi\varepsilon_0 R^3} \left[(\cos kR + kR \sin kR)(\delta_{iz} - 3\hat{R}_i \hat{R}_z) \right.$$
$$\left. - k^2 R^2 \cos kR \left(\delta_{iz} - \hat{R}_i \hat{R}_z \right) \right]. \quad (3.12c)$$

Similarly for the imaginary part,

$$\mathrm{Im}\,(W) = -\frac{\mu}{4\pi\varepsilon_0 R^3} \left[2\mu'_R (\sin kR - kR \cos kR) \cos \vartheta + \mu'_\Theta (\sin kR - kR \cos kR - k^2 R^2 \sin kR) \sin \vartheta \right] \quad (3.13a)$$

$$= -\frac{\mu}{4\pi\varepsilon_0 R^3} \left[(\sin kR - kR \cos kR)(2\mu'_R \cos \vartheta + \mu'_\Theta \sin \vartheta) - \mu'_\Theta k^2 R^2 \sin kR \sin \vartheta \right], \quad (3.13b)$$

to give the final form,

$$\mathrm{Im}\,(W) = \frac{\mu \mu'_i}{4\pi\varepsilon_0 R^3} \left[(\sin kR - kR \cos kR)(\delta_{iz} - 3\hat{R}_i \hat{R}_z) - k^2 R^2 \sin kR \left(\delta_{iz} - \hat{R}_i \hat{R}_z \right) \right]. \quad (3.13c)$$

The quantum amplitudes for the RET process are, therefore,

$$\mathrm{Re}\,(V) = \frac{1}{4\pi\varepsilon_0 R^3} \left[(\cos kR + kR \sin kR)(\delta_{ij} - 3\hat{R}_i \hat{R}_j) - k^2 R^2 \cos kR \left(\delta_{ij} - \hat{R}_i \hat{R}_j \right) \right], \quad (3.14a)$$

$$\mathrm{Im}\,(V) = \frac{1}{4\pi\varepsilon_0 R^3} \left[(\sin kR - kR \cos kR)(\delta_{ij} - 3\hat{R}_i \hat{R}_j) - k^2 R^2 \sin kR \left(\delta_{ij} - \hat{R}_i \hat{R}_j \right) \right]. \quad (3.14b)$$

These are analogous with the real and imaginary expressions of Daniels *et al.*, reproduced in Section II, Eq. (2.1). *Of note is that the arbitrary choice of sign, which can be seen in Eq. (2.1), does not appear in Eq. (3.14a)–(3.14b). In this derivation, the sign takes a definite value for τ_{ij}^-.*

In making this comparison, it must be remembered that the dipole of the energy donor, μ, is placed along the z-axis, so that its only non-zero component is μ_z. This explains the absence of many of the terms in $\hat{R}_x$ and $\hat{R}_y$ which might otherwise have been expected. The relationships between the Cartesian and polar unit vectors for the calculation of $\vec{E}$, above, were those associated for outgoing waves, $\hat{\Theta} \times \hat{\Phi} = \hat{R}$, and time dependence factor of $\exp(-i\omega t)$. The relationships appropriate for incoming waves $\hat{\Theta} \times \hat{\Phi} = -\hat{R}$ and $\exp(-i\omega t)$ give the upper sign seen in Eq. (2.1b).

In the case of outgoing waves, the R dependence can be expressed in terms of Hankel functions of the first kind,

i.e., $h_l^{(1)}(kR) = j_l(kR) + in_l(kR)$ while those for incoming waves in terms of Hankel functions of the second kind, i.e., $h_l^{(2)}(kR) = j_l(kR) - in_l(kR)$. The ambiguous sign of the imaginary part of the coupling tensor in Eq. (2.1) was interpreted from the point of view that both incoming and outgoing waves (i.e., photon absorption and emission) need to be included to calculate the quantum amplitude of the process. In our analysis the incoming and outgoing waves emerge naturally and can be linked directly to one or other of the signs in the imaginary part of Eq. (2.1), up to the phase factor $\exp(\pm i\omega t)$.

B. The general case

The above results are completely general, insofar as quantum amplitudes for any relative orientation of the transition dipole moments can be calculated. We now extend

TABLE I. Components of $\hat{Y}_{12M}$.

M	Θ_{12M}	Φ_{12M}	R_{12M}
+1	$-(1/4\sqrt{\pi})\exp(+i\varphi)\cos\vartheta$	$-(i/4\sqrt{\pi})\exp(+i\varphi)$	$+(1/2\sqrt{\pi})\exp(+i\varphi)\sin\vartheta$
0	$-(1/2\sqrt{2\pi})\sin\vartheta$	0	$-(1/\sqrt{2\pi})\cos\vartheta$
−1	$+(1/4\sqrt{\pi})\exp(-i\varphi)\cos\vartheta$	$-(i/4\sqrt{\pi})\exp(-i\varphi)$	$-(1/2\sqrt{\pi})\exp(-i\varphi)\sin\vartheta$

TABLE II. Classical field of the VSH, $\hat{Y}_{12M}$, $M = x, y, z$.

	Θ_{12M}	Φ_{12M}	R_{12M}
X	$-\mu\cos\vartheta\cos\varphi/4\pi\varepsilon_0 R^3$	$+\mu\sin\varphi/4\pi\varepsilon_0 R^3$	$+\mu\sin\vartheta\cos\varphi/2\pi\varepsilon_0 R^3$
Y	$-\mu\cos\vartheta\sin\varphi/4\pi\varepsilon_0 R^3$	$-\mu\cos\varphi/4\pi\varepsilon_0 R^3$	$+\mu\sin\vartheta\sin\varphi/2\pi\varepsilon_0 R^3$
Z	$+\mu\sin\vartheta/4\pi\varepsilon_0 R^3$	0	$+\mu\cos\vartheta/2\pi\varepsilon_0 R^3$

the calculation for the case of the donor molecule taking on any arbitrary orientation. This further generalization is useful for practical application of the theory, for example, in the cases of energy transfer within a group of randomly oriented molecules. If pair-wise electronic couplings are to be calculated, the equation of Section III A would require reorientation of one of the pair for each interaction. The following development alleviates this problem.

Defining the coupling to an arbitrary orientation is achieved by transforming to a Cartesian coordinate system. In the above derivation, we recall that the transition dipole moment, $\vec{\mu}$, is orientated along the z-axis. Consequently only the z-component is present in the expressions (3.5).

From earlier work,[48] the components of the VSH, $\hat{Y}_{12M}$, $M = +1, 0, -1$, can be seen in Table I.

Using wavefunction basis transformations, Eq. (2.2) and comparison with earlier results for E_R and E_Θ with the dipole aligned along the z-axis, classical electric fields can be obtained by multiplying the components by $\mu/\sqrt{2\pi}\varepsilon_0 R^3$. The results can be found in Table II.

These are the classical electric fields at a point having the spherical polar coordinates ϑ, φ and R. The retarded fields will differ only in the function of R. Thus, a general dipole, $\vec{\mu}$, having components μ_x, μ_y, and μ_z, will contribute to the field as follows:

$$E_\Theta = \left(4\pi\varepsilon_0 R^3\right)^{-1}$$
$$\times \left\{-\mu_x\cos\vartheta\cos\varphi - \mu_y\cos\vartheta\sin\varphi + \mu_z\sin\vartheta\right\},$$
(3.15a)

$$E_\Phi = \left(4\pi\varepsilon_0 R^3\right)^{-1}\left\{+\mu_x\sin\varphi - \mu_y\cos\varphi\right\},$$
(3.15b)

$$E_R = \left(2\pi\varepsilon_0 R^3\right)^{-1}\left\{+\mu_x\sin\vartheta\cos\varphi\right.$$
$$\left. + \mu_y\sin\vartheta\sin\varphi + \mu_z\cos\vartheta\right\}.$$
(3.15c)

As before, we now place a second dipole, $\vec{\mu}'$, at distance R from $\vec{\mu}$ and orientated such that its components in the local axis system $\hat{\Theta}$, $\hat{\Phi}$ and $\hat{R}$ are $\vec{\mu}'_\Theta$, $\vec{\mu}'_\Phi$ and $\vec{\mu}'_R$. The mutual interaction energy, W, of the two dipoles splits naturally into longitudinal, $W_\parallel$ and transverse, $W_\perp$ parts,

$$W_\parallel = -\mu'_R E_R = -\left(\mu'_R/2\pi\varepsilon_0 R^3\right)\left\{+\mu_x\sin\vartheta\cos\varphi + \mu_y\sin\vartheta\sin\varphi + \mu_z\cos\vartheta\right\}$$
(3.16a)

and

$$W_\perp = -\mu'_\Theta E_\Theta - \mu'_\Phi E_\Phi = -\left(\mu'_\Theta/4\pi\varepsilon_0 R^3\right)\left\{-\mu_x\cos\vartheta\cos\varphi - \mu_y\cos\vartheta\sin\varphi + \mu_z\sin\vartheta\right\} - \left(\mu'_\Phi/4\pi\varepsilon_0 R^3\right)\left\{\mu_x\sin\varphi - \mu_y\cos\varphi\right\}.$$
(3.16b)

Inserting the retarded dependence upon R we have

$$W_\parallel = -\frac{\mu'_R k^3}{2\pi\varepsilon_0}\left\{+\mu_x\sin\vartheta\cos\varphi + \mu_y\sin\vartheta\sin\varphi + \mu_z\cos\vartheta\right\}\exp\left(ikR\right)\left[-\frac{i}{(kR)^2} + \frac{1}{(kR)^3}\right]$$
(3.17a)

and

$$W_\perp = -\frac{k^3}{4\pi\varepsilon_0}\left\{\mu'_\Theta\left[-\mu_x\cos\vartheta\cos\varphi - \mu_y\cos\vartheta\sin\varphi + \mu_z\sin\vartheta\right] + \mu'_\Phi\left[\mu_x\sin\varphi - \mu_y\cos\varphi\right]\right\}\exp\left(ikR\right)\left[-\frac{1}{kR} - \frac{i}{(kR)^2} + \frac{1}{(kR)^3}\right].$$
(3.17b)

To express these results in separate real and imaginary parts we first define the symbols,

$$M_R' = \mu_R' \left[+\mu_x \sin\vartheta \cos\varphi + \mu_y \sin\vartheta \sin\varphi + \mu_z \cos\vartheta \right],$$
(3.18a)

$$M_\Theta' = \mu_\Theta' \left[-\mu_x \cos\vartheta \cos\varphi - \mu_y \cos\vartheta \sin\varphi + \mu_z \sin\vartheta \right],$$
(3.18b)

$$M_\Phi' = \mu_\Phi' \left[+\mu_x \sin\varphi - \mu_y \cos\varphi \right].$$
(3.18c)

Now,

$$W_\parallel = -\frac{k^3}{2\pi\varepsilon_0} M_R' \exp(ikR) \left[-\frac{i}{(kR)^2} + \frac{1}{(kR)^3} \right]$$
(3.19)

so that

$$Re\left(W_\parallel\right) = -\frac{k^3}{2\pi\varepsilon_0} M_R' \left[\frac{\sin kR}{(kR)^2} + \frac{\cos kR}{(kR)^3} \right]$$
(3.19a)

and

$$Im\left(W_\parallel\right) = -\frac{k^3}{2\pi\varepsilon_0} M_R' \left[\frac{-\cos kR}{(kR)^2} + \frac{\sin kR}{(kR)^3} \right].$$
(3.19b)

Similarly,

$$W_\perp = -\frac{k^3}{4\pi\varepsilon_0} \{M_\Theta' + M_\Phi'\} (\cos kR + i \sin kR)$$
$$\times \left[-\frac{1}{kR} - \frac{i}{(kR)^2} + \frac{1}{(kR)^3} \right]$$
(3.20)

so that

$$Re\left(W_\perp\right) = -\frac{k^3}{4\pi\varepsilon_0} \{M_\Theta' + M_\Phi'\}$$
$$\times \left[-\frac{\cos kR}{kR} + \frac{\sin kR}{(kR)^2} + \frac{\cos kR}{(kR)^3} \right]$$
(3.20a)

and

$$Im\left(W_\perp\right) = -\frac{k^3}{4\pi\varepsilon_0} \{M_\Theta' + M_\Phi'\}$$
$$\times \left[-\frac{\sin kR}{kR} - \frac{\cos kR}{(kR)^2} + \frac{\sin kR}{(kR)^3} \right].$$
(3.20b)

Summing parallel and transverse parts we have

$$Re\left(W\right) = -\frac{k^3}{4\pi\varepsilon_0} \{2M_R' + M_\Theta' + M_\Phi'\} \left[\frac{\sin kR}{(kR)^2} + \frac{\cos kR}{(kR)^3} \right]$$
$$+ \frac{k^3}{4\pi\varepsilon_0} \{M_\Theta' + M_\Phi'\} \left[\frac{\cos kR}{kR} \right]$$
(3.21a)

and

$$Im\left(W\right) = -\frac{k^3}{4\pi\varepsilon_0} \{2M_R' + M_\Theta' + M_\Phi'\} \left[-\frac{\cos kR}{(kR)^2} + \frac{\sin kR}{(kR)^3} \right]$$
$$+ \frac{k^3}{4\pi\varepsilon_0} \{M_\Theta' + M_\Phi'\} \left[\frac{\sin kR}{kR} \right].$$
(3.21b)

Alternatively, we might write

$$Re\left(W\right) = -\frac{k^3}{2\pi\varepsilon_0} \{M_R'\} \left[\frac{\sin kR}{(kR)^2} + \frac{\cos kR}{(kR)^3} \right]$$
$$+ \frac{k^3}{4\pi\varepsilon_0} \{M_\Theta' + M_\Phi'\} \left[\frac{\cos kR}{kR} - \frac{\sin kR}{(kR)^2} - \frac{\cos kR}{(kR)^3} \right]$$
(3.22a)

and

$$Im\left(W\right) = -\frac{k^3}{2\pi\varepsilon_0} \{M_R'\} \left[-\frac{\cos kR}{(kR)^2} + \frac{\sin kR}{(kR)^3} \right]$$
$$+ \frac{k^3}{4\pi\varepsilon_0} \{M_\Theta' + M_\Phi'\} \left[\frac{\sin kR}{kR} - \frac{\cos kR}{(kR)^2} - \frac{\sin kR}{(kR)^3} \right].$$
(3.22b)

These expressions reduce to Eqs. (3.12c) and (3.13c) when $\mu_x = \mu_y = 0$ and $\mu_z = \mu$.

IV. DISCUSSION

In this work, we present a new formulation of the resonance energy transfer process whereby instead of treating the mediating (virtual) photon as a plane wave with vectors being specified by Cartesian components, a spherical wave approach is employed. This alternative representation for the mediating photon offers new physical insight into the RET process that complements the plane wave formulation. Further, it offers a number of advantages over the plane wave approach for a number of specific applications. In particular where directionality (i.e., orientational factors) is centrally important to the RET process, a description of the process in terms of the polar spherical coordinate system has clear advantages.

The spherical wave approach describes the photon in terms of latitude and longitude angles *via* vector spherical harmonics. The radial function is defined in terms of Hankel functions, where the Hankel function of the first kind describes the outgoing wave when the time dependence has the form $\exp(-i\omega t)$, and consequently Hankel functions of type two describes the incoming wave. Within the context of energy transfer, these processes correspond to the emission and absorption processes. The polarization of the photon is linked to the VSHs with $M = \pm 1$ for transverse waves and $M = 0$ for longitudinal waves.

It is well known that within the framework of QED all intermediate states connecting the initial and final states must be included, when calculating the quantum amplitude for a particular process. In the case of RET, there are two Feynman diagrams associated with two different resonance interactions. The most intuitive one is the transfer of the mediating photon from the initially excited donor to the ground state acceptor. The less intuitive one involves a photon being transferred in the reverse direction. It is interesting to note, that within the VSH-Hankel function formulation of the RET process, that both of these processes can be understood in terms of the time dependent phase term $\exp(\pm i\omega t)$, where $h_l^{(1)}(kR)$ represents an outgoing wave in the case of a negative exponent and an incoming wave in the case of a positive exponent.

While the plane wave approach is natural for considering a donor-acceptor pair separated in space along a well defined vector of separation (i.e., the $\vec{R}$ vector), the spherical wave approach is particularly well suited to situations where there are numerous EET acceptors that are distributed isotropically. For example, EET occurring in condensed phase solutions or quantum plasmonics,[50] a relatively new, technology based, field that seeks to understand and manipulate quantum

properties of light and its interaction with matter at the nanoscale.

One key advantage of the spherical wave analysis is that the interaction separates naturally into transverse and longitudinal field components. This allows a natural way to analyse near- and far-zone RET in terms of orientational effects. Continuing work involves the development of this theory in terms of computational tools that will be beneficial in analysing energy transfer in condensed phase, isotropic and anisotropic, environments.

ACKNOWLEDGMENTS

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