



Article Bridge-Mediated RET between Two Chiral Molecules

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Abstract: Molecular quantum electrodynamics (QED) theory is employed to calculate the rate of resonance energy transfer (RET) between a donor, D, described by an electric dipole and quadrupole, and magnetic dipole coupling, and an identical acceptor molecule, A, that is mediated by a third body, T, which is otherwise inert. A single virtual photon propagates between D and T, and between T and A. Time-dependent perturbation theory is used to compute the matrix element, from which the transfer rate is evaluated using the Fermi golden rule. This extends previous studies that were limited to the electric dipole approximation only and admits the possibility of the exchange of excitation between a chiral emitter and absorber. Rate terms are computed for specific pure and mixed multipole-dependent contributions of D and A for both an oriented arrangement of the three particles and for the freely tumbling situation. Mixed multipole moment contributions, such as those involving electric-magnetic dipole or electric dipole-quadrupole coupling at one center, do not survive random orientational averaging. Interestingly, the mixed electric–magnetic dipole D and A rate term is non-vanishing and discriminatory, exhibiting a dependence on the chirality of the emitter and absorber, and is entirely retarded. It vanishes, however, if D and A are oriented perpendicularly to one another. Near- and far-zone asymptotes of isotropic contributions to the rate are also evaluated, demonstrating radiationless short-range transfer and inverse-square radiative exchange at very large separations.

Keywords: molecular QED; resonance energy transfer; discriminatory effects; mediated exchange

1. Introduction

Fundamental theoretical studies of resonance energy transfer (RET) [1], especially those involving the use of quantum electrodynamics (QED) theory [2–7], have largely concentrated on the exchange of energy taking place between two interacting particles, a donor, D, and an acceptor, A. These species may be atoms, molecules, chromophores, functional groups, or other such material entities that engage with electromagnetic radiation and undergo electronic and/or vibrational excitation and de-excitation to and from quantized energy levels. Migration of energy occurs from the initially excited D, to A, which is initially in its ground state, with A capturing all of the excitation energy in a resonant process. According to QED, energy is conveyed from emitter to absorber at the speed of light through the propagation of a single virtual photon. This is because coupling between matter at the microscopic scale of atoms and molecules is due to electromagnetic forces, which are mediated by gauge bosons. These are the light quanta, a direct manifestation of quantization of the electromagnetic field, which is a key feature of QED. Perturbation theory has been used to evaluate the Fermi golden rule transfer rate as a function of the pair separation distance, R, for oriented and freely tumbling particles [8–16]. From these results, it has been established that at short inter-nuclear distances, the exchange of energy is radiationless, exhibiting an R^{-6} Förster-type dependence, while in the other extreme, corresponding to the far-zone, the rate has inverse square behavior, illustrative of a radiative transfer mechanism.

While a majority of works have understandably focused on RET in free space, considerable effort has also been devoted to exploring the effects of a medium in modifying



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Copyright: © 2021 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the rate [17,18] as environment-influenced energy transfer is the usual situation commonly found in diverse scientific fields and technological applications. An early method to account for the dispersive and dissipative properties of a bath, and a means to introduce the refractive index, was to view the medium as possessing a uniform dielectric constant, with connection to the bulk polarizability made via the Clausius–Mossotti relation [19]. More rigorous treatments have followed. These have included quantizing both the electromagnetic field and a dielectric medium, with the latter viewed as a collection of identical atoms arranged as a lattice, within which a chromophore or a pair of interacting particles is embedded [20–24]. The elementary bosonic excitations of the bath are now medium-dressed photons or polaritons, allowing for individual emission and absorption events to occur. One such particle is exchanged in RET taking place in a surrounding environment, altering the rate relative to its vacuum value through the appearance of a complex refractive index, local field and screening factors, and the correct diminution of the amplitude via exponential decay. This approach has been extended within the framework of macroscopic QED in which the medium is taken to be a linear magnetodielectric [25]. It has recently been applied to compute RET, for instance, in treating coupling to plasmons in nanostructure systems [26-28].

Instead of viewing the direct transfer between D and A taking place in an environment, an alternative approach is to picture exchange mediated by microscopic particles, and to consider how constructing a microscopic many-body theory modifies the rate. The extrapolation of the results obtained for the few-body case to an infinite number of mediators allows a comparison to be made with macroscopic treatments. A few calculations have been performed of the rate mediated by a neutral, polarizable third molecule that either serves as a bridging species, relaying energy between D and A, or is coupled only to D or only to A [29–33], including interference terms between direct and various indirect pathways. In addition, a small number of studies have examined the effect of two additional bridging molecules on RET, and the complicated distance and orientational dependences exhibited by the rate [34–36]. Furthermore, these three-body, free-space QED results have been supplemented by accounting for a dielectric medium using the polariton exchange approach, in which amplitude and phase damping, vibrational relaxation, and dissipative effects on the rate were investigated [24,37,38]. Interest in three-center RET has been driven by potential applications involving sensitization and energy pooling in organic systems, as well as up-conversion and down-conversion in rare-Earth doped materials [39–41], in addition to testing mixed QM/MM methods for treating a solvent [42].

Until now, the problem of RET between two chiral molecules mediated by a third body has not been considered. This is the aim of the present contribution. As in previous studies, the mediator is taken to be achiral, characterized by its electric dipole polarizability. To deal with the potential optical activity of D and A, the electric dipole approximation is relaxed for these two species, with magnetic dipole and electric quadrupole coupling terms included in the description of the response properties of the emitter and absorber molecules. This will not only allow a comparison to be made with previous work involving RET modified by one or two mediators in the electric dipole approximation, but also with earlier molecular QED calculations of discriminatory pair RET [43,44]. In these last works, interference between electric and magnetic dipole coupling terms led to a transfer rate that depended on the handedness of the donor and acceptor, changing sign when its mirror image form replaces one enantiomer. It is examined whether such behavior is replicated in the mediated case. The paper is organized as follows: first the problem is set up within the framework of molecular QED theory and basic equations are given. Time-dependent perturbation theory is used to evaluate the matrix element for mediated RET. This is done together in Section 2. Specific higher-order multipole moment-dependent contributions of D or A contributing to the oriented or isotropic Fermi golden rule rate are then extracted in Sections 3 and 4, with special emphasis placed on the term proportional to the handedness of the emitter or absorber in order to elucidate possible discriminatory effects. A summary is given in Section 5.

2. QED Matrix Element for Third Body-Mediated RET between Two Chiral Molecules

Consider RET between two chiral molecules, one serving as the donor species, D, located at \overrightarrow{R}_D , and the second, A, positioned at \overrightarrow{R}_A , playing the role of acceptor entity. If Dand A are not identical, then their energy spectra need to overlap. Because symmetry plays a special part in classifying whether a molecule is chiral or not, spectroscopic selection rules are less stringent for such species relative to non-chiral or achiral substances, allowing multipole moment contributions other than the electric dipole moment to contribute to numerous processes involving the coupling of light with matter. D is assumed to initially be in the excited electronic state $|m^D>$, with energy E_m^D , while A is in the ground state $|0^A>$, with energy E_0^A . An amount of energy $E_{m0} = E_m - E_0 = hck_{m0}$ is transferred, with k_{m0} being the wave number of the transition associated with de-excitation in D. This quantity of energy is gained by the absorber, which becomes excited to state $|m^A>$, while the emitter decays to the ground state, $|0^D>$.

Let the exchanged energy be mediated by a third particle, *T*, positioned at \hat{R}_T , which serves to relay excitation between *D* and *A*. *T* is electrically polarizable and may undergo virtual transitions from the ground state $|0^T\rangle$ to excited levels $|r^T\rangle$, but is otherwise inert, remaining in the ground state when not interacting. In the multipolar formalism of molecular QED theory [3,4,6], the total Hamiltonian operator for the system comprising the three particles, the radiation field, and their mutual interaction, is written as

$$H = \sum_{\xi} H_{mol}(\xi) + H_{rad} + \sum_{\xi} H_{int}(\xi), \ \xi = D, A, T.$$
(1)

The first term in Equation (1) is the molecular Hamiltonian of particle ξ , $H_{mol}(\xi)$, familiar from quantum chemistry and which is expressed as a sum of kinetic and intra-molecular potential energy contributions for a collection of non-relativistic charged particles grouped into atoms or molecules ξ . A characteristic feature of QED is the placing of the electromagnetic field on an equal footing with matter, with both subject to the axioms of quantum mechanics. This leads to the explicit appearance in Equation (1) of the Hamiltonian operator for the radiation field, H_{rad} . One form for the total energy of the field is given by

$$H_{rad} = \frac{1}{2\varepsilon_0} \int \{ \vec{d}^{\perp 2}(\vec{r}) + \varepsilon_0^2 c^2 \vec{b}^2(\vec{r}) \} d^3 \vec{r}, \qquad (2)$$

where $\vec{d}^{\perp}(\vec{r})$ and $\vec{b}(\vec{r})$ are microscopic transverse electric displacement and magnetic fields, respectively. In QED, the electromagnetic field is pictured as a sum of independent simple harmonic oscillators, whose quantization is straightforward in either the particle or wave viewpoints. This results in photons, which are completely characterized by their individual mode designation \vec{k} , λ , where \vec{k} is the wave vector, signifying the propagation direction of light, and λ is its index of polarization. These first two terms of Equation (1) constitute the unperturbed Hamiltonian, whose solutions are assumed to be known. They correspond to the problem of matter in the absence of radiation, and the propagation of electromagnetic radiation in free space, respectively.

Energy eigenstates $|m^{\xi}\rangle$ for a particle ξ in a state described by one or more quantum numbers m^{ξ} , with energy E_{m}^{ξ} , are employed as base states for matter, while radiation states are specified by $|n(\vec{k},\lambda)\rangle$, which details the number of photons in the field of mode \vec{k}, λ , with *n* being the number operator whose eigenvalues are 0, 1, 2, Because the unperturbed Hamiltonian is separable, the base states employed to monitor the evolution of the system under the influence of the perturbation operator, $H_{int} = \sum_{\xi} H_{int}(\xi)$, are product molecule-field states of the form $|mol\rangle \otimes |field\rangle =$

 $|mol; field \rangle = |m^{\xi}, m'^{\xi'}, \ldots; n(\vec{k}, \lambda), n'(\vec{k'}, \lambda'), \ldots \rangle$. The state of the composite system at some final time, t_f , $|f\rangle$, given that at the initial time, t_i , it was in the initial state $|i\rangle$,

Turning to the last term in Equation (1), the perturbation operator, which describes the coupling between light and matter, takes the following explicit form: for the emitter and the absorber, both of which are chiral, the first few terms of the multipolar expansion of the electric polarization and magnetization fields are retained, yielding

$$H_{int}(\xi) = -\varepsilon_0^{-1} \mu_i(\xi) d_i^{\perp}(\vec{R}_{\xi}) - m_i(\xi) b_i(\vec{R}_{\xi}) - \varepsilon_0^{-1} Q_{ij}(\xi) \nabla_j d_i^{\perp}(\vec{R}_{\xi}), \ \xi = D, A$$
(3)

where Roman indices denote Cartesian tensor components in the space-fixed frame of reference, and Einstein's summation convention is in force for indices that repeat. In expression (3), $\mu_i(\xi)$, $m_i(\xi)$, and $Q_{ij}(\xi)$ are the electric dipole moment operator, the magnetic dipole moment operator, and the electric quadrupole moment operator, respectively. The multipole moments couple directly to the electromagnetic fields. A convenient form to express these microscopic Maxwell field operators is as a sum over Fourier modes, with expansions

$$\vec{d}^{\perp}(\vec{r}) = i \sum_{\vec{k},\lambda} \left(\frac{hck\varepsilon_0}{2V} \right)^{1/2} [\vec{e}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k})e^{i\vec{k}\cdot\vec{r}} - \vec{e}^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k})e^{-i\vec{k}\cdot\vec{r}}], \quad (4)$$

and

$$\vec{b}(\vec{r}) = i \sum_{\vec{k},\lambda} \left(\frac{hk}{2\varepsilon_0 cV} \right)^{1/2} [\vec{b}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k})e^{i\vec{k}\cdot\vec{r}} - \vec{b}^{(\lambda)}(\vec{k})a^{\dagger(\lambda)}(\vec{k})e^{-i\vec{k}\cdot\vec{r}}].$$
(5)

Appearing in these last two expressions are the second quantized raising and lowering operators for a \vec{k} , λ mode photon, $a^{\dagger(\lambda)}(\vec{k})$ and $a^{(\lambda)}(\vec{k})$, respectively, with $\vec{e}^{(\lambda)}(\vec{k})$ being the complex unit electric polarization vector, $\vec{b}^{(\lambda)}(\vec{k})$ is its magnetic counterpart, and V is the volume of the radiation quantization box, which serves to restrict the number of allowed field modes to a countable infinity.

Because the third body, *T*, acts as a bridge between *D* and *A*, scattering virtual photons, it is advantageous to employ the following form for the interaction operator, $H_{int}(T)$,

$$H_{int}(T) = -\varepsilon_0^{-2} \alpha_{ij}(T) d_i^{\perp}(\vec{R}_T) d_j^{\perp}(\vec{R}_T), \qquad (6)$$

which is seen to be quadratic in the electric displacement field. The mediator responds to radiation through its ground state frequency-dependent electric dipole polarizability tensor

$$\alpha_{ij}(T) = \alpha_{ij}(T; \pm k_1, \pm k_2) = \sum_r \left\{ \frac{\mu_i^{0r}(T)\mu_j^{r0}(T)}{E_{r0} \mp hck_1} + \frac{\mu_j^{0r}(T)\mu_i^{r0}(T)}{E_{r0} \mp hck_2} \right\},\tag{7}$$

where the matrix element of the electric dipole moment operator between electronic states $|0^{T}\rangle$ and $|r^{T}\rangle$ of *T* is abbreviated to $\mu_{i}^{0r}(T) = \langle 0^{T} | \mu_{i}(T) | r^{T} \rangle$. Since a single virtual photon traverses between *D* and *T*, and between *T* and *A*, the interaction Hamiltonian Equation (6) is an effective two-photon perturbation operator [45]. Employing it will help to simplify the computation of the matrix element by reducing the number of Feynman-like diagrams that have to be drawn and summed over, which is beneficial when solving higher-order processes. This type of coupling Hamiltonian has been used to similar good effect in the evaluation of the Casimir–van der Waals dispersion potential, which is attributed to two virtual photon exchanges [46–49], and its radiation-induced analog [50,51].

To complete the statement of the problem, the final item required is the specification of the initial and final states. These may be written as

$$|i\rangle = |m^{D}, 0^{A}, 0^{T}\rangle; |f\rangle = |0^{D}, m^{A}, 0^{T}\rangle,$$
(8)

corresponding to the migration of electronic energy from *D* to *A* resonantly, with energy E_{m0} , with the mediator *T* remaining unexcited before and after the transfer process. No photons—real or virtual—are present at times $t < t_i$ and $t > t_f$.

Let the single virtual photon exchanged between *D* and *T* be of mode \vec{p} , ε , and the one propagating between *T* and *A* be of mode $\vec{p'}$, ε' . With the interaction Hamiltonians given by Equations (3) and (6), the matrix element for mediated RET between two chiral molecules is evaluated using the third-order perturbation theory formula

$$M_{fi} = \sum_{I,II} \frac{\langle f | H_{int} | II \rangle \langle II | H_{int} | I \rangle \langle I | H_{int} | i \rangle}{E_{iI} E_{III}},$$
(9)

with $H_{int} = \sum_{\xi} H_{int}(\xi)$, $\xi = D$, A, and T, and where the sum in Equation (9) is carried out over all intermediate states that link $|f \rangle \leftarrow |i \rangle$. Written in the denominator of Equation (9) are differences in energy between initial and intermediate states, $E_{iI} = E_i - E_I$, etc. The computation of the probability amplitude for the process under consideration may be aided by drawing time-ordered diagrams depicting the sequence of photon emission/absorption events, with the total number being equal to the number of terms in the sum of Equation (9). In the present example, because the mediator interacts with radiation via the effective two-photon coupling (Equation (6)), only six Feynman-like diagrams contribute. They may be obtained from diagrams of the type shown in Figure 1d of [37].

On using the standard calculational techniques of molecular QED theory, the matrix element is found to be

$$\begin{split} M_{fi} &= -\sum_{\vec{p}, \vec{e}} \sum_{\vec{p}', \vec{e'}} \left(\frac{p}{2\epsilon_0 V} \right) \left(\frac{p'}{2\epsilon_0 V} \right) \alpha_{rs}(T; -p, -p') \\ &\times \{ [\mu_i^{0m}(D)e_i^{(e)}(\vec{p}) + \frac{1}{c}m_i^{0m}(D)b_i^{(e)}(\vec{p}) + ip_j Q_{ij}^{0m}(D)e_i^{(e)}(\vec{p})] \\ &\times [\mu_k^{m0}(A)e_k^{(e')}(\vec{p}') + \frac{1}{c}m_k^{m0}(A)b_k^{(e')}(\vec{p}') + ip'_l Q_{kl}^{m0}(A)e_k^{(e')}(\vec{p}')] \bar{e}_r^{(e)}(\vec{p})\bar{e}_s^{(e')}(\vec{p}') \frac{e^{i\vec{p}\cdot\vec{R}}e^{i\vec{p}'\cdot\vec{R}'}}{(p+k_{m0})(p'-k_{m0})} \\ &+ [\mu_i^{0m}(D)\bar{e}_i^{(e)}(\vec{p}) + \frac{1}{c}m_k^{m0}(A)\bar{b}_k^{(e')}(\vec{p}') - ip_j Q_{ij}^{0m}(D)\bar{e}_i^{(e)}(\vec{p})] \\ &\times [\mu_k^{m0}(A)\bar{e}_k^{(e')}(\vec{p}') + \frac{1}{c}m_k^{m0}(A)\bar{b}_k^{(e')}(\vec{p}') - ip_j Q_{ij}^{0m}(D)\bar{e}_i^{(e')}(\vec{p}')] e_r^{(e)}(\vec{p})e_s^{(e')}(\vec{p}') \frac{e^{-i\vec{p}\cdot\vec{R}}e^{-i\vec{p}'\cdot\vec{R}'}}{(p-k_{m0})(p'+k_{m0})} \\ &+ [\mu_i^{0m}(D)\bar{e}_i^{(e)}(\vec{p}) + \frac{1}{c}m_i^{0m}(D)\bar{b}_i^{(e)}(\vec{p}) - ip_j Q_{ij}^{0m}(D)\bar{e}_i^{(e)}(\vec{p})] \\ &\times [\mu_k^{m0}(A)e_k^{(e')}(\vec{p}') + \frac{1}{c}m_i^{m0}(A)b_k^{(e')}(\vec{p}') + ip'_l Q_{kl}^{m0}(A)e_k^{(e')}(\vec{p}')]e_r^{(e)}(\vec{p})\bar{e}_s^{(e')}(\vec{p}') \frac{e^{-i\vec{p}\cdot\vec{R}}e^{i\vec{p}'\cdot\vec{R}'}}{(p-k_{m0})(p'-k_{m0})} \\ &+ [\mu_i^{0m}(D)\bar{e}_i^{(e)}(\vec{p}) + \frac{1}{c}m_i^{0m}(D)b_i^{(e)}(\vec{p}) - ip_j Q_{ij}^{0m}(D)\bar{e}_i^{(e)}(\vec{p})] \\ &\times [\mu_k^{m0}(A)\bar{e}_k^{(e')}(\vec{p}') + \frac{1}{c}m_i^{m0}(A)b_k^{(e')}(\vec{p}') - ip_j Q_{ij}^{0m}(D)\bar{e}_i^{(e)}(\vec{p})] \\ &\times [\mu_k^{m0}(A)\bar{e}_i^{(e')}(\vec{p}') + \frac{1}{c}m_i^{m0}(A)\bar{b}_k^{(e')}(\vec{p}') - ip_j Q_{ij}^{0m}(D)\bar{e}_i^{(e)}(\vec{p})] \\ &\times [\mu_k^{m0}(A)\bar{e}_k^{(e')}(\vec{p}') + \frac{1}{c}m_i^{m0}(A)\bar{b}_k^{(e')}(\vec{p}') - ip_j Q_{ij}^{0m}(D)\bar{e}_i^{(e)}(\vec{p})] \\ &\times [\mu_k^{m0}(A)\bar{e}_k^{(e')}(\vec{p}') + \frac{1}{c}m_k^{m0}(A)\bar{b}_k^{(e')}(\vec{p}') - ip_j Q_{ij}^{0m}(A)\bar{e}_k^{(e')}(\vec{p}')] \bar{e}_r^{(e)}(\vec{p})\bar{e}_s^{(e')}(\vec{p}') \frac{e^{i\vec{p}\cdot\vec{R}}e^{-i\vec{p}'\cdot\vec{R}'}}{(p+k_{m0})(p'-k_{m0})} \\ &+ [\mu_i^{0m}(A)\bar{e}_k^{(e')}(\vec{p}') + \frac{1}{c}m_k^{m0}(A)\bar{b}_k^{(e')}(\vec{p}') - ip_j Q_{ij}^{0m}(A)\bar{e}_k^{(e')}(\vec{p}')] \bar{e}_r^{(e)}(\vec{p})\bar{e}_s^{(e')}(\vec{p}') \frac{e^{i\vec{p}\cdot\vec{R}}e^{-i\vec{p}'\cdot\vec{R}'}}{(p+k_{m0})(p'+k_{m0})} \\ &+ [\mu_i^{0m}(A)\bar{e}_k^{(e')}(\vec{p}') + \frac{1}{c}m_k^{m0}(A)\bar$$

where the inter-particle displacement vectors \vec{R} and \vec{R}' are defined as $\vec{R} = \vec{R}_D - \vec{R}_T$ and $\vec{R}' = \vec{R}_A - \vec{R}_T$, respectively.

To proceed further in the calculation of the matrix element, the sums over the virtual photon modes $\overrightarrow{p}, \varepsilon$ and $\overrightarrow{p}', \varepsilon'$ must be evaluated. For the polarization index sums, use is made of the identities [3]

$$\sum_{\varepsilon} e_i^{(\varepsilon)}(\vec{p}) \overline{e}_j^{(\varepsilon)}(\vec{p}) = \sum_{\varepsilon} b_i^{(\varepsilon)}(\vec{p}) \overline{b}_j^{(\varepsilon)}(\vec{p}) = \delta_{ij} - \hat{p}_i \hat{p}_j, \tag{11}$$

and

$$\sum_{\varepsilon} e_i^{(\varepsilon)}(\vec{p}) \bar{b}_j^{(\varepsilon)}(\vec{p}) = \varepsilon_{ijk} \hat{p}_k, \tag{12}$$

where ε_{ijk} is the Levi-Civita alternating tensor. The leading term of Equation (10), namely, the matrix element for RET between an electric dipole donor and an electric dipole acceptor mediated by an electric dipole polarizable third body, has been evaluated previously [29–32].

New features arise with the inclusion of higher multipole moments. By way of illustration, the contribution from Equation (10) proportional to " $[\vec{\mu}(D)\vec{m}(A) + \vec{m}(D)\vec{\mu}(A)]\alpha(T)$ " is extracted. Carrying out the polarization sums using the first relation of Equations (11), and Equation (12), this term is

$$\frac{1}{c} \sum_{\overrightarrow{p}} \sum_{\overrightarrow{p'}} \left(\frac{p}{2\varepsilon_0 V} \right) \left(\frac{p'}{2\varepsilon_0 V} \right) \alpha_{kl}(T; -p, -p') \\
\times \left[\mu_i^{0m}(D) m_j^{m0}(A) (\delta_{ik} - \hat{p}_i \hat{p}_k) \varepsilon_{jls} \hat{p}'_s + m_i^{0m}(D) \mu_j^{m0}(A) \varepsilon_{iks} \hat{p}_s(\delta_{jl} - \hat{p}'_j \hat{p}'_l) \right] \\
\times \left\{ \frac{e^{i\overrightarrow{p}\cdot\overrightarrow{R}} e^{i\overrightarrow{p}\cdot\overrightarrow{R}'}}{(p+k_{m0})(p'-k_{m0})} + \frac{e^{-i\overrightarrow{p}\cdot\overrightarrow{R}} e^{-i\overrightarrow{p'}\cdot\overrightarrow{R}'}}{(p-k_{m0})(p'+k_{m0})} + \frac{e^{-i\overrightarrow{p}\cdot\overrightarrow{R}} e^{i\overrightarrow{p'}\cdot\overrightarrow{R}'}}{(p-k_{m0})(p'-k_{m0})} + \frac{e^{i\overrightarrow{p}\cdot\overrightarrow{R}} e^{-i\overrightarrow{p}\cdot\overrightarrow{R}'}}{(p+k_{m0})(p'+k_{m0})} \right\}.$$
(13)

The four terms within braces of the last expression may be written as a product of factors involving one virtual photon momentum variable only so that the \vec{p} and \vec{p}' and sums are now independent:

$$\frac{1}{c} \sum_{\substack{\vec{p} \ \vec{p}'}} \left(\frac{p}{2\varepsilon_0 V} \right) \left(\frac{p'}{2\varepsilon_0 V} \right) \alpha_{kl}(T; -p, -p') \\
\times [\mu_i^{0m}(D) m_j^{m0}(A) (\delta_{ik} - \hat{p}_i \hat{p}_k) \varepsilon_{jls} \hat{p}'_s + m_i^{0m}(D) \mu_j^{m0}(A) \varepsilon_{iks} \hat{p}_s(\delta_{jl} - \hat{p}'_j \hat{p}'_l)] \\
\times \{ \frac{e^{i\vec{p} \cdot \vec{R}}}{p + k_{m0}} + \frac{e^{-i\vec{p} \cdot \vec{R}}}{p - k_{m0}} \} \{ \frac{e^{i\vec{p}' \cdot \vec{R}'}}{p' - k_{m0}} + \frac{e^{-i\vec{p}' \cdot \vec{R}'}}{p' + k_{m0}} \}.$$
(14)

Converting the sum over discrete virtual photon wave vectors to a continuous variable via the relation,

$$\sum_{\overrightarrow{p}} \to \frac{V}{(2\pi)^3} \int d^3 \overrightarrow{p}, \qquad (15)$$

and performing the necessary angular averages, the wave vector sums may be evaluated to give \vec{r}

$$\sum_{\vec{p}} \left(\frac{p}{2\varepsilon_0 V} \right) (\delta_{ij} - \hat{p}_i \hat{p}_j) \{ \frac{e^{i\vec{p}\cdot\vec{R}}}{p - k_{m0}} + \frac{e^{-i\vec{p}\cdot\vec{R}}}{p + k_{m0}} \} = -V_{ij}(k_{m0}, \vec{R}),$$
(16)

and

$$\frac{1}{c}\sum_{\overrightarrow{p}}\left(\frac{p}{2\varepsilon_0 V}\right)\varepsilon_{ijk}\hat{p}_k\left\{\frac{e^{i\overrightarrow{p}\cdot\overrightarrow{R}}}{p-k_{m0}}+\frac{e^{-i\overrightarrow{p}\cdot\overrightarrow{R}}}{p+k_{m0}}\right\}=-U_{ij}(k_{m0},\overrightarrow{R}).$$
(17)

On the right-hand side of the result Equation (16) is the familiar retarded resonant electric dipole–dipole interaction tensor, $V_{ij}(k_{m0}, \vec{R})$, defined by

$$V_{ij}(k,\vec{r}) = -\frac{1}{4\pi\epsilon_0}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\frac{e^{ikr}}{r} = \frac{1}{4\pi\epsilon_0 r^3}[(\delta_{ij} - 3\hat{r}_i\hat{r}_j)(1 - ikr) - (\delta_{ij} - \hat{r}_i\hat{r}_j)k^2r^2]e^{ikr}.$$
 (18)

Appearing in Equation (17) is the tensor

$$U_{ij}(k,\vec{r}) = -\frac{ik}{4\pi\varepsilon_0 c}\varepsilon_{ijk}\nabla_k \frac{e^{ikr}}{r} = \frac{1}{4\pi\varepsilon_0 cr^3}\varepsilon_{ijk}\hat{r}_k[ikr+k^2r^2]e^{ikr},$$
(19)

which features in RET between electric and magnetic dipole moments; it is entirely retarded, vanishing when k = 0 [3,4,43]. The contribution Equation (14) thus becomes

$$[\mu_i^{0m}(D)m_j^{m0}(A)V_{ik}(k_{m0},\vec{R})U_{jl}(k_{m0},\vec{R}') + m_i^{0m}(D)\mu_j^{m0}(A)U_{ik}(k_{m0},\vec{R})V_{jl}(k_{m0},\vec{R}')]\alpha_{kl}(T;-k_{m0},+k_{m0}).$$
(20)

Returning to Equation (10) and focusing on the pure and mixed dipolar terms only, using the identities Equations (11) and (12), and the results Equations (16) and (17), the electric and magnetic dipole-dependent matrix element is found to be

$$M_{fi}^{\mu+m} = [-\mu_i^{0m}(D)\mu_j^{m0}(A)V_{ik}^R V_{jl}^{R'} + \mu_i^{0m}(D)m_j^{m0}(A)V_{ik}^R U_{jl}^{R'} + m_i^{0m}(D)\mu_i^{m0}(A)U_{ik}^R V_{il}^{R'} - m_i^{0m}(D)m_j^{m0}(A)U_{ik}^R U_{ll}^{R'}]\alpha_{kl}^{R},$$
(21)

where to simplify the expression, the following shorthand notation is introduced: $V_{ij}^R = V_{ij}(k_{m0}, \vec{R}), U_{ij}^R = U_{ij}(k_{m0}, \vec{R})$, and $\alpha_{kl}^T = \alpha_{kl}(T; -k_{m0}, +k_{m0})$.

A similar procedure is used to obtain contributions dependent upon the electric quadrupole moment. Only pure and mixed electric multipole moment terms of Equation (10) are extracted, with higher-order mixed magnetic dipole–electric quadrupole factors being neglected. Use is made of the result

$$\sum_{\vec{p}} \left(\frac{p}{2\varepsilon_0 V} \right) (\delta_{ij} - \hat{p}_i \hat{p}_j) \nabla_k \{ \frac{e^{i\vec{p}\cdot\vec{R}}}{p + k_{m0}} + \frac{e^{-i\vec{p}\cdot\vec{R}}}{p - k_{m0}} \} = -V_{ijk}(k_{m0}, \vec{R}),$$
(22)

which features in quadrupolar RET [52], with $V_{ijk}(k, \vec{r})$ defined as

$$V_{ijk}(k,\vec{r}) = -\frac{1}{4\pi\epsilon_0}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\nabla_k \frac{e^{ikr}}{r} = \frac{1}{4\pi\epsilon_0 r^4} [(\delta_{ij} - \hat{r}_i\hat{r}_j)\hat{r}_k(-ik^3r^3 + k^2r^2) + (\delta_{ij}\hat{r}_k + \delta_{ik}\hat{r}_j + \delta_{jk}\hat{r}_i - 5\hat{r}_i\hat{r}_j\hat{r}_k)(k^2r^2 + 3ikr - 3)]e^{ikr}.$$
(23)

Thus, the electric dipole and quadrupole-dependent contribution to the matrix element is given by

$$M_{fi}^{\mu+Q} = [-\mu_i^{0m}(D)\mu_k^{m0}(A)V_{ir}^R V_{ks}^{R'} - \mu_i^{0m}(D)Q_{kl}^{m0}(A)V_{ir}^R V_{ksl}^{R'} + Q_{ij}^{0m}(D)\mu_k^{m0}(A)V_{irj}^R V_{ks}^{R'} + Q_{ij}^{0m}(D)Q_{kl}^{m0}(A)V_{irj}^R V_{ksl}^{R'}]a_{rs}^{T},$$
(24)

where the shorthand notation $V_{ijk}^R = V_{ijk}(k_{m0}, \vec{R})$ is introduced. Note that the leading electric dipole–dipole term appears as the first term in Equation (24), just as in Equation (21). This completes the evaluation of the matrix element for RET between an electric dipole, quadrupole, and magnetic dipole donor and acceptor molecule mediated by a third molecule. Specific contributions to the transfer rate are extracted in the sections that follow.

3. Dipolar Contributions to the Mediated Rate

For weak radiation–matter coupling, in which a perturbative approximation is invoked to solve the QED eigenvalue problem via the computation of the matrix element, M_{fi} , the rate of RET may be obtained from the Fermi golden rule formula:

$$\Gamma = \frac{2\pi\rho_f}{h} |M_{fi}|^2,\tag{25}$$

where Γ is the rate, and ρ_f is the density of final states. To keep the length of rate results manageable, specific multipole moment-dependent contributions will be considered separately.

The first term to be examined is the rate between an electric dipole donor and an acceptor that is characterized by terms proportional to the product of transition electric and magnetic dipole moments, i.e., " $\vec{\mu}\vec{m} + \vec{m}\vec{\mu}$ ". The rate for the three species in fixed orientation relative to one another is

$$\Gamma^{(\mu\mu)^{D}-(\mu m+m\mu)^{A}} = \frac{2\pi\rho_{f}}{h}\mu_{i}^{0m}(D)\overline{\mu}_{i'}^{m0}(D) \times [\mu_{j}^{0m}(A)m_{j'}^{m0}(A)V_{jl}^{R'}\overline{U}_{j'l'}^{R'} - \mu_{j'}^{0m}(A)m_{j}^{m0}(A)U_{jl}^{R'}\overline{V}_{j'l'}^{R'}] \times V_{ik}^{R}\overline{V}_{i'k'}^{R}\alpha_{kl}^{T}\overline{\alpha}_{k'l'}^{T},$$
(26)

where the overbar denotes the complex conjugate quantity, and use has been made of the relations $m_i^{0m} = -m_i^{m0} = \overline{m}_i^{m0}$, for an imaginary magnetic dipole moment operator and real molecular wave functions. Explicit distance and orientational dependences of Equation (26) are obtained on inserting the geometric tensors $V_{ij}^{R/R'}$ and $U_{ij}^{R/R'}$.

To obtain the rate formula applicable to species that are freely tumbling, as in the gaseous or liquid phases, an orientational average must be performed on Equation (26). The averages over D and A involve using the result for the average of a second-rank Cartesian tensor since they each involve a product of dipole moments. Hence

$$<\mu_{i}^{0m}(D)\overline{\mu}_{i'}^{m0}(D)>=rac{1}{3}\delta_{ii'}|\overset{\rightarrow}{\mu}^{m0}(D)|^{2},$$
 (27)

and

$$<\mu_{j}^{0m}(A)m_{j'}^{m0}(A)> = \frac{1}{3}\delta_{jj'}[\overrightarrow{\mu}^{0m}(A)\cdot\overrightarrow{m}^{m0}(A)],$$
 (28)

where the chevron brackets indicate an orientationally averaged quantity. From Equation (26), it is seen that the mediator appears in the rate as the product of its dynamic polarizability and its complex conjugate, each of which are second-rank tensors. A free orientational average of the mediator thus requires use of the result for the average of a fourth-rank Cartesian tensor [53],

$$<\alpha_{kl}^{T}\overline{\alpha}_{k'l'}^{T}>=\frac{1}{30}\{(4\delta_{kl}\delta_{k'l'}-\delta_{kl'}\delta_{k'l}-\delta_{kk'}\delta_{ll'})\alpha_{\lambda\lambda}^{T}\overline{\alpha}_{\mu\mu}^{T}+[-2\delta_{kl}\delta_{k'l'}+3(\delta_{kl'}\delta_{k'l}+\delta_{kk'}\delta_{ll'})]\alpha_{\lambda\mu}^{T}\overline{\alpha}_{\lambda\mu}^{T}\},$$

$$(29)$$

using the index symmetry properties of the polarizability tensor, with Greek subscripts referring to Cartesian tensor components in the body-fixed frame. The result Equation (29) will be utilized in all of the remaining calculations of isotropic transfer rates. Inserting the last three relations in Equation (26) and contracting with the product of V and U tensors results in the isotropic rate vanishing, that is,

$$<\Gamma^{(\mu\mu)^D - (\mu m + m\mu)^A} >= 0.$$
 (30)

Unsurprisingly, interchanging the role of *D* and *A* also produces a vanishing randomly averaged rate. That is,

$$<\Gamma^{(\mu m+m\mu)^D-(\mu\mu)^A}>=0.$$
 (31)

On taking advantage of the fact that the electric and magnetic dipole moments are both vectors, the isotropic rate between a magnetic dipole donor particle and an electric dipole–magnetic dipole acceptor species, and the rate between an electric dipole–magnetic dipole donor and a magnetic dipole acceptor, both mediated by an electric dipole polarizable third body, *T*, also vanish on free orientational averaging, that is,

$$<\Gamma^{(mm)^{D}-(\mu m+m\mu)^{A}}>=<\Gamma^{(\mu m+m\mu)^{D}-(mm)^{A}}>=0.$$
 (32)

We now return to Equation (21) and extract the contribution to the rate proportional to the product of electric and magnetic dipole moments at both the emitter and absorber sites. For oriented *D*, *A*, and *T*, this is given by the expression $\Gamma(\mu m + m\mu)^{D} - (\mu m + m\mu)^{A} -$

$$\begin{aligned} & \frac{2\pi\rho_{f}}{h} \{\mu_{i}^{0m}(D)m_{i'}^{m0}(D)[\mu_{j'}^{0m}(A)m_{j'}^{m0}(A)U_{jl}^{R'}\overline{V}_{j'l'}^{R'} - \mu_{j}^{0m}(A)m_{j'}^{m0}(A)V_{jl}^{R'}\overline{U}_{j'l'}^{R'}]V_{ik}^{R}\overline{U}_{i'k'}^{R} \\ & +\mu_{i'}^{0m}(D)m_{i}^{m0}(D)[\mu_{j}^{0m}(A)m_{j'}^{m0}(A)V_{jl}^{R'}\overline{U}_{j'l'}^{R'} - \mu_{j'}^{0m}(A)m_{j}^{m0}(A)U_{jl}^{R'}\overline{V}_{j'l'}^{R'}]U_{ik}^{R}\overline{V}_{i'k'}^{R}\}\alpha_{kl}^{T}\overline{\alpha}_{k'l'}^{T}, \end{aligned}$$
(33)

with explicit distance and orientational behavior following from substituting the geometric tensors.

To find the isotropic rate, the orientational averages in Equations (28) and (29) are applied to Equation (33) and the product of tensors involving V and U are contracted. The

transfer rate between two electric–magnetic dipole particles mediated by an electric dipole polarizable third molecule is found to be

$$<\Gamma^{(\mu m+m\mu)^{D}-(\mu m+m\mu)^{A}} > = -\frac{8\pi\rho_{f}}{27hc^{2}}\frac{1}{(4\pi\varepsilon_{0})^{4}}\frac{k_{m0}^{8}}{R^{2}R'^{2}}(\hat{R}\cdot\hat{R}')[\overrightarrow{\mu}^{0m}(D)\cdot\overrightarrow{m}^{m0}(D)][\overrightarrow{\mu}^{0m}(A)\cdot\overrightarrow{m}^{m0}(A)][\alpha_{\lambda\lambda}^{T}\overline{\alpha}_{\mu\mu}^{T}-\alpha_{\lambda\mu}^{T}\overline{\alpha}_{\lambda\mu}^{T}].$$
(34)

This rate is clearly discriminatory, dependent upon the chirality of the emitter and receiver, which manifests through the pseudoscalar quantity $[\overset{\rightarrow 0m}{\mu}(\xi) \cdot \overset{\rightarrow m0}{m}(\xi)]$, $\xi = D, A$, which changes sign when one enantiomer is replaced by its mirror-image structure. A number of other interesting features emerge from the result Equation (34). The rate vanishes if the acceptor is oriented perpendicularly relative to the donor and has its maximum value when D, T, and A are collinear. Similarly, if the product of the diagonal components of the polarizability tensor of the mediator is equal to its product of off-diagonal elements, the rate again vanishes. While this may be achieved in a two-level truncation scheme, a multi-level model of T is needed to ensure that the relay of energy occurs. Expression Equation (34) is retarded, as evidenced by the factor k_{m0}^8 , indicative of radiative migration of energy. Further confirmation is provided by the inverse square dependence of the rate on each of the inter-particle displacements, *R* and *R'*. Hence, no near-zone limit exists. This is to be expected since there is no coupling between static electric and magnetic dipoles. The result Equation (34) complements discriminatory pair RET between two optically active molecules [43,44]. Dispersion energy shifts between two electric-magnetic dipole polarizable molecules are also discriminatory [54–58].

A contribution that is of an identical order of magnitude to that considered in the last example, Equations (33) and (34), is the rate between an electric dipole donor and a magnetic dipole acceptor, mediated by a third-body *T*. From Equation (21), the rate for an oriented arrangement of the three particles is

$$\Gamma^{(\mu\mu)^{D}-(mm)^{A}} = \frac{2\pi\rho_{f}}{h}\mu_{i}^{0m}(D)\overline{\mu}_{i'}^{0m}(D)m_{j}^{m0}(A)\overline{m}_{j'}^{m0}(A)\alpha_{kl}^{T}\overline{\alpha}_{k'l'}^{T}V_{ik}^{R}\overline{V}_{i'k'}^{R}U_{jl}^{R'}\overline{U}_{j'l'}^{R'}.$$
 (35)

In addition to Equations (27) and (29), the following orientational average over products of magnetic dipole moments associated with center ξ is necessary to compute the rate applicable to a fluid sample,

$$< m_i^{0m}(\xi)\overline{m}_{i'}^{m0}(\xi) > = \frac{1}{3}\delta_{ii'}|\overrightarrow{m}^{0m}(\xi)|^2,$$
 (36)

yielding the isotropic rate result

$$< \Gamma^{(\mu\mu)^{D}-(mm)^{A}} > = \frac{\pi\rho_{f}}{135hc^{2}} \frac{1}{(4\pi\epsilon_{0})^{4}} \frac{1}{(RR')^{6}} |\vec{\mu}^{Um}(D)|^{2} |\vec{m}^{m0}(A)|^{2} \\ \times (\{[3-9(\hat{R}\cdot\hat{R}')^{2}](k^{2}R'^{2}+k^{4}R'^{4})+[5-15(\hat{R}\cdot\hat{R}')^{2}](k^{4}R^{2}R'^{2}+k^{6}R^{2}R'^{4}) \\ +[-1+3(\hat{R}\cdot\hat{R}')^{2}](k^{6}R^{4}R'^{2}+k^{8}R^{4}R'^{4})\}\alpha^{T}_{\lambda\lambda}\overline{\alpha}^{T}_{\mu\mu} \\ +\{[41-3(\hat{R}\cdot\hat{R}')^{2}](k^{2}R'^{2}+k^{4}R'^{4})+[15-5(\hat{R}\cdot\hat{R}')^{2}](k^{4}R^{2}R'^{2}+k^{6}R^{2}R'^{4}) \\ +[13+(\hat{R}\cdot\hat{R}')^{2}](k^{6}R^{4}R'^{2}+k^{8}R^{4}R'^{4})\}\alpha^{T}_{\lambda\mu}\overline{\alpha}^{T}_{\lambda\mu}),$$

$$(37)$$

where $k = k_{m0}$. It is informative to evaluate the asymptotic limits of result Equation (37) corresponding to short and large relative separation distances. In the near zone, $kR \ll 1$ and $kR' \ll 1$, yielding the asymptote

$$< \Gamma^{(\mu\mu)^{D} - (mm)^{A}} >_{NZ} \sim \frac{\pi \rho_{f}}{135hc^{2}} \frac{1}{(4\pi\epsilon_{0})^{4}} \frac{k^{2}}{R^{6}R'^{4}} |\overset{\rightarrow}{\mu}^{0m}(D)|^{2} |\vec{m}^{m0}(A)|^{2} \\ \times ([3 - 9(\hat{R} \cdot \hat{R}')^{2}] \alpha^{T}_{\lambda\lambda} \overline{\alpha}^{T}_{\mu\mu} + [41 - 3(\hat{R} \cdot \hat{R}')^{2}] \alpha^{T}_{\lambda\mu} \overline{\alpha}^{T}_{\lambda\mu}),$$
(38)

which is also not a true near-zone limit since U_{ij} is retarded, and with $k^2 = k_{m0}^2$ appearing explicitly. Interestingly, the short-range rate exhibits Förster-like R^{-6} dependence due to electric dipole–dipole transfer between *D* and *T*, and R'^{-4} behavior arising from exchange between electric dipole *T* and magnetic dipole *A*. At very large inter-particle displacements, kR >> 1 and kR' >> 1, giving rise to the far zone approximated form of the rate

$$< \Gamma^{(\mu\mu)^{D} - (mm)^{A}} >_{FZ} \sim \frac{\pi\rho_{f}}{135hc^{2}} \frac{1}{(4\pi\varepsilon_{0})^{4}} \frac{k^{8}}{R^{2}R'^{2}} |\vec{\mu}^{0m}(D)|^{2} |\vec{m}^{m0}(A)|^{2} \\ \times \{ [-1 + 3(\hat{R} \cdot \hat{R}')^{2}] \alpha_{\lambda\lambda}^{T} \overline{\alpha}_{\mu\mu}^{T} + [13 + (\hat{R} \cdot \hat{R}')^{2}] \alpha_{\lambda\mu}^{T} \overline{\alpha}_{\lambda\mu}^{T} \},$$
(39)

displaying characteristic inverse square behavior on each of R and R', indicative of sequential real photon emission from D to A via T.

From the results Equations (35) and (37), it is straightforward to obtain the mediated transfer rate between a magnetic dipole emitter and an electric dipole acceptor; simply interchange \hat{R} and \hat{R}' , and R and R'. The same holds for the asymptotically limiting forms Equations (38) and (39).

The final pure dipolar contribution to the third body-mediated rate to be considered is that between a magnetic dipole donor and a magnetic dipole acceptor, the magnetic analog of the leading pure electric dipole case, which has been examined previously [29–32]. For an oriented configuration, the rate from Equation (21) is given by

$$\Gamma^{(mm)^{D}-(mm)^{A}} = \frac{2\pi\rho_{f}}{h} m_{i}^{0m}(D) m_{i'}^{m0}(D) m_{j}^{0m}(A) m_{j'}^{m0}(A) \alpha_{kl}^{T} \overline{\alpha}_{k'l'}^{T} U_{ik}^{R} \overline{U}_{i'k'}^{R} U_{jl}^{R'} \overline{U}_{j'l'}^{R'}.$$
 (40)

Employing the rotational averages Equations (29) and (36) and contracting with the geometrical tensors, the mediated rate for a freely tumbling system is

$$<\Gamma^{(mm)^{D}-(mm)^{A}} >= \frac{\pi\rho_{f}}{135h} \frac{1}{(4\pi\epsilon_{0}c)^{4}} \frac{1}{R^{6}R'^{6}} |\vec{m}^{0m}(D)|^{2} |\vec{m}^{m0}(A)|^{2} \times \{[-1+3(\hat{R}\cdot\hat{R}')^{2}] \alpha^{T}_{\lambda\lambda} \overline{\alpha}^{T}_{\mu\mu} + [13+(\hat{R}\cdot\hat{R}')^{2}] \alpha^{T}_{\lambda\mu} \overline{\alpha}^{T}_{\lambda\mu} \} [k^{4}R^{2}R'^{2} + k^{6}(R^{2}R'^{4} + R^{4}R'^{2}) + k^{8}R^{4}R'^{4}],$$
(41)

with $k = k_{m0}$.

In the near zone, kR and kR' are both a lot less than unity so that the dominant contribution from the polynomial factor is $k^4R^2R'^2$, yielding the limit

$$<\Gamma^{(mm)^{D}-(mm)^{A}}>_{NZ} \sim \frac{\pi\rho_{f}}{135h} \frac{1}{(4\pi\epsilon_{0}c)^{4}} \frac{k^{4}}{R^{4}R'^{4}} |\vec{m}^{0m}(D)|^{2} |\vec{m}^{m0}(A)|^{2} \times \{[-1+3(\hat{R}\cdot\hat{R}')^{2}]\alpha_{\lambda\lambda}^{T}\overline{\alpha}_{\mu\mu}^{T} + [13+(\hat{R}\cdot\hat{R}')^{2}]\alpha_{\lambda\mu}^{T}\overline{\alpha}_{\lambda\mu}^{T}\},$$
(42)

which is not a true near-zone limit due to the presence of the radiative factor k^4 , but which exhibits inverse fourth power dependence on each displacement variable. In the far zone, the rate takes the form

$$<\Gamma^{(mm)^{D}-(mm)^{A}}>_{FZ} \sim \frac{\pi\rho_{f}}{135\hbar} \frac{1}{(4\pi\varepsilon_{0}c)^{4}} \frac{k^{8}}{R^{2}R'^{2}} |\vec{m}^{0m}(D)|^{2} |\vec{m}^{m0}(A)|^{2} \times \{[-1+3(\hat{R}\cdot\hat{R}')^{2}]\alpha_{\lambda\lambda}^{T}\overline{\alpha}_{\mu\mu}^{T} + [13+(\hat{R}\cdot\hat{R}')^{2}]\alpha_{\lambda\mu}^{T}\overline{\alpha}_{\lambda\mu}^{T}\},$$
(43)

illustrative of a radiative exchange mechanism due to the inverse square behavior of R and R'.

4. Electric Dipole and Quadrupole Contributions to the Mediated Rate

Pure electric dipole and electric quadrupole contributions to the third body-mediated rate, as well as various mixed contributions, may be obtained from the matrix element, $M_{fi}^{\mu+Q}$, Equation (24). Individual terms are again considered separately.

The first contribution to be studied is the rate term proportional to a donor that is an electric dipole emitter, and a mixed electric dipole–quadrupole acceptor, namely between " $(\mu\mu)^{D}$ " and " $(\mu Q + Q\mu)^{A}$ ". Hence, for the three bodies in fixed mutual orientation,

$$\Gamma^{(\mu\mu)^{D}-(\muQ+Q\mu)^{A}} = \frac{2\pi\rho_{f}}{h} [\mu_{i}^{0m}(D)\mu_{i'}^{0m}(D)\mu_{k}^{m0}(A)Q_{k'l'}^{m0}(A)V_{ir}^{R}\overline{V}_{i'r'}^{R}V_{ks}^{R'}\overline{V}_{k's'l'}^{R'} + \mu_{i}^{0m}(D)Q_{kl}^{0m}(D)Q_{kl}^{m0}(A)\mu_{k'}^{R}\overline{V}_{i'r'}^{R}V_{ksl}^{R'}\overline{V}_{k's'}^{R'}]\alpha_{rs}^{R}\overline{\alpha}_{r's'}^{T},$$
(44)

with explicit distance and orientation dependences obtained on inserting the respective geometric tensors from Equations (18) and (23). To obtain the isotropic rate, the averages over D and T may be performed using the results Equations (27) and (29), respectively. For A, however, an average over a third-rank Cartesian tensor is needed. This is given by

$$<\mu_i^{0m}(\xi)Q_{jk}^{m0}(\xi)>=\frac{1}{6}\varepsilon_{ijk}\varepsilon_{\lambda\mu\nu}\mu_{\lambda}^{0m}(\xi)Q_{\mu\nu}^{m0}(\xi),\tag{45}$$

which vanishes because the electric quadrupole moment is symmetric in the indices μ and ν , while the Levi-Civita tensor is anti-symmetric in this pair. Thus

$$<\Gamma^{(\mu\mu)^D-(\mu Q+Q\mu)^A}>=0.$$
 (46)

Based on symmetry considerations, the isotropic rate also vanishes when the characteristics of *D* and *A* are switched relative to the previous case, that is,

$$<\Gamma^{(\mu Q+Q\mu)^D-(\mu\mu)^A}>=0.$$
 (47)

Using index symmetry of the electric quadrupole moment and index anti-symmetry of the alternating tensor, it is easily seen that the following isotropic electric quadrupole-dependent contributions to the rate are also zero,

$$<\Gamma^{(\mu Q+Q\mu)^{D}-(QQ)^{A}}> = <\Gamma^{(QQ)^{D}-(\mu Q+Q\mu)^{A}}> = <\Gamma^{(\mu Q+Q\mu)^{D}-(\mu Q+Q\mu)^{A}}> = 0.$$
(48)

The last of these three written in Equation (48) is the analog of the discriminatory rates Equations (33) and (34) evaluated in the previous section involving the interference of electric and magnetic dipole coupling terms. While the electric dipole–quadrupole counterpart does not survive orientational averaging, the rate for fixed mutual orientation of the three bodies does depend on the chirality of *D* and *A*. From the matrix element Equation (24), the rate is

$$\Gamma^{(\mu Q+Q\mu)^{D}-(\mu Q+Q\mu)^{A}} =
-\frac{2\pi\rho_{f}}{h} \{\mu_{i}^{0m}(D)Q_{i'j'}^{0m}(D)[\mu_{k}^{m0}(A)Q_{k'l'}^{m0}(A)V_{ks}^{R'}\overline{V}_{k's'l'}^{R'} + Q_{kl}^{m0}(A)\mu_{k'}^{m0}(A)V_{ksl}^{R'}\overline{V}_{k's'}^{R'}]V_{ir}^{R}\overline{V}_{i'r'j'}^{R} +
+Q_{ij}^{0m}(D)\mu_{i'}^{0m}(D)[Q_{kl}^{m0}(A)\mu_{k'}^{m0}(A)V_{ksl}^{R'}\overline{V}_{k's'}^{R'} + \mu_{k}^{m0}(A)Q_{k'l'}^{m0}(A)V_{ks}^{R'}\overline{V}_{k's'l'}^{R'}]V_{irj}^{R}\overline{V}_{i'r'}^{R}] \}\alpha_{rs}^{T}\overline{\alpha}_{r's'}^{T}.$$
(49)

The only surviving quadrupolar-dependent contributions to the isotropic rate are of the type " $(\mu\mu)^D - (QQ)^A$ ", " $(QQ)^D - (\mu\mu)^A$ ", and the pure quadrupole coupling term at each *D* and *A* center, " $(QQ)^D - (QQ)^A$ ". These are now evaluated. For a pure electric dipole donor and a pure electric quadrupole absorber, the oriented rate term from the matrix element Equation (24) is

$$\Gamma^{(\mu\mu)^D - (QQ)^A} = \frac{2\pi\rho_f}{h} \mu_i^{0m}(D) \mu_{i'}^{m0}(D) Q_{kl}^{m0}(A) Q_{k'l'}^{m0}(A) \alpha_{rs}^T \overline{\alpha}_{r's'}^T V_{ir}^R \overline{V}_{i'r'}^R V_{ksl}^{R'} \overline{V}_{k's'l'}^{R'}.$$
 (50)

To derive the rate applicable to freely tumbling molecules, the rotational averages Equations (27) and (29) are again used for *D* and *T*, respectively; for the product of electric quadrupole moments of *A*, the following fourth-rank Cartesian tensor average is employed:

$$< Q_{kl}^{0m}(A)Q_{k'l'}^{m0}(A) >= \frac{1}{10} (\delta_{kl'}\delta_{k'l} + \delta_{kk'}\delta_{ll'})Q_{\rho\sigma}^{0m}(A)Q_{\rho\sigma}^{m0}(A),$$
(51)

on making use of the symmetric and traceless properties of the tensor $Q_{ij}^{0m}(\xi)$. Substituting the results for the averages, contracting indices, and multiplying the geometric tensors using relations Equations (18) and (23) yields the isotropic rate formula

$$< \Gamma^{(\mu\mu)^{D}-(QQ)^{A}} >= \frac{\pi\rho_{f}}{450h} \frac{1}{(4\pi\varepsilon_{0})^{4}} \frac{1}{R^{6}R'^{8}} |\vec{\mu}^{00m}(D)|^{2} Q_{\rho\sigma}^{0m}(A) Q_{\rho\sigma}^{m0}(A) \times [\alpha_{\lambda\lambda}^{T} \overline{\alpha}_{\mu\mu}^{T} \{-4[54 - 243(\hat{R} \cdot \hat{R}')^{2}] - 108[1 - 3(\hat{R} \cdot \hat{R}')^{2}]k^{2}R'^{2} - 360[1 - 3(\hat{R} \cdot \hat{R}')^{2}]k^{2}R^{2} + 72[1 - 3(\hat{R} \cdot \hat{R}')^{2}]k^{4}R^{4} - [21 + 9(\hat{R} \cdot \hat{R}')^{2}]k^{4}R'^{4} + 18[1 - 45(\hat{R} \cdot \hat{R}')^{2}]k^{4}R^{2}R'^{2} + 3[1 - 3(\hat{R} \cdot \hat{R}')^{2}]k^{6}R'^{6} - 3[9 + 5(\hat{R} \cdot \hat{R}')^{2}]k^{6}R^{2}R'^{4} - 18[1 + 3(\hat{R} \cdot \hat{R}')^{2}]k^{6}R^{4}R'^{2} + [13 - 15(\hat{R} \cdot \hat{R}')^{2}]k^{8}R^{2}R'^{6} - 3[3 - (\hat{R} \cdot \hat{R}')^{2}]k^{8}R^{4}R'^{4} + 3[1 + (\hat{R} \cdot \hat{R}')^{2}]k^{10}R^{4}R'^{6} \} + \alpha_{\lambda\mu}^{T}\overline{\alpha}_{\lambda\mu}^{T} \{3528 + 324(\hat{R} \cdot \hat{R}')^{2} + [684 + 108(\hat{R} \cdot \hat{R}')^{2}]k^{2}R'^{2} + 360[3 + (\hat{R} \cdot \hat{R}')^{2}]k^{2}R^{2} + 72[17 - (\hat{R} \cdot \hat{R}')^{2}]k^{4}R^{4} + [89 - 3(\hat{R} \cdot \hat{R}')^{2}]k^{4}R'^{4} + [198 + 270(\hat{R} \cdot \hat{R}')^{2}]k^{4}R^{2}R'^{2} + [41 - 3(\hat{R} \cdot \hat{R}')^{2}]k^{6}R'^{6} + [23 - 5(\hat{R} \cdot \hat{R}')^{2}]k^{6}R^{2}R'^{4} + 18[13 - (\hat{R} \cdot \hat{R}')^{2}]k^{6}R^{4}R'^{2} + 5[3 - (\hat{R} \cdot \hat{R}')^{2}]k^{8}R^{2}R'^{6} + 29[1 + (\hat{R} \cdot \hat{R}')^{2}]k^{8}R^{4}R'^{4} + [1 + (\hat{R} \cdot \hat{R}')^{2}]k^{10}R^{4}R'^{6} \}],$$
(52)

which holds for all *R* and *R'* outside the charge overlap region, with $k = k_{m0}$. A true near-zone limit of Equation (52) arises since static coupling is possible between electric multipoles. Retaining the pertinent wave vector independent terms, the isotropic rate valid at short separations between particles is

$$<\Gamma^{(\mu\mu)^{D}-(QQ)^{A}}>_{NZ}\sim\frac{\pi\rho_{f}}{450h}\frac{1}{(4\pi\varepsilon_{0})^{4}}\frac{1}{R^{6}R^{\prime8}}|\vec{\mu}^{0m}(D)|^{2}Q^{0m}_{\rho\sigma}(A)Q^{m0}_{\rho\sigma}(A) \times \{-4\alpha^{T}_{\lambda\lambda}\overline{\alpha}^{T}_{\mu\mu}[54-243(\hat{R}\cdot\hat{R}')^{2}]+\alpha^{T}_{\lambda\mu}\overline{\alpha}^{T}_{\lambda\mu}[3528+324(\hat{R}\cdot\hat{R}')^{2}]\},$$
(53)

which exhibits R^{-6} behavior indicative of near-zone dipole–dipole transfer between *D* and *T*, and R'^{-8} near-zone dipole–quadrupole exchange between *T* and *A*. At the other distance extreme, approximating kR and kR' to be much greater than unity gives rise to the far-zone asymptote

$$<\Gamma^{(\mu\mu)^{D}-(QQ)^{A}}>_{FZ}\sim\frac{\pi\rho_{f}}{450h}\frac{1}{(4\pi\varepsilon_{0})^{4}}\frac{k^{10}}{R^{2}R'^{2}}|\vec{\mu}^{0m}(D)|^{2}Q^{0m}_{\rho\sigma}(A)Q^{m0}_{\rho\sigma}(A)\{3\alpha^{T}_{\lambda\lambda}\overline{\alpha}^{T}_{\mu\mu}+\alpha^{T}_{\lambda\mu}\overline{\alpha}^{T}_{\lambda\mu}\}[1+(\hat{R}\cdot\hat{R}')^{2}],$$
(54)

which displays characteristic inverse square dependences on *R* and *R'*. It should be noted that the oriented and isotropic rates for the case " $(QQ)^D - (\mu\mu)^A$ " may be obtained from Equations (50) and (52) on interchanging *R* and *R'*, and \hat{R} and \hat{R}' .

The final surviving isotropic-mediated rate involving the electric quadrupole moment to be calculated is the term that is dependent upon the pure quadrupole moment of *D* and the pure quadrupole of *A*. From the matrix element Equation (24), the rate for the three bodies in fixed relative orientation is

$$<\Gamma^{(QQ)^{D}-(QQ)^{A}}>=\frac{2\pi\rho_{f}}{h}Q_{ij}^{0m}(D)Q_{i'j'}^{m0}(D)Q_{kl}^{0m}(A)Q_{k'l'}^{m0}(A)\alpha_{rs}^{T}\overline{\alpha}_{r's'}^{T}V_{irj}^{R}\overline{V}_{ksl}^{R'}\overline{V}_{k's'l'}^{R'}.$$
(55)

Using Equation (29) for the average over the electric dipole polarizability of *T*, and the result Equation (51) for both *D* and *A*, contracting the tensors and multiplying the product of four $V_{ijk}^{R/R'}$ factors from Equation (23), of which twelve such terms ensue, produces the isotropic rate formula

$$< \Gamma^{(QQ)^{D} - (QQ)^{A}} > = \frac{\pi \rho_{f}}{1500h} \frac{1}{(4\pi\varepsilon_{0})^{4}} \frac{1}{R^{8}R'^{8}} Q_{\nu\pi}^{0m}(D) Q_{\nu\sigma}^{m0}(D) Q_{\rho\sigma}^{0m}(A) Q_{\rho\sigma}^{m0}(A) \times \{\alpha_{\lambda\lambda}^{T} \overline{\alpha}_{\mu\mu}^{T} [-1 + 3(\hat{R} \cdot \hat{R}')^{2}] (5184 + 2592k^{2}(R^{2} + R'^{2}) + 1080k^{4}(R^{4} + R'^{4}) + 1296k^{4}R^{2}R'^{2} -72k^{6}(R^{6} + R'^{6}) + 540k^{6}R^{2}R'^{2}(R^{2} + R'^{2}) + 225k^{8}R^{4}R'^{4} - 36k^{8}R^{2}R'^{2}(R^{4} + R'^{4}) -15k^{10}R^{4}R'^{4}(R^{2} + R'^{2}) + k^{12}R^{6}R'^{6}) + \alpha_{\lambda\mu}^{T} \overline{\alpha}_{\lambda\mu}^{T} (2592[41 + 2(\hat{R} \cdot \hat{R}')^{2}] + 2592[8 + (\hat{R} \cdot \hat{R}')^{2}]k^{2}(R^{2} + R'^{2}) + 1080[3 + (\hat{R} \cdot \hat{R}')^{2}]k^{4}(R^{4} + R'^{4}) + 1296[3 + (\hat{R} \cdot \hat{R}')^{2}]k^{4}R^{2}R'^{2} + 72[17 - (\hat{R} \cdot \hat{R}')^{2}]k^{6}(R^{6} + R'^{6}) + 540[1 + (\hat{R} \cdot \hat{R}')^{2}]k^{6}R^{2}R'^{2}(R^{2} + R'^{2}) + 45[1 + 5(\hat{R} \cdot \hat{R}')^{2}]k^{8}R^{4}R'^{4} + 36[7 - (\hat{R} \cdot \hat{R}')^{2}]k^{8}R^{2}R'^{2}(R^{4} + R'^{4}) + 15[3 - (\hat{R} \cdot \hat{R}')^{2}]k^{10}R^{4}R'^{4}(R^{2} + R'^{2}) + [13 + (\hat{R} \cdot \hat{R}')^{2}]k^{12}R^{6}R'^{6})\},$$

$$(56)$$

which holds beyond the overlap of wave functions associated with *D*, *T*, and *A*.

Asymptotic limits of the general result Equation (56) readily follow from making the approximations appropriate to the near and far zones. At short R and R',

$$<\Gamma^{(QQ)^{D}-(QQ)^{A}}>_{NZ}\sim\frac{5184\pi\rho_{f}}{1500h}\frac{1}{(4\pi\epsilon_{0})^{4}}\frac{1}{R^{8}R'^{8}}Q_{\nu\pi}^{0m}(D)Q_{\nu\pi}^{m0}(D)Q_{\rho\sigma}^{0m}(A)Q_{\rho\sigma}^{m0}(A) \times\{[-1+3(\hat{R}\cdot\hat{R}')^{2}]\alpha_{\lambda\lambda}^{T}\bar{\alpha}_{\mu\mu}^{T}+\frac{1}{2}[41+2(\hat{R}\cdot\hat{R}')^{2}]\alpha_{\lambda\mu}^{T}\bar{\alpha}_{\lambda\mu}^{T}\},$$
(57)

exhibiting inverse eighth power dependence on each of the inter-particle separation distances. In the far zone, on the other hand, radiative transfer leads to inverse square distance dependences,

$$<\Gamma^{(QQ)^{D}-(QQ)^{A}}>_{FZ} \sim \frac{\pi\rho_{f}}{1500h} \frac{1}{(4\pi\varepsilon_{0})^{4}} \frac{k^{12}}{R^{2}R'^{2}} Q_{\nu\pi}^{0m}(D) Q_{\nu\pi}^{m0}(D) Q_{\rho\sigma}^{0m}(A) Q_{\rho\sigma}^{m0}(A) \times \{[-1+3(\hat{R}\cdot\hat{R}')^{2}]\alpha_{\lambda\lambda}^{T}\overline{\alpha}_{\mu\mu}^{T} + [13+(\hat{R}\cdot\hat{R}')^{2}]\alpha_{\lambda\mu}^{T}\overline{\alpha}_{\lambda\mu}^{T}\}.$$
(58)

5. Summary

The problem of RET mediated by a passive, polarizable third body has been tackled within the framework of molecular QED theory. Previous work [29–32], which was limited to the electric dipole approximation being made for the emitter and receiver particles, has been extended to include the effects of magnetic dipole and electric quadrupole interaction terms. A host of pure and mixed multipole moment terms now contribute to the rate, including transfer relayed between two chiral molecules, of particular interest in the present study. To account for the mediation of energy between two optically active molecules, it was necessary to include magnetic dipole and electric quadrupole coupling terms to describe the donor and acceptor. While these multipole moments are smaller than the electric dipole by a factor of the fine structure constant, limiting the treatment of the process to only the leading electric dipole coupling term, as in earlier work [29–32], does not result in any discriminatory effects occurring.

A single virtual photon propagating between D and T, and another such particle traversing between T and A, are responsible for the conveyance of energy. The total matrix element was evaluated using diagrammatic time-dependent perturbation theory. To reduce the number of possible time-ordered sequences of emission and absorption events attributable to differing multipole moments, an effective two-photon coupling Hamiltonian that was proportional to the polarizability of T and depended quadratically on the electric displacement field was employed for the mediator molecule. Hence, only six Feynman-like diagrams needed to be evaluated and summed over at the third order of perturbation theory. The transfer rate, applicable to both oriented and isotropic systems was computed via the Fermi golden rule, which applies when the coupling between radiation and matter, and between particles, is weak, and for durations longer than the inverse frequency of the decay transition but less than the inverse rate.

If the donor or acceptor is either pure electric or pure magnetic dipolar, and the other is mixed electric–magnetic dipolar, and vice versa, the rate vanishes on orientational aver-

aging, with all other dipolar combinations surviving tumble averaging. The contribution proportional to the mixed electric-magnetic dipole moments of A and D is discriminatory, depending on the handedness of the emitter and absorber species through the pseudoscalar $[\mu^{0m}(\xi) \cdot \vec{m}^{m0}(\xi)], \xi = D, A$, with the rate changing sign when one enantiomer is replaced by its antipode and increasing in direct proportion to this quantity. Interestingly, the rate was found to be a maximum if the two chiral molecules and the mediator are collinear, and is zero if one enantiomer is perpendicular to the other. A possible system of interest is 3-methylcyclopentanone, which has been employed in studying the enhancement of the discriminatory dispersion interaction in the presence of a chiral surface [59]. Of the contributions to the rate proportional to the pure or mixed combinations of electric dipole and quadrupole moments of D and A, only pure dipole or pure quadrupole moments at either D or A survive free orientational averaging, all other possibilities producing a zero isotropic rate. For those permutations of moments that led to non-vanishing orientationally averaged rate formulae, near- and far-zone limiting forms were calculated. In each case, the expected short-range radiationless, Förster-type of transfer manifested, corresponding to static coupling between electric-electric and magnetic-magnetic multipoles. At very long range, the rates exhibited inverse square behavior on each inter-particle displacement, indicative of radiative transfer. Both mechanisms are well known from pair transfer theory [4].

In the microscopic model developed, energy is transferred directly between the transmitter and receiver, or indirectly through the mediator, which in the spatial configuration chosen, relays energy between the two sites. Other possible transfer pathways involving T coupling only to D or only to A will be considered in future to assess the importance of the bridge-assisted mechanism. More challenging is to add one extra mediator, to see the effect on the rate from two inert polarizable particles relative to direct and three-body contributions to transfer between chiral donor and acceptor. The present and future studies will enable connections to be made with macroscopic treatments of the surroundings, which often involve the environment being taken to have a uniform dielectric constant, though little work has been done examining chiroptical effects. From the microscopic point of view, the addition and rigorous accounting of more and more mediators will ultimately lead to results applicable to a bulk medium with the Clausius–Mossotti equation linking the macroscopic polarizability of the bath to its refractive index and dispersive properties.

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