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2

Unified theory of radiative and radiationless energy transfer

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2.1   INTRODUCTION

The resonance transfer of energy between chemical species separated beyond wavefunction overlap has, until quite recently, commonly been regarded as being mediated by one of two distinct mechanisms: radiationless transfer, generally associated with the names of Perrin [46], Förster [23], Dexter [19] and Galanin [24, 25], and radiative transfer. The former applies over short distances and is characterized by an inverse sixth-power dependence on the separation between the donor and acceptor; the latter is a longer-range effect characterized by an inverse square law. Within the framework of a unified theory [4, 6, 7, 8, 10, 11, 26, 37, 38, 53], it has emerged that both are but limits of a more general mechanism which operates over all distances. This includes an intermediate range over which some degree of competition between the two traditional mechanisms might have been envisaged – and where it transpires that a third, previously hidden, interaction gains equal prominence. However, the new approach offers a number of other advantages beyond its greater compass. In particular, it can properly accommodate the dielectric influence of the medium across which energy transfer takes place [37], it lends itself to the rigorous analysis of energy transfer dynamics [38, 52], and it can be incorporated into stochastic theories of ensemble energy transport [15]. Further, it is a theory

which has successfully expedited the resolution of a number of serious conceptual and other problems latent in earlier treatments. It is the purpose of this chapter to summarize the key features of the modern theoretic development, to identify results in a form amenable to direct implementation, and to highlight the paradigm shift in the conceptualization of resonance energy transfer.

2.2 BACKGROUND

2.2.1 Theoretical framework

The framework within which the unified theory naturally emerges is quantum electrodynamics (QED) [28], best implemented in the molecular formulation largely due to Craig and Thirunamachandran [16]. This is a theory in which both matter and radiation are subject to quantum development, in contrast to the more familiar semiclassical approach where radiation is treated as a classical electromagnetic field. Quantum electrodynamics is in fact the only theory in which the photon concept has any legitimacy, despite the latter's invocation at some point in almost every semiclassical description. It is a theory in which retardation is also naturally accommodated, reflecting the finite speed of signal propagation. It is such retardation features, for example, which are responsible for modifying at mesoscopic distances the inverse sixth-power distance-dependence of the London potential (the attractive part of the 6–12 Lennard–Jones potential) to the correct and experimentally verified form given by the Casimir–Polder formula – in which the asymptotic behavior at large distances proves to be of inverse seventh-power form [16, 42]. Lastly, QED is a theory in which matter and radiation, treated on a common footing, together comprise a closed dynamical system, as illustrated in Fig. 2.1 for the simple case of photon absorption. Notwithstanding the theory's intrinsic logical appeal, it is the incorporation of retardation features in particular which vindicates the application to resonance energy transfer. It is this aspect which proves crucial in identifying the link between radiationless and radiative transport of excitation energy – it also clarifies their relationship to the classical model of dipole coupling [5].

2.2.2 Historical development

More than a half century has elapsed since the first pioneering attempts by Kikuchi [39], Fermi [21], Heitler and Ma [30] and Hamilton [27] to address by quantum electrodynamical methods the theory of resonance energy transfer. It was clearly not the intention in the earliest studies, concentrating on the longer-range (far zone) energy transfer, to forge any link between the so-called radiative and radiationless mechanisms. In the 1960s, Avery [10] and Gomberoff and
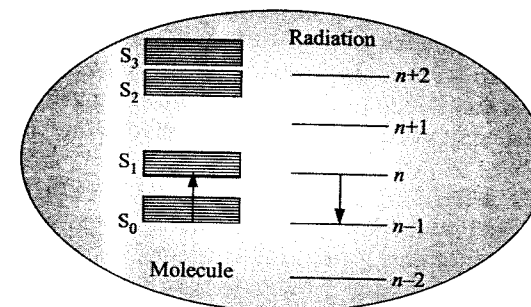
Figure 2.1 A representation of the absorption of light by a molecular system, emphasizing the quantum-electrodynamical view of the molecule plus the radiation as a single closed system. The molecule undergoes an upward transition from its ground to its first excited singlet state, while the radiation experiences a transition from a state with n photons to one with $n-1$

Power [26] made the first attempts to extend the Förster theory of the short-range radiationless energy transfer [2, 23–25] to arbitrary transfer distances, to include long-range radiative transfer. Such a unified approach to radiative and radiationless energy transfer received a considerable boost of interest in the 1980s [4, 8, 9, 11, 17, 47] and 1990s [6, 7, 14, 18, 35, 52, 53]. Through such studies it has been demonstrated [35, 11, 8, 7, 6, 4] that, in the far zone, the unified mechanism for energy transfer equates to emission of a photon by a donor molecule and subsequent recapture of the photon by an acceptor, thus proving the equivalence of the so-called radiationless and radiative mechanisms. In other developments [44, 54, 18, 38, 52], the time evolution of the transfer dynamics has been explicitly considered within the framework of the unified theory, analysing in detail the transfer dynamics beyond the rate regime.

Another important raft of issues relates to the incorporation within the unified theory of the effects of the surrounding medium. Although a handful of sporadic attempts to accommodate medium effects in excitation transfer has appeared previously [7, 10, 17], it was the case until quite recently that most QED theories totally ignored the influence of such effects. The 1989 treatment by Craig and Thirunamachandran [17], incorporating effects of a third molecule in the energy transfer between a selected pair of molecules, led to a new discussion of the way to include dielectric characteristics. It was suggested from macroscopic arguments that the vacuum dielectric permittivity ϵ_0 entering the rate of excitation transfer *in vacuo* should be replaced by its medium counterpart ϵ to represent the screening. Nevertheless, in using this prescriptive approach other important medium effects, such as local fields, energy losses due to the absorbing medium, and influences on the character of the transfer rates in passing from the near to the far zone, were not considered. More recently, a QED theory was developed

by us [37, 38] which systematically dealt with these issues by microscopically including the molecular medium. In contrast to the conventional QED theories in which energy transfer is cast in terms of the intermolecular propagation of virtual photons, the new theory has been formulated by invoking the concept of bath polaritons ("medium-dressed" photons) mediating the process. The medium effects have been shown to play an important role in making the unified theory self-consistent [35, 37, 38]. In fact, it was a systematic treatment of the surrounding medium that made it possible to solve the problem of potentially infinite ensemble rates of energy transfer associated with the far zone inverse square law, as will be discussed in detail in Section 2.5.

2.2.3 Physical basis

Before proceeding further, it is worth saying something about the electronic basis for these interactions. Although usually couched in terms of a coupling between molecules, the theory to be described here is valid for energy transfer between any two species with a distinct electronic integrity – for convenience and generality we can simply refer to them as the donor and acceptor. The theory thus embraces not only intermolecular transfer, but also transfer between chromophores within any larger structure such as a protein or other host structure – provided that these chromophores are not electronically coupled by a resonance structure such as a conjugated chain. As it is generally most convenient to consider electronic properties in terms of electric dipoles, quadrupoles, etc., we shall deal in the common multipolar (Power–Zienau–Woolley) form of QED. A key feature of this formulation is the exact cancelation of all intermolecular coulombic (longitudinal) interactions [16], so that any process involving two or more electrically neutral species invokes the creation and annihilation of virtual photons: in the jargon of particle physics, where QED is more often applied, we would say that these are the gauge bosons that mediate intermolecular interaction. If that sounds daunting, the calculations which it engenders in the case of resonance energy transfer nonetheless prove remarkably straightforward.

2.2.4 Layers of complexity

To develop a usable and general result for the rate of energy exchange in a real system, it is most instructive and convenient to progressively refine a working model by inclusion of salient detail. The plan in the following sections of this chapter is therefore to work as follows:

• The first stage (Section 2.3) is to define the basic concepts of the unified theory, subsequently providing the derivation of the transition matrix

element for energy transfer between a pair of chromophores separated by an arbitrary distance R. This leads to identification of the radiative R^{-1} term featured in the quantum amplitude for the transition (the transition matrix element), along with the near-zone R^{-3} contribution. At this stage, neither the effect of the surrounding medium nor the vibrational structure for each of the transfer species is explicitly included.

• The next step (Section 2.4) is to include the effects of energy-level structure for each donor and acceptor. Accordingly, the transfer rate is represented in terms of the overlap integral between the donor fluorescence and the acceptor absorption spectra, establishing a connection with the Förster theory of radiationless energy transfer. The subsequent consideration of the range-dependence of the fluorescence depolarization illustrates the general theory.

• The third element (Section 2.5) is accommodation of the electronic influence of the absorbing molecular medium between the donor and acceptor sites. This is reflected in refractive and dissipative effects on the transfer of excitation energy, rectifying the otherwise anomalous R^{-2} dependence of the transfer rates between the selected pair at large separation. Using the corrected pair rates one can calculate (Section 2.5.2) the total rate of decay of an initially excited molecule due to the energy transfer to the surrounding medium. The contributions due to energy transfer in the far zone are then identified as the rate of spontaneous emission in the absorbing medium, the effects of the surrounding medium being incorporated on a fully microscopic basis.

• Finally, Section 2.6 analyses in detail the transfer dynamics for a pair of species in a dielectric medium. Starting from a general consideration of the time evolution, a connection is first established with the temporal basis of the previous sections that describe the process in terms of the energy transfer rates. Attention is then focused on situations that do not fit into the rate regime, and where different dynamical aspects are apparent.

2.3   THE BASIS OF THE UNIFIED THEORY

2.3.1 General formulation

In the multipolar (Power–Zienau–Woolley) formulation of QED [16, 50, 57], the Coulomb interaction between molecules is represented by the propagation of transverse virtual photons, and it is the coupling between the molecules and the quantized radiation field which is responsible not only for molecular absorption and emission, but also for intermolecular energy transfer. In this formalism, the Hamiltonian for the system can generally be written as

$$H = H_{\text{rad}} + \sum_X H_{\text{mol}}(X) + \sum_X H_{\text{int}}(X), \qquad (2.1)$$

where H_{rad} is the Hamiltonian for the radiation field and $H_{mol}(X)$ is the Hamiltonian for molecule X, the summations being over all molecules of the system. The coupling between the molecular subsystem and the quantized field is represented by a set of terms $H_{int}(X)$ that describe the interaction of the field with the individual molecules. For general purposes, it is sufficient to express the interaction terms in the electric dipole approximation, although the formalism that we employ is perfectly amenable to the incorporation of higher multipole terms [52]. Thus we write

$$H_{int}(X) = -\varepsilon_0^{-1}\boldsymbol{\mu}(X) \cdot \mathbf{d}^\perp(\mathbf{R}_X), \qquad (2.2)$$

where $\boldsymbol{\mu}(X)$ is the electric dipole operator of the molecule X positioned at $\mathbf{R}_X$, and $\mathbf{d}^\perp(\mathbf{R}_X)$ is the electric displacement operator calculated at the molecular site. The latter displacement operator and the radiation Hamiltonian may be cast as [16]

$$\mathbf{d}^\perp(\mathbf{R}) = i\sum_{\mathbf{k},\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{1/2}\mathbf{e}^{(\lambda)}(\mathbf{k})\left\{a^{(\lambda)}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R}} - a^{(\lambda)^-}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{R}}\right\} \qquad (2.3)$$

and

$$H_{rad} = \sum_{\mathbf{k},\lambda}a^{(\lambda)+}(\mathbf{k})a^{(\lambda)}(\mathbf{k})\hbar ck + e_{vac}, \qquad (2.4)$$

where in each expression a sum is taken over radiation modes characterized by wave-vector $\mathbf{k}$ and polarization vector $\mathbf{e}^{(\lambda)}(\mathbf{k})$ (with $\lambda = 1, 2$); $a^{(\lambda)+}(\mathbf{k})$ and $a^{(\lambda)}(\mathbf{k})$ are the corresponding operators for creation and annihilation of a photon, V is the quantization volume, and e_{vac} is the energy of the photon vacuum.

2.3.2 Energy transfer between a donor and acceptor pair in vacuum

In this and the next sections, we shall analyse the energy transfer between a pair of species (to be referred to as donor and acceptor, labeled by D and A) without taking into account the influences of other molecules comprising the surrounding medium [4, 6, 7, 8, 9, 10, 11, 16, 18, 26]. In such a situation the general Hamiltonian Eqn 2.1 reduces to the following:

$$H = H^0 + V, \qquad (2.5)$$

with

$$H^0 = H_{rad} + H_{mol}(D) + H_{mol}(A) \qquad (2.6)$$

and

$$V = H_{int}(D) + H_{int}(A). \qquad (2.7)$$

To represent the energy transfer from D to A, the initial and final state vectors are chosen to be the following eigenvectors of the zero-order Hamiltonian H^0:

$$|I\rangle = |D^*\rangle|A\rangle|0\rangle, \quad |F\rangle = |D\rangle|A^*\rangle|0\rangle, \qquad (2.8)$$

the corresponding energies being

$$E_I = e_{D^*} + e_A + e_{vac}, \quad E_F = e_D + e_{A^*} + e_{vac}, \qquad (2.9)$$

where $|0\rangle$ denotes the photon vacuum, $|D^*\rangle$ and $|D\rangle$ label the initial and final states of the donor, $|A\rangle$ and $|A^*\rangle$ are the corresponding state vectors of the acceptor (the asterisk referring to a molecule in an electronically excited state), and e_{D^*} and e_A (e_D and e_{A^*}) are the appropriate energies of the donor and acceptor in their initial (final) states. For generality, the state vectors of donor and acceptor are considered to implicitly contain vibrational contributions that are normally separable from the electronic parts on the basis of the Born–Oppenheimer principle, both for the ground and excited electronic molecular states. The vibronic sublevels will be explicitly included into the theory in the following section.

In passing, we note that the conventional (semiclassical) theories of radiationless energy transfer [2, 23, 25] do not consider photon states, and the energy transfer appears as a first-order process induced by an instantaneous Coulomb interaction. Such an approach is justified in the near zone, i.e. when the distance R of donor–acceptor separation is much less than the reduced wavelength $\lambda = \lambda/2\pi$, λ being the wavelength corresponding to the transfer energy. In the QED formalism employed here, the quantized electromagnetic field is treated on an equal footing to the molecular subsystem, both subsystems comprising a united dynamical system described by the full Hamiltonian H. Here the energy transfer emerges as a second-order process mediated by intermolecular propagation of virtual photons (see Fig. 2.2), and the theory is no longer restricted to the near zone of the separation distances R. The rate of excitation energy transfer, associated with the initial and final states of Eqn 2.8, can be generally written using the Fermi Golden Rule (see Section 2.6 for more detail; and, for example, [21, 51]), as

$$W_{FI} = \frac{2\pi}{\hbar}|\langle F|T|I\rangle|^2\delta(E_I - E_F), \qquad (2.10)$$
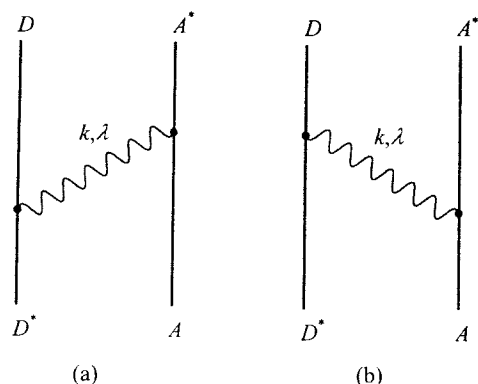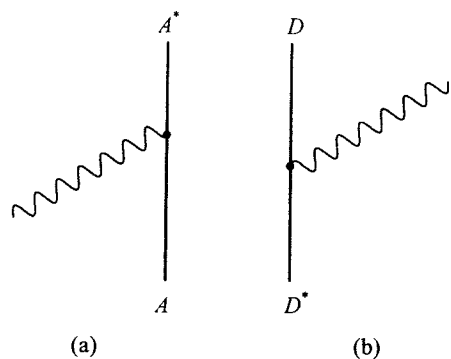
Figure 2.2 The two time-ordered diagrams for resonance energy transfer, time progressing upward. In both cases the virtual photon labeled k, λ mediates the transfer of energy from the initially excited donor D^* to the acceptor A

where T is the transition operator, given by

$$T = V + V \frac{1}{E_1 - H^0 + \mathrm{i}s} V + \ldots = T^{(1)} + T^{(2)} + \ldots \quad (S \to +0) \quad (2.11)$$

and the higher order terms can be neglected for our purposes. In the QED approach, the first-order term $T^{(1)} \equiv V$, representing photoabsorption and photoemission by individual molecules (Fig. 2.3), does not contribute to the transfer rate as given by Eqns 2.10 and 2.11. It is the second-order contribution

Figure 2.3 Time-ordered diagrams for (a) photoabsorption and (b) photoemission

$T^{(2)}$ that is the leading term responsible for the resonance energy transfer in question. Using Eqns 2.4–2.9, the second-order transition matrix element reads

$$\langle F|T^{(2)}|I \rangle = \frac{1}{\hbar} \sum_{\mathbf{k},\lambda} \sum_{q=1}^{2} \frac{\langle F|V|M_q(\mathbf{k},\lambda) \rangle \langle M_q(\mathbf{k},\lambda)|V|I \rangle}{(-1)^{q+1}cK - ck + \mathrm{i}s}, \quad (2.12)$$

with

$$\hbar cK = e_{A^*} - e_A = e_{D^*} - e_D > 0 \quad (2.13)$$

being the transfer energy. Here $|M_p(\mathbf{k},\lambda)\rangle$ $(q = 1, 2)$ denote the intermediate states in which both donor and acceptor are either in the ground $(q = 1)$ or in the excited $(q = 2)$ electronic states:

$$|M_1(\mathbf{k},\lambda)\rangle = |D\rangle|A\rangle|\mathbf{k},\lambda\rangle \quad (2.14)$$

and

$$|M_2(\mathbf{k},\lambda)\rangle = |D^*\rangle|A^*\rangle|\mathbf{k},\lambda\rangle, \quad (2.15)$$

the radiation field being promoted to a one-photon state:

$$|\mathbf{k},\lambda\rangle \equiv a^{(\lambda)^-}(\mathbf{k})|0\rangle. \quad (2.16)$$

The two types of intermediate state correspond to the two possible sequences of transitions undergone by the donor and acceptor. In the first case $(q = 1)$, the transition $D^* \to D$ precedes the transition $A^* \to A^*$, as in Fig. 2.2a, whereas in the second case $(q = 2)$ one has the opposite ordering, as in Fig. 2.2b. The latter sequence represents an apparently anomalous situation in which the upward transition of the acceptor A is accompanied by the creation of a virtual photon, and the subsequent annihilation of the photon induces the downward transition by the donor $D^* \to D$. Nevertheless, both types of transition must be included in the theory according to the normal rules of time-dependent perturbation theory. The precision with which the law of energy conservation has to apply to the virtual photons is determined by the time–energy Uncertainty Principle: $\delta E \delta t \geqslant \hbar$, where $\delta t = R/c$ is the time necessary for a photon to cover the distance between the donor and acceptor, giving

$$\delta E \geqslant \frac{\hbar cK}{KR}. \quad (2.17)$$

Consequently, the contribution due to intermediate states of the second type, Fig. 2.2b, is of essential importance in the near zone $(KR \ll 1)$, for which the

energy uncertainty δE greatly exceeds the energy transferred, $\hbar cK$. At large separations ($KR \gg 1$), where a virtual photon mediating the interaction between the donor and acceptor exists for a time that appreciably exceeds the duration of the optical cycle, the photon acquires real character: $\delta E \ll \hbar cK$. In such a situation, the contribution associated with Fig. 2.2b diminishes to a point at which it can be considered negligible.

Substituting Eqns 2.2, 2.8, 2.9, and 2.14–2.16 into Eqn 2.12, one arrives at the following expression for the transition matrix element:

$$\langle F|T^{(2)}|I\rangle = \mu_{A_l}^{\text{full}} \, \theta_{lj}^{\text{vac}}(K,\mathbf{R}) \mu_{D_j}^{\text{full}}, \tag{2.18}$$

with

$$\theta_{lj}^{\text{vac}}(K,\mathbf{R}) = \frac{1}{\hbar\varepsilon_0^2} \sum_{\mathbf{k},\lambda} \left[\frac{\langle 0|d_l^-(\mathbf{R}_A)|\mathbf{k},\lambda\rangle\langle \mathbf{k},\lambda|d_j^-(\mathbf{R}_D)|0\rangle}{cK - ck + \mathrm{i}s} \right.$$
$$\left. - \frac{\langle 0|d_j^-(\mathbf{R}_D)|\mathbf{k},\lambda\rangle\langle \mathbf{k},\lambda|d_l^-(\mathbf{R}_A)|0\rangle}{cK + ck - \mathrm{i}s} \right] \quad (\mathbf{R} = \mathbf{R}_A - \mathbf{R}_D) \tag{2.19}$$

and

$$\boldsymbol{\mu}_D^{\text{full}} = \langle D|\boldsymbol{\mu}(D)|D^*\rangle, \qquad \boldsymbol{\mu}_A^{\text{full}} = \langle A^*|\boldsymbol{\mu}(A)|A\rangle. \tag{2.20}$$

where implied summation over the repeated Cartesian indices (l and j) is assumed, and where $\boldsymbol{\mu}_D^{\text{full}}$ and $\boldsymbol{\mu}_A^{\text{full}}$ are the transition dipole moments of the donor and acceptor, respectively. The superscript "full" indicates that the molecular state vectors entering the transition dipoles of Eqn 2.20 contain both electronic and vibrational contributions, as made explicit in the following section. Here also $\theta_{lj}^{\text{vac}}(K,\mathbf{R})$ is the tensor for the retarded dipole–dipole coupling between the donor and acceptor in vacuum: modifications to the tensor by the surrounding molecular medium will be considered in Section 2.5. Using Eqn 2.3 for the displacement operator and performing summation over the photon polarizations ($\lambda = 1,2$), the tensor Eqn 2.19 reduces to

$$\theta_{lj}^{\text{vac}}(K,\mathbf{R}) = \sum_{\mathbf{k}} \frac{(\delta_{lj} - \hat{k}_l\hat{k}_j)k}{2\varepsilon_0 V} \left[\frac{\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{R}}}{K - k + \mathrm{i}s'} - \frac{\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{R}}}{K + k - \mathrm{i}s'} \right] \quad (\mathbf{R} = \mathbf{R}_A - \mathbf{R}_D), \tag{2.21}$$

where $\hat{\mathbf{k}} = \mathbf{k}/k$ is the unit vector along the wave-vector $\mathbf{k}$, and $s' = s/c \to +0$ is the new infinitesimal. Replacing the sum over $\mathbf{k}$ by an integral and performing the angular integration, Eqn 2.21 can be written as

$$\theta_{lj}^{\text{vac}}(K,\mathbf{R}) = \left(-\nabla^2\delta_{lj} + \nabla_l\nabla_j\right)\frac{1}{4\pi^2\varepsilon_0} G(K,R), \tag{2.22}$$

where

$$G(K,R) = \int_0^\infty \frac{\sin(kR)}{R}\left[\frac{1}{K - k + \mathrm{i}s'} - \frac{1}{K + k - \mathrm{i}s'}\right]\mathrm{d}k \tag{2.23}$$

$$= \frac{1}{2\mathrm{i}R}\int_{-\infty}^\infty \left[\frac{\mathrm{e}^{\mathrm{i}kR}}{K - k + \mathrm{i}s'} - \frac{\mathrm{e}^{\mathrm{i}kR}}{K + k + \mathrm{i}s'}\right]\mathrm{d}k \tag{2.24}$$

is the Green function, the sign of the infinitesimal s' being reversed in the nonresonant term of the original integral in Eqn 2.23 to expand the integration contour to negative values of k in Eqn 2.24. The expanded contour of integration can be closed up by a large semicircle in the upper complex half-plane, subsequently calculating the residue at $k = K + \mathrm{i}s'$ to yield

$$G(K,R) = -\pi\frac{\exp(\mathrm{i}KR)}{R}. \tag{2.25}$$

It is noteworthy that the imaginary infinitesimal featured in the transition matrix element, Eqn 2.11 and the subsequent equations, emerges intrinsically from the time-dependent analysis of the problem, as will be demonstrated in Section 2.6. It is the presence of such an infinitesimal s' that ensures the correct bypassing of poles in Eqns 2.23 and 2.24. Thus, one automatically avoids analytic problems associated with the choice of the integration contour of the Green function, discussed previously [8].

Using Eqn 2.25, the electromagnetic tensor, Eqn 2.22, now takes the final form

$$\theta_{lj}^{\text{vac}}(K,\mathbf{R}) = \frac{K^3\mathrm{e}^{\mathrm{i}KR}}{4\pi\varepsilon_0}\left[\left(\delta_{ij} - 3\hat{R}_i\hat{R}_j\right)\left(\frac{1}{K^3R^3} - \frac{i}{K^2R^2}\right) - \left(\delta_{ij} - \hat{R}_i\hat{R}_j\right)\frac{1}{KR}\right], \tag{2.26}$$

with $\hat{\mathbf{R}} = \mathbf{R}/R$. The above tensor, whose role in the first-order dispersion forces was much earlier established by Stephen [55], contains the R^{-3} term characteristic of the near zone, the radiative R^{-1} term operating in the far zone, as well as an R^{-2} contribution that plays an important role at critical retardation distances: $KR \simeq 1$. Note that the long- and short-range terms are characterized by different orientational dependencies: this factor will lead to the range dependence of the fluorescence anisotropy, to be discussed in Section 2.4.2.

2.4 SPECTRAL FEATURES

2.4.1 Connection with the Förster theory

According to the Born–Oppenheimer Principle, the molecular state vectors can be separated into electronic and vibrational parts, as

$$|\mathbf{D}^*\rangle = |\mathbf{D}_{el}^*\rangle|\varphi_{D^*}^{(n)}\rangle, \qquad |\mathbf{D}\rangle = |\mathbf{D}_{el}\rangle|\varphi_D^{(r)}\rangle, \qquad (2.27)$$

$$|\mathbf{A}\rangle = |\mathbf{A}_{el}\rangle|\varphi_A^{(m)}\rangle, \qquad |\mathbf{A}^*\rangle = |\mathbf{A}_{el}^*\rangle|\varphi_A^{(p)}\rangle, \qquad (2.28)$$

where the subscript "el" refers to the electronic part of the state vectors, the indices n, r, m, and p specifying the vibrational, rotational, etc. sublevels of the transfer species D and A. The transition dipole moments, Eqn 2.20, then split into electronic and vibrational contributions, as

$$\boldsymbol{\mu}_D^{full} = \langle \mathbf{D}_{el}|\boldsymbol{\mu}(\mathbf{D})|\mathbf{D}_{el}^*\rangle\langle\varphi_D^{(r)}|\varphi_{D^*}^{(n)}\rangle = \boldsymbol{\mu}_D\langle\varphi_D^{(r)}|\varphi_{D^*}^{(n)}\rangle, \qquad (2.29)$$

$$\boldsymbol{\mu}_A^{full} = \langle \mathbf{A}_{el}^*|\boldsymbol{\mu}(\mathbf{A})|\mathbf{A}_{el}\rangle\langle\varphi_{A^*}^{(p)}|\varphi_A^{(m)}\rangle = \boldsymbol{\mu}_A\langle\varphi_{A^*}^{(p)}|\varphi_A^{(m)}\rangle, \qquad (2.30)$$

where, according to the Condon Principle, the dipole operators of the donor and acceptor, $\boldsymbol{\mu}$ (D) and $\boldsymbol{\mu}$ (A) respectively, are assumed not to depend on the vibrational degrees of freedom, $\boldsymbol{\mu}_D$ and $\boldsymbol{\mu}_A$ being the appropriate electronic parts of the transition matrix elements.

Substituting the transition dipoles, Eqns 2.29 and 2.30, into Eqn 2.18, the full rate of donor–acceptor transfer reads, after performing the necessary averaging over the initial molecular states and summing over the final molecular states in Eqn 2.10,

$$W_{DA} = \frac{2\pi}{\hbar}\sum_{n,m,r,p}\rho_{D^*}^{(n)}\rho_A^{(m)}|\langle\varphi_D^{(r)}|\varphi_{D^*}^{(n)}\rangle\langle\varphi_{A^*}^{(p)}|\varphi_A^{(m)}\rangle|^2|\mu_{A_i}\mu_{D_j}|^2|\theta_{ij}^{vac}(K,\mathbf{R})|^2$$

$$\delta\left(e_{D_n^*} + e_{A_m} - e_{D_r} - e_{A_p^*}\right). \qquad (2.31)$$

Here, $\rho_{D^*}^{(n)}$ and $\rho_A^{(m)}$ are the population distribution functions of the initial vibrational states of the donor and acceptor respectively, the vibrational indices also being included in the energies of the initial and final states that feature in the energy-conserving delta function. In analogy to the Förster theory [2, 25], the pair transfer rate, Eqn 2.31, can be expressed, using Eqn 2.26 for $\theta_{ij}^{vac}(K,\mathbf{R})$, in terms of the overlap integral between the donor and acceptor spectra:

$$W_{DA} = \frac{9}{8\pi c^2\tau_D}\int_0^\infty F_D(\omega)\sigma_A(\omega)\omega^2 g^{vac}(\omega,\mathbf{R})d\omega, \qquad (2.32)$$

with

$$g^{vac}(\omega,\mathbf{R}) = \eta_3^2\frac{c^6}{\omega^6 R^6} + \left(\eta_3^2 - 2\eta_1\eta_3\right)\frac{c^4}{\omega^4 R^4} + \eta_1^2\frac{c^2}{\omega^2 R^2}. \qquad (2.33)$$

In the above equations,

$$\sigma_A(\omega) = \frac{\pi\omega\mu_A^2}{3\varepsilon_0 c}\sum_{m,p}\rho_A^{(m)}|\langle\varphi_{A^*}^{(p)}|\varphi_A^{(m)}\rangle|^2\delta\left(e_{A_p^*} - e_{A_m} - \hbar\omega\right) \qquad (2.34)$$

and

$$F_D(\omega) = \frac{\omega^3\tau_D\mu_D^2}{3\varepsilon_0\pi c^3}\sum_{n,r}\rho_{D^*}^{(n)}|\langle\varphi_D^{(r)}|\varphi_{D^*}^{(n)}\rangle|^2\delta\left(e_{D_n^*} - e_{D_r} - \hbar\omega\right), \qquad (2.35)$$

are, respectively, the cross-section for the acceptor absorption and the donor emission spectra (the latter $F_D(\omega)$ normalized to unity), τ_D being the radiative lifetime of the donor. Here also

$$\eta_q = (\hat{\boldsymbol{\mu}}_A \cdot \hat{\boldsymbol{\mu}}_D) - q\left(\hat{\mathbf{R}} \cdot \hat{\boldsymbol{\mu}}_A\right)\left(\hat{\mathbf{R}} \cdot \hat{\boldsymbol{\mu}}_D\right) \qquad (q = 1,3) \qquad (2.36)$$

are the orientational factors, the carets referring to unit vectors. In passing we note that the orientational factor η_3 that characterizes the near-zone transfer is identical to the kappa whose square is the familiar short-range orientational factor; see, for example, Chapter 4.

The rate equation 2.32 accommodates contributions due to both radiation-less and radiative energy transfer. In the near zone, Eqn 2.35 reduces to the usual Förster rate for nonradiative energy transfer [2, 25]:

$$W_{DA}^{Först} = \frac{9c^4\eta_3^2}{8\pi\tau_D R^6}\int_0^\infty F_D(\omega)\sigma_A(\omega)\omega^{-4}\,d\omega, \qquad (2.37)$$

characterized by an R^{-6} distance dependence and the orientational factor η_3^2 (kappa squared). In the far zone, Eqn 2.32 provides the radiative result $W_{DA} \propto \eta_1^2/R^2$. It is noteworthy that the two limiting cases differ not only in their distance dependence, but also in their orientational factors. This leads to a completely different transfer-induced fluorescence depolarization in these two cases, an issue to be discussed in detail in the following subsection. Note also that although the effects of retardation are contained in the pair-rate Eqn 2.32, the result has been derived without taking into account the influence of mole-cules other than the donor and acceptor: the effects of the intervening medium will be considered in Section 2.5.

We conclude this subsection with a remark concerning nonrigid systems that have fast rotational motion of the donor and acceptor. In such a situation, the factor $g^{\text{vac}}(\omega, \mathbf{R})$ that enters Eqn 2.32 should be replaced by its orientational average:

$$g_{av}^{\text{vac}}(\omega, \mathbf{R}) = \frac{2}{9}\left(\frac{3c^6}{\omega^6 R^6} + \frac{c^4}{\omega^4 R^4} + \frac{c^2}{\omega^2 R^2}\right). \tag{2.38}$$

The factor $g_{av}^{\text{vac}}(\omega, \mathbf{R})$ is then related to the excitation transfer function $A(K, R)$ introduced in [8, 4]. as

$$g_{av}^{\text{vac}}(\omega, \mathbf{R}) = \left(\frac{4\pi\varepsilon_0 c^3}{3\omega^3}\right)^2 A(\omega/c, R). \tag{2.39}$$

2.4.2 Range-dependence of the fluorescence depolarization

In this subsection we shall consider the polarization character of the system fluorescence [25]. applying the unified approach to determine the depolarization of fluorescence through acceptor decay following radiative or radiationless energy transfer. For the usual nonradiative (Förster) mechanism, the transfer rate depends only weakly on the average mutual orientation of the donors and acceptors (see Eqn 2.41 below for the average of the appropriate orientational factor). This is the reason for the well-known and considerable (1/25) reduction of fluorescence anisotropy following a single act of energy transfer in an isotropic or randomly oriented system [2, 25]. By contrast, in the radiative mechanism, the energy transfer between species with parallel transition dipoles is greatly preferred. leading to a smaller loss of polarization in a randomly oriented system (compare Eqn 2.40, in which the angle-dependent term is weighted by a factor of 7]. Consequently, the residual anisotropy following a single act of photon reabsorption is substantially (seven times) greater than in the case of nonradiative transfer.

Here, following [6]. a general formula will be derived which connects and accommodates the above limiting cases, also providing results that are valid for intermediate distances where neither radiative nor radiationless transfer dominates. Note that the rotational depolarization is assumed to be negligible. In order to arrive at a formula that exhibits the effects of the relative donor–acceptor orientation in an ensemble, it is necessary to average the pair-rate, Eqn 2.32, over the orientation of the radius vector $\mathbf{R}$, keeping a fixed mutual orientation between the donor and acceptor. We then obtain the following results for the rotational averages of the orientational factors featured in Eqn 2.33.

$$\overline{\eta_1^2} = \tfrac{1}{15}(7\cos^2\theta + 1), \qquad \overline{\eta_3^2} = \tfrac{1}{5}(\cos^2\theta + 3) \tag{2.40, 2.41}$$

and

$$\overline{\eta_1\eta_3} = \tfrac{1}{3}\overline{\eta_3^2}, \tag{2.42}$$

where $\cos\theta = \hat{\boldsymbol{\mu}}_A \cdot \hat{\boldsymbol{\mu}}_D$. Substituting the above averages into Eqns 2.32 and 2.33, we thus obtain

$$\overline{W(R)} \propto (3y_6 + y_4 + 7y_2)\cos^2\theta + (9y_6 + 3y_4 + y_2). \tag{2.43}$$

with

$$y_n = \frac{c^{n-2}}{R^n}\int_0^\infty \omega^{(2-n)} F_D(\omega)\sigma_A(\omega)\mathrm{d}\omega \quad (n = 2, 4, 6). \tag{2.44}$$

Therefore, the properly normalized function for the orientational distribution of excited acceptors is given by

$$f(\theta, R) = \frac{3}{10}\frac{(3 + \widetilde{K^2}R^2 + 7\widetilde{K^4}R^4)\cos^2\theta + (9 + 3\widetilde{K^2}R^2 + \widetilde{K^4}R^4)}{3 + \widetilde{K^2}R^2 + \widetilde{K^4}R^4}, \tag{2.45}$$

with

$$\widetilde{K^n} = \frac{\displaystyle\int_0^\infty (\omega/c)^n F_D(\omega)\sigma_A(\omega)\omega^{-4}\,\mathrm{d}\omega}{\displaystyle\int_0^\infty F_D(\omega)\sigma_A(\omega)\omega^{-4}\,\mathrm{d}\omega}. \tag{2.46}$$

Of special interest is the fluorescence anisotropy, defined by

$$r = \frac{I_{II} - I_\perp}{I_{II} + 2I_\perp}, \tag{2.47}$$

where I_{II} and $I_\perp$ are components of the fluorescence intensity polarized, respectively, parallel to and perpendicular to the polarization of the excitation light. In the case where fluorescence occurs directly from the molecule which absorbs the incident light (the donor), the anisotropy is designated r_0; where fluorescence occurs following a single-step transfer of energy to another molecule (the acceptor), the anisotropy is designated r_1. The value of r_0, if intramolecular relaxation of the donor produces no change of electronic state, has its theoretical maximum of 0.4 [2, 25].

Here it is the result for r_1 which is of principal interest; the fluorescence anisotropy following a chain of energy transfer events can be directly calculated from this result. In terms of r_0, the acceptor anisotropy r_1 can be expressed as

$$r_1 = \langle P_2(\cos\theta)\rangle r_0, \tag{2.48}$$

where $P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$ is the second-order Legendre polynomial, and the angular brackets denote the orientational average,

$$\langle P_2(\cos\theta)\rangle = \frac{1}{2}\int_0^\pi P_2(\cos\theta)f(\theta)\sin\theta\,\mathrm{d}\theta. \tag{2.49}$$

Substituting Eqn 2.45 into Eqn 2.49, we obtain the following most general result for the fluorescence anisotropy:

$$r_1(R) = \frac{r_0}{25}\frac{7\widetilde{K^4}R^4 + \widetilde{K^2}R^2 + 3}{\widetilde{K^4}R^4 + \widetilde{K^2}R^2 + 3}. \tag{2.50}$$

The above equation is valid for arbitrary separations R. As shown in Eqns 2.55 and 2.56 below, the familiar near- and far-zone results are the asymptotes of this formula. It is to be pointed out that, in general, the residual anisotropy depends not only on the transfer distance, but also on the shapes of the spectral lines through the averages $\widetilde{K^2}$ and $\widetilde{K^4}$ featured in Eqn 2.50. However, as the widths of the absorption and emission lines are considerably less than the photon frequency, Eqn 2.50 can be rewritten without significant loss of generality as

$$r_1(R) = \frac{r_0}{25}\frac{7\widetilde{K}^4R^4 + \widetilde{K}^2R^2 + 3}{\widetilde{K}^4R^4 + \widetilde{K}^2R^2 + 3}, \tag{2.51}$$

where $\widetilde{K}$ is the averaged value of K calculated by use of Eqn 2.46 with $n = 1$. In the case in which the absorption and emission lines are of Gaussian shape,

$$F_D(\omega) \propto \omega^3\exp\left[(\omega - \omega_D)^2/2\sigma^2\right], \qquad \sigma_A(\omega) \propto \omega\exp\left[(\omega - \omega_A)^2/2\sigma^2\right], \tag{2.52}$$

we have

$$\widetilde{K^2} = \widetilde{K}^2\left[1 + (\sigma/\tilde\omega)^2/2\right], \qquad \widetilde{K^4} = \widetilde{K}^4\left[1 + 3(\sigma/\tilde\omega)^2 + 3(\sigma/\tilde\omega)^4/4\right]. \tag{2.53, 2.54}$$

This means that if, for instance, the ratio $\sigma/\tilde\omega$ is equal to 0.1, the error made using the relationship of Eqn 2.51 instead of the exact result, Eqn 2.50, is less

than a few percent. Further, both formulas provide the correct asymptotes at small and large distances, as follows.

$\widetilde{K}R \ll 1$. Here, Eqns 2.50 and 2.51 reproduce the usual Galanin result,

$$r_1 \equiv r_1^{\text{nonrad}} = r_0/25. \tag{2.55}$$

$\widetilde{K}R \gg 1$. Here we arrive at the result for the fluorescence depolarization associated with radiative energy transfer from the donor to an acceptor in the far zone:

$$r_1 \equiv r_1^{\text{rad}} = 7r_0/25. \tag{2.56}$$

The distance-dependence of the relative anisotropy r_1/r_0 calculated according to Eqn 2.51 is presented in Fig. 2.4. One can see the anisotropy rise to significant values at distances much less than those normally associated with radiative energy transfer. For instance, with a donor–acceptor separation of $R = 1.5/\widetilde{K} = 0.75\lambda/\pi$, the relative anisotropy r_1/r_0 attains the value of 3/25, which is considerably higher than the result for radiationless transfer, as follows from Eqn 2.51.

In connection with multiphoton fluorescence energy transfer, any microscopically disordered system exhibits the same sevenfold increase in fluorescence
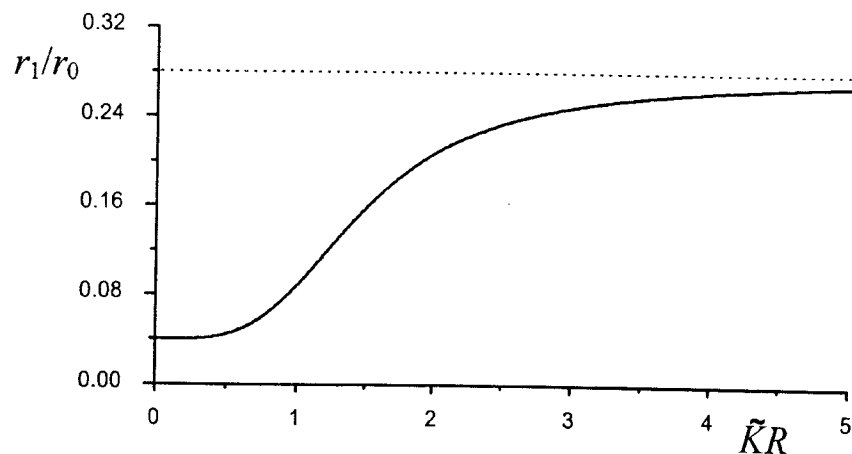
Figure 2.4 The distance-dependence of relative fluorescence anisotropy, displaying the increase associated with the onset of significant retardation on progressing from "radiationless" transfer at short distances to long-range "radiative" transfer. The abscissa values $\widetilde{K}R$ signify the donor–acceptor distance R divided by the "reduced wavelength" $\lambda/2\pi$, where λ is the wavelength corresponding to the transferred energy

anisotropy as the donor–acceptor distance increases from the near-zone to the far-zone range. However, the detailed dependence on the relative orientations of the participating donor transition moments adds considerable complexity to the results, even in the two-photon case [3].

2.5   REFRACTION AND DISSIPATION

In deriving the pair rate, Eqn 2.32, the influence of molecules other than the selected donor and acceptor has not been taken into account. Therefore, straightforward application of such pair rates to any ensemble can lead to erroneous conclusions, the most dramatic fact being the prediction of a potentially infinite donor decay rate, calculated as the sum of contributions to all surrounding acceptors (by analogy with the Förster theory of radiationless energy transfer [2, 25]). The problem arises because the pair rates, Eqn 2.35, behave as R^{-2} in the far zone, whereas for a uniform distribution the number of acceptors in a shell centered on the donor grows as R^2. In this section, contributions due to other molecules are systematically included into the pair rates, providing *inter alia* a resolution to the above problem.

2.5.1   Influence of the molecular medium on the pair rates

Let us return to the general Hamiltonian, Eqn 2.1, which describes an ensemble of molecules (atoms or chromophore groups) coupled with the quantized radiation field. To deal with excitation transfer between a selected pair of molecules D and A, we shall now divide the full system into two parts. One subsystem comprises the selected pair of species D and A; another subsystem (to be referred to as the polariton bath) contains the quantized electromagnetic field and the remaining molecules that constitute the surrounding medium. Note that the molecules of the medium may, but do not necessarily, differ in type from D and A. With regard to the chosen partitioning of the system, the full Hamiltonian of Eqn 2.1 splits into a zero-order Hamiltonian and interaction operator, as

$$H = H^0 + V,\tag{2.57}$$

with

$$H^0 = H_{\mathrm{bath}} + H_{\mathrm{mol}}(D) + H_{\mathrm{mol}}(A),\tag{2.58}$$

$$V = H_{\mathrm{int}}(D) + H_{\mathrm{int}}(A),\tag{2.59}$$

and

$$H_{\mathrm{bath}} = H_{\mathrm{rad}} + \sum_{X \neq D,A} [H_{\mathrm{mol}}(X) + H_{\mathrm{int}}(X)],\tag{2.60}$$

where the latter H_{bath} is the "bath" Hamiltonian that contains the radiation Hamiltonian H_{rad}, as well as contributions due to all molecules other than the donor and acceptor, the interaction Hamiltonians $H_{\mathrm{int}}(X)$ being given by Eqns 2.2 and 2.3.

The partitioning of Eqns 2.57–2.59 has the same form as Eqns 2.5–2.7 employed for energy transfer *in vacuo*, subject to the replacement $H_{\mathrm{rad}} \rightarrow H_{\mathrm{bath}}$. Consequently, one can readily modify the previous Eqns 2.8–2.20 to suit the present situation. Specifically, the state vector $|0\rangle$ featured in the initial conditions, Eqn 2.8, now represents the ground state of the polariton bath (a combined system of the radiation field and the molecular medium), e_{vac} being the corresponding zero-point energy of the bath. Next, the transition matrix element, Eqn 2.12, and the state vectors for the intermediate states, Eqns 2.14 and 2.15, modify as follows:

$$\langle F|T^{(2)}|I\rangle = \frac{1}{\hbar}\sum_{\sigma}\sum_{q=1}^{2}\frac{\langle F|V|M_q(\sigma)\rangle\langle M_q(\sigma)|V|I\rangle}{(-1)^{q+1}cK - \Pi_\sigma + is},\tag{2.61}$$

$$|M_1(\sigma)\rangle = |D\rangle|A\rangle|\sigma\rangle,\tag{2.62}$$

and

$$|M_2(\sigma)\rangle = |D^*\rangle|A^*\rangle|\sigma\rangle,\tag{2.63}$$

where

$$\hbar\Pi_\sigma = e_\sigma - e_{\mathrm{vac}},\tag{2.64}$$

is the excitation energy of the bath (i.e. the difference in energies between its excited and ground states). Here the index σ refers to the excited states of the bath that are accessible though a single action of the interaction operator V on the ground-state vector $|0\rangle$. Accordingly, the energy transfer is now regarded as being mediated by the elementary excitations of the bath (virtual polaritons) rather than by virtual photons of the "pure" electromagnetic field. The two types of intermediate states, Eqns 2.62 and 2.63, again correspond to the two time-orderings (Fig. 2.5) showing two different patterns for mediation of the intermolecular coupling by a medium-dressed photon (a bath polariton).

By analogy with Eqns 2.18 and 2.19, the transition matrix element can now be represented as

$$\langle F|T^{(2)}|I\rangle = \mu_{A_l}^{\mathrm{full}}\theta_{lj}(K,\mathbf{R})\mu_{D_j}^{\mathrm{full}},\tag{2.65}$$
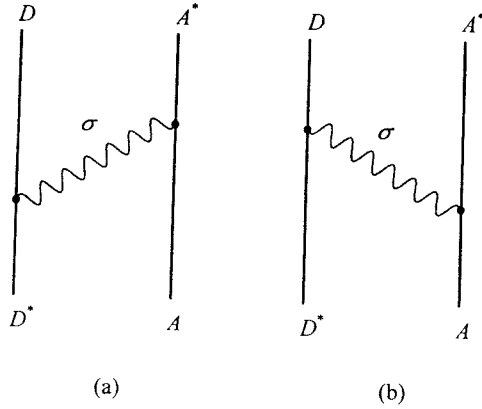
(a)   (b)

Figure 2.5   Time-ordered diagrams for polariton-mediated energy transfer

where

$$\theta_{lj}(K,\mathbf{R}) = \frac{1}{\hbar\varepsilon_0^2}\sum_\sigma\left[\frac{\langle 0|d_l^\perp(\mathbf{R}_A)|\sigma\rangle\langle\sigma|d_j^\perp(\mathbf{R}_D)|0\rangle}{cK - \Pi_\sigma + is} - \frac{\langle 0|d_j^\perp(\mathbf{R}_D)|\sigma\rangle\langle\sigma|d_l^\perp(\mathbf{R}_A)|0\rangle}{cK + \Pi_\sigma - is}\right]$$

(2.66)

is the tensor for the retarded dipole–dipole coupling between a pair of molecules within the medium: here the influences of the material medium arise through the detailed form of the eigenstates and the eigenenergies of the bath tensor $\theta_{lj}(K,\mathbf{R})$ by invoking the Green function formalism [37]. As an alternative, explicit summation over the normal modes σ can be performed in Eqn 2.66; this can be achieved by expanding (in terms of the normal modes of the dielectric medium [33, 34]) the local displacement operators $d_l^\perp(\mathbf{R}_A)$ and $d_l^\perp(\mathbf{R}_D)$ that enter Eqn 2.66. By either method, one arrives at the same result, Eqn 2.68, presented below. For instance, applying the Green function technique, the tensor of Eqn 2.66 is found to be [37]

$$\theta_{lj}(K,\mathbf{R}) = \frac{1}{n^2}\left(\frac{n^2+2}{3}\right)^2\sum_\mathbf{k}\frac{(\delta_{lj} - \hat{k}_l\hat{k}_j)k}{2\varepsilon_0 V}\left[\frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{nK - k + is'} - \frac{e^{-i\mathbf{k}\cdot\mathbf{R}}}{nK + k - is'}\right],$$

(2.67)

where $n \equiv n(cK)$ is the refractive index of the medium given by Eqns 2.69–2.70 below. One can now repeat steps similar to those for the vacuum case,

Eqns 2.21–2.26, to yield the following final result for the retarded tensor of the dipole–dipole coupling in the dielectric medium:

$$\theta_{lj}(K,\mathbf{R}) = \frac{1}{n^2}\left(\frac{n^2+2}{3}\right)^2\theta_{lj}^{\text{vac}}(nK,\mathbf{R}).$$

(2.68)

The tensor of Eqn 2.68 accommodates a screening contribution n^{-2} and a local field (Lorenz) factor $(n^2+2)/3$. In addition, the result contains the tensor $\theta_{lj}^{\text{vac}}(nK,\mathbf{R})$ with the same structure as the vacuum tensor, Eqn 2.26, the argument $y = nK$ now, however, being scaled by the refractive index n, as given by

$$n^2 = 1 + \frac{\alpha\rho/\varepsilon_0}{1 - \alpha\rho/3\varepsilon_0},$$

(2.69)

where $\rho = N/V$ in turn is the number of molecules X per unit volume, and α is the molecular polarisability (calculated at the transfer frequency $\omega = cK$):

$$\alpha \equiv \alpha_X(cK) = \frac{1}{3\hbar}\sum_{m,p}\rho_X^{(m)}\left[\frac{\mu_X^2|\langle\varphi_{X^*}^{(p)}|\varphi_X^{(m)}\rangle|^2}{e_{X_p^*} - e_{X_m} - cK - is} + \frac{\mu_X^2|\langle\varphi_{X^*}^{(p)}|\varphi_X^{(m)}\rangle|^2}{e_{X_p^*} - e_{X_m} + cK + is}\right].$$

(2.70)

In this representation, the quantity s is considered to be a small though a finite parameter that reflects the natural widths of each molecular line: replacement of an infinitesimal s by its finite counterpart to can be justified on rigorous dynamical grounds, as discussed in Section 2.6 (in which connection, the width s is labeled by another letter, η). Here also the indices m and p label the sublevels (vibrational, etc.) of the ground and excited state manifolds for the species X comprising the medium, μ_X is the electronic part of the transition dipole, as in Eqn 2.30, $e_{X_p^*} - e_{X_m}$ represent the excitation energies, and $\rho_X^{(m)}$ are the population distributions of the vibrational sublevels in the ground electronic state of the molecule X. It is noteworthy that an arbitrary number of vibrational sublevels can be accommodated for each molecule X of the medium in the framework of the formalism applied [33, 34, 37]. This includes *inter alia* a situation in which the molecular sublevels form a dense (quasi-continuum) set. In such a case, the molecular polarizability, Eqn 2.70, acquires an imaginary part in the absorbing areas of the spectrum, making the refractive index, Eqn 2.68, a complex quantity:

$$n = n' + in''.$$

(2.71)

The derivation of the tensor represented by Eqns 2.67 and 2.68 is based on a microscopic theory [33, 34, 37] in which the molecules of the medium are

considered to be all of the same type, regularly placed to form a simple cubic lattice, and characterized by the same isotropic polarizabilities $\alpha^X \equiv \alpha$. Such a model may also describe a common situation in which nonisotropic species are randomly oriented in their sites. The resulting Eqn 2.68 seems, however, not to be sensitive to the possible lack of translational symmetry as well, as long as the vibrational widths of the spectral lines exceed the characteristic energies of resonance coupling between the molecules comprising the medium. It is therefore expected that the transition matrix element given by Eqns 2.65 and 2.68, should adequately describe the transfer of energy in a variety of amorphous media constituted of randomly situated and oriented molecules, and characterized by some energetic disorder as well. For such systems, the quantity α that enters Eqn 2.69 is to be understood as an averaged polarizability for all of the species X that constitute the medium:

$$\alpha = \bar{\alpha}^X = N^{-1} \sum_X \alpha^X, \qquad (2.72)$$

N being the total number of molecules in the system. The subsequent analysis is also consistent with such a definition of the polarizability α.

The full rate of donor–acceptor transfer is again given by Eqn 2.31, subject to replacement of the tensor for the electromagnetic coupling in the vacuum by the tensor for the coupling in the medium, as $\theta_{lj}^{\text{vac}}(K, \mathbf{R}) \rightarrow \theta_{lj}(K, \mathbf{R})$. Using Eqn 2.68 for $\theta_{ij}(K, \mathbf{R})$, the pair rate can be expressed, as in Eqn 2.32, in terms of the overlap integral between the donor and acceptor spectra:

$$W_{DA} = \frac{9}{8\pi c^2 \tau_D} \int_0^\infty F_D(\omega)\sigma_A(\omega)\omega^2 g(\omega, \mathbf{R}) e^{-2n''\omega R/c} \, d\omega, \qquad (2.73)$$

with $n \equiv n(\omega)$ and

$$
\begin{aligned}
g(\omega, \mathbf{R}) &= |n|^2 \left| \eta_3 \left[\left(\frac{c}{n\omega R}\right)^3 - i\left(\frac{c}{n\omega R}\right)^2 \right] - n_1 \frac{c}{n\omega R} \right|^2 \\
&= \frac{1}{|n|^4} \left\{ \eta_3^2 \frac{c^6}{\omega^6 R^6} + 2\eta_3^2 n'' \frac{c^5}{\omega^5 R^5} + \left[\eta_3^2 |n|^2 - 2\eta_1 \eta_3 (n'^2 - n''^2) \right] \right. \\
&\quad \left. \times \frac{c^4}{\omega^4 R^4} + 2\eta_1 \eta_3 n'' |n|^2 \frac{c^3}{\omega^3 R^3} + \eta_1^2 |n|^4 \frac{c^2}{\omega^2 R^2} \right\},
\end{aligned}
\qquad (2.74)
$$

where the quantities

$$\sigma_A(\omega) = \frac{\pi \omega \mu_A^2}{3\varepsilon_0 c} \frac{1}{n'} \left| \frac{n^2 + 2}{3} \right|^2 \sum_{m,p} \rho_A^{(m)} \left| \left\langle \varphi_{A^*}^{(p)} | \varphi_A^{(m)} \right\rangle \right|^2 \delta(e_{A_p^*} - e_{A_m} - \hbar\omega) \qquad (2.75)$$

and

$$F_D(\omega) = \frac{\omega^3 \tau_D \mu_D^2}{3\varepsilon_0 \pi c^3} n' \left| \frac{n^2 + 2}{3} \right|^2 \sum_{n,r} \rho_{D^*}^{(n)} \left| \left\langle \varphi_D^{(r)} | \varphi_{D^*}^{(n)} \right\rangle \right|^2 \delta(e_{D_n^*} - e_{D_r} - \hbar\omega), \qquad (2.76)$$

can be identified (see Section 2.5.2), respectively, as the absorption cross-section of the acceptor and the emission spectrum of donor, both quantities being corrected for the electronic influence of the medium. The latter $F_D(\omega)$ is again normalized to unity in the sense

$$\int F_D(\omega) d\omega = 1. \qquad (2.77)$$

The normalization constant τ_D – to be explicitly presented in Eqn 2.94 below – represents the radiative lifetime of the donor in the absorbing medium, as will be demonstrated in the following subsection. In this way, dielectric influences of the material medium feature in the pair rate, Eqn 2.73, through the refractive modifications of the spectral functions $F_D(\omega)$ and $\sigma_A(\omega)$, as well as through the factors $g(\omega, \mathbf{R})$ and $e^{-2n''\omega R/c}$. The latter exponential factor represents the Beer's law losses in the absorbing medium. This factor will be demonstrated to play a vital role at large separations between the transfer species, providing a physically sensible total rate of energy transfer to all the surrounding acceptors (see Section 2.5.2).

The pair rate, Eqn 2.73, can be presented meaningfully as the following sum of three terms:

$$W_{DA} = W_{DA}^{\text{Först}} + W_{DA}^I + W_{DA}^{\text{Far zone}}. \qquad (2.78)$$

The first term,

$$W_{DA}^{\text{Först}} = \frac{9c^4 \eta_3^2}{8\pi \tau_D R^6} \int_0^\infty F_D(\omega)\sigma_A(\omega)|n|^{-4}\omega^{-4} e^{-2n''\omega R/c} \, d\omega, \qquad (2.79)$$

represents the familiar Förster rate of energy transfer which is characterized by an R^{-6} distance dependence. Such a rate is the dominant contribution in the near zone ($KR \ll 1$) where the exponential factor $e^{-2n''\omega R/c}$ is close to unity and can therefore be disregarded. Consequently, the spectral integral of Eqn 2.79 is weighted by the factor $|n|^{-4}$ in the near zone, in agreement with the standard theory of radiationless energy transfer [2, 25]. Note that the local field-factors featured in the coupling tensor, Eqn 2.68, are now contained in the spectral functions $F_D(\omega)$ and $\sigma_A(\omega)$. The third term in Eqn 2.78,

$$W_{DA}^{\text{Far zone}} = \frac{9\eta_1^2}{8\pi \tau_D R^2} \int_0^\infty F_D(\omega)\sigma_A(\omega) e^{-2n''\omega R/c} \, d\omega, \qquad (2.80)$$

behaving as R^{-2}, dominates in the far zone ($KR \gg 1$). It is characterized by the overlap integral between the donor emission and acceptor absorption spectra, weighted by the Beer's law factor. The rate, Eqn 2.80, can be identified as the rate of radiative (far-zone) energy transfer involving spontaneous emission by a donor, propagation of the emitted photon through the absorbing medium, followed by its absorption at the acceptor. The factors $F_D(\omega) \cdot e^{-2n''\omega R/c}$ and $\sigma_A(\omega)$ characterize the corresponding processes.

Lastly, the middle term of the pair-rate equation 2.78, W_{DA}^I, due to the remaining terms in the function of Eqn 2.74, becomes important at intermediate distances where $KR \simeq 1$. In general, this intermediate contribution contains not only the usual R^{-4} term [4, 8, 10, 11, 17, 26], but also additional terms in odd powers of R (i.e. R^{-3} and R^{-5}). However, in the case of a weakly absorbing medium ($n'' \ll n'$) one can disregard the latter odd rank terms to arrive at the following approximate expression:

$$W_{DA}^I = \frac{9c^2(\eta_3^2 - 2\eta_1\eta_3)}{8\pi\tau_D R^4} \int_0^\infty F_D(\omega)\sigma_A(\omega)|n|^{-2}\omega^{-2}e^{-2n''\omega R/c}\,d\omega. \quad (2.81)$$

For any such weakly absorbing medium, the function $g(\omega, \mathbf{R})$ that enters the pair rate, Eqn 2.73, can be written approximately as

$$g(\omega, \mathbf{R}) = |n|^2 g^{vac}(|n|\omega, \mathbf{R}), \quad (2.82)$$

$g^{vac}(|n|\omega, \mathbf{R})$ being its vacuum counterpart defined by Eqn 2.33, but with the argument ω now scaled by the modulus of the complex refractive index $|n|$. Finally, one can readily extend Eqn 2.51, which characterizes the range-dependence of fluorescence anisotropy in vacuum, for the depolarization that is taking place in the medium. Specifically, in the case of a weakly absorbing medium, one then has

$$r_1(R) = \frac{r_0}{25} \frac{7|n|^4 \tilde{K}^4 R^4 + |n|^2 \tilde{K}^2 R^2 + 3}{|n|^4 \tilde{K}^4 R^4 + |n|^2 \tilde{K}^2 R^2 + 3}, \quad (2.83)$$

i.e. the wave-vector $\tilde{K}$ appears to be scaled by $|n|$, modifying to some extent the characteristic scale of distances. As such, the position at which the onset of significant retardation modifies the fluorescence anisotropy can be still closer than the vacuum formula would suggest.

2.5.2 Spontaneous emission as far-zone energy transfer

Consider the decay of an excited state of donor D through energy transfer to the surrounding species X. By summing up all appropriate pair rates, the full decay rate is

$$\Gamma_D = \sum_{X \neq D} W_{DX}, \quad (2.84)$$

where W_{DX} is the rate of excitation transfer between a pair of molecules D and X, as explicitly presented in the previous subsection (with $X \equiv A$). Using Eqn 2.78 for the pair rates, the decay rate of Eqn 2.84 can be cast as

$$\Gamma_D = \tilde{\Gamma}_D^{Först} + \Gamma_D^{Far\,zone}, \quad (2.85)$$

with

$$\tilde{\Gamma}_D^{Först} = \sum_{X \neq D} (W_{DX}^{Forst} + W_{DX}^I), \quad (2.86)$$

and

$$\Gamma_D^{Far\,zone} = \sum_{X \neq D} W_{DX}^{Far\,zone} \quad (2.87)$$

The former decay rate $\tilde{\Gamma}_D^{Först}$ contains contributions due to the Förster pair rates modified by the intermediate terms W_{DX}^I, the tilde over Γ reflecting such a modification. The constituent pair rates have been explicitly presented in Eqns 2.79 and 2.81 of the previous subsection.

In what follows, we shall concentrate on the latter decay rate $\Gamma_D^{Far\,zone}$ associated with far-zone (radiative) energy transfer. The far-zone transfer may be viewed [4, 10, 11, 35, 36] as spontaneous emission of a photon followed by its subsequent recapture by a distant acceptor. Adopting such a concept, we shall regard the contribution $\Gamma_D^{Far\,zone}$ as the rate of spontaneous emission in the absorbing medium. The approach is in a certain sense related to absorber theory [20, 45, 56] in which spontaneous emission is seen to be the result of direct interaction between the emitting atom and "the Universe," the latter acting as a perfect absorber at all emitted frequencies. In our situation, the surrounding medium does indeed act as a perfect absorber, even at extremely low concentrations of the absorbing species (or, alternatively, for an almost transparent condensed medium), as long as the system dimensions are large enough to insure eventual recapture of the emitted photon. For such a weakly absorbing medium, the rate $\Gamma_D^{Far\,zone}$ will be demonstrated to reproduce exactly the familiar rate [31, 33, 34, 40, 43] for the spontaneous emission in a transparent dielectric.

To obtain the proper decay rate $\Gamma_D^{Far\,zone}$ using Eqn 2.87, the pair transfer rates $W_{DX}^{Far\,zone}$ should not only reflect effects due to retardation, but also incorporate influences of the surrounding medium, as in the previous section. Following [35, 36], we shall demonstrate that $\Gamma_D^{Far\,zone}$ does indeed represent the

rate of spontaneous emission in the absorbing medium. For this purpose, we shall substitute Eqn 2.80 for the pair rate $W_{DA}^{\text{Far zone}}$ (with $A \equiv X$) into Eqn 2.87, to yield

$$\Gamma_D^{\text{Far zone}} = \frac{9}{8\pi\tau_D} \int_0^\infty F_D(\omega) \sum_X R^{-2} \eta_1^2 \sigma_X(\omega) e^{-2n''\omega R/c} \, d\omega, \qquad (2.88)$$

with $\mathbf{R} \equiv \mathbf{R}_{XD}$. The decay rate $\Gamma_D^{\text{Far zone}}$ is built up of a large number of the pair rates operating predominantly in the far zone. Hence the summation over the molecules X can be changed to an integral over the radius vector $\mathbf{R}$, giving

$$\Gamma_D^{\text{Far zone}} = \frac{1}{\tau_D} \int_0^\infty d\omega \, F_D(\omega)\sigma(\omega) \int_0^\infty d\,\text{Re}^{-2n''\omega R/c} \qquad (2.89)$$

$$= \frac{c}{2\tau_D} \int_0^\infty d\omega \, F_D(\omega)\sigma(\omega)/\omega n'', \qquad (2.90)$$

where in Eqn 2.89 orientational averaging has been carried out $(\eta_1^2 \rightarrow \langle\eta_1^2\rangle = 2/9)$, and the cross-section of the molecular absorption $\sigma_X(\omega)$ has been replaced by its ensemble average, as given by

$$\sigma(\omega) \equiv \bar{\sigma}_X(\omega) = \frac{\omega}{c}\frac{1}{n'}\left|\frac{n^2+2}{3}\right|^2 \frac{\bar{\alpha}''_x}{\varepsilon_0}. \qquad (2.91)$$

The relationship of Eqn 2.91 has been written exploiting Eqn 2.75 for $\sigma_A(\omega)$ (with $A \equiv X$), with constraints due to the energy-conserving delta functions expressed in terms of the imaginary part of the molecular polarizability $\bar{\alpha}''_X \equiv \alpha''$ using Eqn 2.70 for α_X. The imaginary part α'' is in turn related to the complex refractive index n, given by Eqn 2.69, as

$$n'' = \frac{1}{2n'}\left|\frac{n^2+2}{3}\right|^2 \frac{\alpha''\rho}{\varepsilon_0}, \qquad (2.92)$$

so that Eqn 2.91 reduces to

$$\sigma(\omega) \equiv \bar{\sigma}_x(\omega) = n''2\omega/c\rho. \qquad (2.93)$$

In writing Eqn 2.92, use has been made of the generalized definition, Eqn 2.72, for the molecular polarizability α.

Equation 2.93 can be identified as the usual relationship between the imaginary part of the complex refractive index and the absorption cross-section. In this way, the quantity $\sigma(\omega)$ defined by Eqn 2.75 is indeed seen to represent the

cross-section of molecular absorption in the lossy medium. Substituting Eqn 2.93 into Eqn 2.90, using Eqn 2.76 for $F_D(\omega)$ and the normalization condition Eqn 2.77, one finds

$$\Gamma_D^{\text{Far zone}} = \tau_D^{-1} = \sum_{n,r} (\tau_D^{rn})^{-1} \rho_{D'}^{(n)}, \qquad (2.94)$$

with

$$(\tau_D^{rn})^{-1} = \frac{\omega^3 \mu_D^2}{3\hbar\varepsilon_0\pi c^3} n' \left|\frac{n^2+2}{3}\right|^2 \left|\langle\varphi_D^{(r)}|\varphi_{D'}^{(n)}\rangle\right|^2. \qquad (2.95)$$

The rate $\Gamma_D^{\text{Far zone}} = \tau_D^{-1}$ as given by Eqns 2.94 and 2.95 represents the full rate of spontaneous emission by the donor, and so involves summation over the final levels and averaging over the initial levels of the donor, labeled respectively by r and n, $\rho_{D'}^{(n)}$ being the population distribution of the vibrational levels of donor in the initially excited electronic state. The constituent terms $(\tau_D^{rn})^{-1}$ represent the partial rates of spontaneous emission associated with downward transitions of the donor between the specific levels n and r, where in each of these terms the refractive index is to be calculated at the appropriate frequency $(e_{D_n^r} - e_{D_r})/\hbar$.

The emission rates, Eqn 2.95, manifestly accommodate contributions due to the absorbing dielectric medium, including the local field factor. It is noteworthy that the present analysis is based on a microscopic QED theory [35, 37], the relationship Eqn 2.95 supporting previous phenomenological methods [12, 13] used to introduce local field corrections to the rates of spontaneous emission in an absorbing medium. In the limit where $\alpha'' \rightarrow 0$, $n'' \rightarrow 0$, the far-zone rate given in Eqns 2.94 and 2.95 reduces smoothly to the usual result for spontaneous emission in a transparent medium [31, 33, 34, 40, 43], there being a vanishing contribution due to the decay in the near and intermediate zones: $\tilde{\Gamma}_D^{\text{Först}} \rightarrow 0$. In other words, the present analysis reproduces in full the rate of spontaneous emission in transparent dielectrics $n'' = 0$, including *inter alia* the case of free space: $n'' = 0$, $n' = 1$. Here, free space is be to viewed as a limit in which the density of the absorbing species goes to zero, while the size of the system goes to infinity, so that the emitted photon is eventually recaptured somewhere in the system. It is noteworthy that in order to arrive at a sensible result for $\Gamma_D^{\text{Far zone}} = \tau_D^{-1}$, such as that given by Eqns 2.94 and 2.95, the influences of the absorbing medium are necessarily to be reflected in the pair transfer rates comprising the decay rate equation 2.87. In fact, it is the exponential factor $\exp(-2n''\omega R/c)$, which represents absorption losses at the intervening medium, that helps avoid the potentially infinite decay rate $\Gamma_D^{\text{Far zone}}$ (given by Eqn 2.87) due to the R^{-2} factor featured in the constituent pair rates, Eqn 2.80. Note also that the same result, Eqns 2.94 and 2.95, can be reproduced for the

rate of spontaneous emission τ_D^{-1} in terms of another microscopic method that involves calculation of the quantum flow from the emitting molecule D in the absorbing medium [36].

2.6 DYNAMICS OF ENERGY TRANSFER BETWEEN A PAIR OF MOLECULES IN A DIELECTRIC MEDIUM

In previous sections, the transfer dynamics has been described in terms of well-defined rates for intermolecular energy transfer. It is the purpose of the current section to pursue in more detail temporal aspects of the energy transfer between a pair of species in a dielectric medium, through explicit consideration of the QED time evolution. A distinctive aspect of the approach developed in [38] is that it affords a combined analysis of rate and nonrate regimes, in the context of examining the influence of the dielectric medium on a microscopic basis. The theory is built on the foundation established in the previous section. Again, the approach exploits the concept of energy transfer mediated by bath polaritons. The theory also makes use of the microscopically derived tensor, Eqn 2.68, for the retarded and medium-dressed dipole–dipole coupling, now with regard to the dynamical behavior. The present section not only extends consideration beyond the rate description, but also re-examines conditions for that regime itself. That leads to incorporation of an energy renormalization for both of the ground and excited states of the transfer species, due to the interaction of these species with the molecules that belong to the medium, and also with each other. That is a feature not reflected in direct application of the ordinary Fermi Golden Rule.

The section is organized as follows. In the next subsection the Heitler–Ma method [1, 28–30] for describing the quantum time evolution is first outlined, and subsequently reformulated to suit our current purposes, technical details of the derivation being placed in two appendices. Consequently, the basic equations for time evolution acquire a form that is more symmetric with respect to the initial and final states. Subsection 2.6.2 concentrates on the transfer dynamics between a pair of molecules in the molecular medium, starting from general considerations and leading to an analysis of both the rate regime and beyond. Note that the nonrate regime features in situations that lack an intrinsic density of molecular states for the participating species.

2.6.1 General description of time evolution

Consider the quantum dynamics of a system with a time-independent Hamiltonian that is separable as the sum of a zero-order Hamiltonian H^0 and an interaction term V (such as that defined by Eqn 2.57 in the previous section),

where the eigenvectors of H_0 include, *inter alia*, both the initial state $|I\rangle$ and the final state $|F\rangle$ for the process. For reasons which will become apparent later, we shall commence work in the Schrödinger representation rather than the more common interaction representation. The state vector of the system then evolves at positive times from the state $|I\rangle$ at $t = +0$ as

$$S(t)|I\rangle = \Theta(t)e^{-iHt/t}|I\rangle \tag{2.96}$$

$$= -\frac{1}{2\pi i}\int_{-\infty}^{+\infty} d\varepsilon\, e^{-i\varepsilon t/\hbar}(\varepsilon - H + i\eta)^{-1}|I\rangle \quad (\eta \to +0). \tag{2.97}$$

$\Theta(t)$ being the unit step (Heaviside) function. Strictly, the quantity η is a positive infinitesimal, yet for finite times it may be considered to be a finite quantity that obeys the following: $\eta t/\hbar \ll 1$ (i.e. η should be kept much less than the inverse lifetime for the excited states). Under this condition, introduction of a finite η does not influence the quantum dynamics governed by Eqn 2.97. Retention of a finite value for η plays an important role in smoothing spectral lines. This makes the refractive index given by Eqns 2.69 and 2.70 a complex quantity in absorbing areas of the spectrum, comprising contributions due to densely spaced molecular sublevels of vibrational or other origin for each electronic transition. Note that the smoothing parameter η was labeled s in the previous sections.

The Heitler–Ma method [1, 28–30] may now be employed, giving (see Appendix A)

$$\langle F|(\varepsilon - H + i\eta)^{-1}|I\rangle = \frac{U_{FI}(\varepsilon)}{(\varepsilon - E_F + i\eta)(\varepsilon - E_1 + \frac{1}{2}i\hbar\Gamma_I(\varepsilon) + i\eta)}. \tag{2.98}$$

Here $U_{FI}(\varepsilon) \equiv \langle F|U(\varepsilon)|I\rangle$ and $\Gamma_I(\varepsilon) \equiv \langle I|\Gamma(\varepsilon)|I\rangle$ are, respectively, the matrix elements of the off-diagonal transition operator $U(\varepsilon)$ and the diagonal damping operator $\Gamma(\varepsilon)$, both determined by the following recurrence relation:

$$U(\varepsilon) - \frac{i}{2}\hbar\Gamma(\varepsilon) = V + V(\varepsilon - H^0 + i\eta)^{-1}U(\varepsilon). \tag{2.99}$$

For present purposes it is more convenient to represent the above in a non-recursive format, as

$$[U(\varepsilon) - \frac{i}{2}\hbar\Gamma(\varepsilon)]|I\rangle = \left[V + VP_I(\varepsilon - H^0 - P_I VP_I + i\eta)^{-1}P_I V\right]|I\rangle. \tag{2.100}$$

where the projection (idempotent) operator,

$$P_I = 1 - |I\rangle\langle I|, \tag{2.101}$$

identifies the exclusion of contributions by the initial state in the perturbation expansion of Eqn 2.100. Recasting the transition matrix element in a form in which the perturbational contribution by the final state also no longer explicitly features, one arrives at (see Appendix B)

$$U_{FI}(\varepsilon) = \frac{\varepsilon - E_F + i\eta}{\varepsilon - E_F - \frac{i}{2}\hbar\Gamma'_F + i\eta} U'_{FI}, \tag{2.102}$$

where the newly defined quantities on the right, U'_{FI} and Γ'_F, both have implicit ε-dependence and are given by

$$U'_{FI} \equiv \langle F|\Big[V + VP_IP_F(\varepsilon - H^0 - P_IP_FVP_IP_F + i\eta)^{-1}P_IP_FV\Big]|I\rangle, \tag{2.103}$$

$$-\frac{i}{2}\hbar\Gamma'_F \equiv \langle F|\Big[V + VP_IP_F(\varepsilon - H^0 - P_IP_FVP_IP_F + i\eta)^{-1}P_IP_FV\Big]|F\rangle, \tag{2.104}$$

with

$$P_F = 1 - |F\rangle\langle F|. \tag{2.105}$$

Finally, calling on Eqns 2.97, 2.98 and 2.102, one finds the following probability amplitude for the transition $|I\rangle \rightarrow |F\rangle$:

$$\langle F|S(t)|I\rangle = -\frac{1}{2\pi i}\int_{-\infty}^{+\infty} d\varepsilon\, U'_{FI}\, e^{-i\varepsilon t/\hbar}\Big(\varepsilon - E_F + \frac{i}{2}\hbar\Gamma'_F + i\eta\Big)^{-1}$$
$$\Big(\varepsilon - E_I + \frac{i}{2}\hbar\Gamma_I + i\eta\Big)^{-1}, \tag{2.106}$$

which is an exact result. Here, the presence of both Γ_I and Γ'_F in the energy denominators explicitly accommodates the damping corrections and energy renormalization of the initial and final states. Consequently, the transfer amplitude as presented above has a form that is obviously more symmetric with respect to the initial and final states than would result from direct substitution of Eqn 2.98 into Eqn 2.97. Still, there is some dissymmetry with respect to these states, reflected by the prime on Γ'_F. The retention of this dissymmetry will be of vital importance in the case of sharp energy levels for the donor and acceptor, i.e. where the participating transfer species lack an intrinsic density of molecular states; this aspect is to be considered in subsection 2.6.2.2.

2.6.2   Transfer dynamics

The dynamical system of interest has been defined by the Hamiltonian, Eqns 2.57–2.60. For the representation of energy transfer between the donor and

acceptor molecules in the dielectric medium, the initial and final state vectors and their energies are again (as in the previous section) considered to have the form of Eqns 2.8 and 2.9, which characterize the energy transfer *in vacuo*, where the state vector $|0\rangle$ is again to be understood as the ground state of the polariton bath (the combined system of the radiation field and the molecular medium), e_{vac} being the corresponding zero-point energy of such a bath. Because of the two-center character of the interaction operator, Eqn 2.59, it is convenient to carry out the corresponding partitioning in Eqns 2.100 and 2.104, writing

$$-\frac{i}{2}\hbar\Gamma_I(\varepsilon) = \Delta e_{D^*} + \Delta e_A - \frac{i}{2}\hbar\gamma_{D^*} - \frac{i}{2}\hbar\Gamma_{D^*A}, \tag{2.107}$$

$$-\frac{i}{2}\hbar\Gamma'_F(\varepsilon) = \Delta e_D + \Delta e_{A^*} - \frac{i}{2}\hbar\gamma_{A^*} - \frac{i}{2}\hbar\Gamma'_{DA^*}, \tag{2.108}$$

Here, one center contributions, denoted by a single index D (or A), are due to the terms that contain only one operator V_D (or V_A) in the perturbation expansions of Eqns 2.100 and 2.104. Such contributions have already been separated into real energy shifts and imaginary damping terms in the above equations. For instance, Δe_{D^*} and γ_{D^*} represent, respectively, the bath-induced level shift (energy renormalization) and the damping factor for the excited molecular state $|D^*\rangle$, there being no imaginary (damping) contributions for the ground molecular states $|D\rangle$ and $|A\rangle$. Each such energy renormalization (Δe_{D^*}, Δe_A, Δe_D, and Δe_{A^*}) embodies not only the radiative (Lamb) shift [16, 28, 42], but the also the contribution due to the dispersion interaction between the donor D (or acceptor A) and the molecular medium. Note that the dispersion energy appears now in the second order of perturbation, rather than the usual fourth order [16, 48, 49], as the coupling of the radiation field with the medium has already been included in the zero-order Hamiltonian H^0, given by Eqns 2.58 and 2.60. Here, we shall not consider the explicit structure of these energy shifts, which are to be treated as the parameters of the theory. The remaining (complex) quantities Γ_{D^*A} and Γ'_{DA^*} are two-center contributions resulting from cross-terms (containing both V_D and V_A) that emerge in the perturbation expansions of Eqns 2.100 and 2.104.

By making use of Eqns 2.107 and 2.108, the probability amplitude for the energy transfer, Eqn 2.106, becomes

$$\langle F|\tilde{S}(t)|I\rangle = -\frac{1}{2\pi i\hbar}\int_{-\infty}^{+\infty} d\omega$$
$$\frac{U'_{FI}(\omega)e^{-i(\omega - \omega_{A^*})t}}{(\omega - \omega_{A^*} + (i/2)\gamma_{A^*} + (i/2)\Gamma'_{DA^*} + i\eta')(\omega - \omega_{D^*} + (i/2)\gamma_{D^*} + (i/2)\Gamma_{D^*A} + i\eta')}$$
$$(\eta' \rightarrow +0), \tag{2.109}$$

where

$$\omega = (\varepsilon - e_D - e_A - \Delta e_D - \Delta e_A - e_{\mathrm{vac}})/\hbar \qquad (2.110)$$

is a new variable, and

$$\omega_{D'} = (e_{D'} + \Delta e_{D'} - e_D - \Delta e_D)/\hbar, \qquad \omega_{A'} = (e_{A'} + \Delta e_{A'} - e_A - \Delta e_A)/\hbar \qquad (2.111, 2.112)$$

are the excitation frequencies of the donor and acceptor. The frequencies $\omega_{D'}$ and $\omega_{A'}$ incorporate level shifts for both the ground and excited molecular states. Finally, in Eqn 2.109 transformation has been carried out to a modified interaction representation, as

$$\langle F|\tilde{S}(t)|I\rangle = \langle F|S(t)|I\rangle \exp(-\mathrm{i}(E_F + \Delta E_F)t/\hbar), \qquad (2.113)$$

the term "modified" referring to renormalization by the medium of the final state energy $E_F = e_D + e_{A'}$ by the amount $\Delta E_F = \Delta e_D + \Delta e_{A'}$.

Now, we turn our attention to the transition matrix element $U'_{FI}(\omega)$, which in the present study will be represented through an effective second-order contribution, as

$$U'_{FI}(\omega) \approx U^{(2)}_{FI}(\omega) = \mu^{\mathrm{full}}_{A_l}\theta'_{lj}(\omega/c, \mathbf{R})\mu^{\mathrm{full}}_{D_j}. \qquad (2.114)$$

with

$$\theta'_{lj}(\omega/c, \mathbf{R}) = \frac{1}{\hbar\varepsilon_0^2}\sum_\sigma \left[\frac{\langle 0|d_l^\perp(\mathbf{R}_A)|\sigma\rangle\langle\sigma|d_j^\perp(\mathbf{R}_D)|0\rangle}{\omega - \prod_\sigma + \mathrm{i}\eta'} + \frac{\langle 0|d_j^\perp(\mathbf{R}_D)|\sigma\rangle\langle\sigma|d_l^\perp(\mathbf{R}_A)|0\rangle}{\omega - \omega_{D'} - \omega_{A'} - \prod_\sigma + \mathrm{i}\eta'} \right]$$
$$(\mathbf{R} = \mathbf{R}_A - \mathbf{R}_D),$$

$$(2.115)$$

where implied summation over the repeated Cartesian indices (l and j) is assumed, μ^{full}_D and μ^{full}_A being the transition dipoles given by Eqn 2.20. As in the previous section, here $\hbar\prod_\sigma = e_\sigma - e_{\mathrm{vac}}$ is the excitation energy of the bath, the index σ denoting excited (single polariton) states of the bath accessible from the ground state $|0\rangle$ by single action of the local displacement operator $\mathbf{d}^\perp(\mathbf{R}_X)(X = D, A)$. Within the range of frequencies ω close to molecular transition frequencies $\omega_{D'}$ and $\omega_{A'}$, the energy denominator $(\omega - \omega_{D'} - \omega_{A'} - \prod_s + \mathrm{i}\eta)$ may be replaced by $(-\omega - \prod_s + \mathrm{i}\eta)$ in the nonresonant term of Eqn 2.115.[†]

[†] It follows from the time–energy Uncertainty Principle that retention of the original form (Eqn 2.115) is important only for times which are less than the inverse molecular transition frequency, ω_D^{-1}, generally on the femtosecond timescale.

Consequently, the above tensor of Eqn 2.115 reduces to that relating to retarded dipole–dipole coupling in the medium:

$$\theta'_{l,j}(\omega/c, \mathbf{R}) \approx \theta_{l,j}(\omega/c, \mathbf{R}), \qquad (2.116)$$

the latter tensor, $\theta_{l,j}(\omega/c, \mathbf{R})$, being defined by Eqn 2.66. Using Eqns 2.68 and 2.26, the tensor $\theta_{l,j}(\omega/c, \mathbf{R})$ reads explicitly

$$\theta_{l,j}(\omega/c, \mathbf{R}) = n\left(\frac{n^2 + 2}{3}\right)^2 \frac{\omega^3 e^{\mathrm{i}n\omega R/c}}{4\pi c^3\varepsilon_0}\left[(\delta_{ij} - 3\hat{R}_i\hat{R}_j)\left(\frac{c^3}{n^3\omega^3 R^3} - \frac{\mathrm{i}c^2}{n^2\omega^2 R^2}\right) - (\delta_{ij} - \hat{R}_i\hat{R}_j)\frac{c}{n\omega R}\right].$$

$$(2.117)$$

where $n \equiv n(\omega)$ is the complex relative index given by Eqns 2.69 and 2.70.

It is noteworthy that one can relate the matrix element $U^{(2)}_{FI}(\omega)$ (given by Eqns 2.114 and 2.117) to the transition matrix element considered in the previous section (see Eqn 2.65), as

$$\langle F|T^{(2)}|I\rangle \equiv U^{(2)}_{FI}(\omega_{D'}), \qquad (2.118)$$

where $U^{(2)}_{FI}(\omega)$ is to be taken at the emission frequency $\omega = \omega_{D'} = cK \approx \omega_{A'}$. In the context of time evolution, it is important to retain the ω-dependence featured in the exponential phase factor $\exp(\mathrm{i}n\omega R/c)$ of the matrix element $U^{(2)}_{FI}(\omega)$. This leads to appearance of a time lag in the initial arrival of the excitation at the acceptor A, due to the finite speed of signal propagation. The remainder of the transition element $U^{(2)}_{FI}(\omega)$, together with other ω-dependent parameters that enter Eqn 2.109, will at this stage be evaluated at the resonant frequency, $\omega = \omega_{A'} \approx \omega_{D'}$. Linearizing the exponent,

$$n(\omega)\omega R/c \approx [n(\omega_{A'})\omega_{A'} R/c] + [(\omega - \omega_{A'})R/v_g], \qquad (2.119)$$

with

$$\frac{1}{v_g} = \frac{\mathrm{d}}{\mathrm{d}\omega}\left(\frac{n\omega}{c}\right)\Big|_{\omega = \omega_{A'}}, \qquad (2.120)$$

and re-defining the origin of time $\tau = (t - R/v_g)$, the transfer amplitude, Eqn 2.109, takes the form

$$\langle F|\tilde{S}(t)|I\rangle = -\frac{1}{2\pi\hbar i}\int_{-\infty}^{+\infty}d\omega\, U_{FI}^{(2)}(\omega_{A^.})e^{-i(\omega-\omega_{A^.})\tau}$$

$$\left(\omega - \omega_{A^.} + \frac{i}{2}\gamma_{A^.} + i\eta'\right)\left(\omega - \omega_{D^.} + \frac{i}{2}\gamma_{D^.} + i\eta'\right)^{-1} \qquad (2.121)$$

$$= \hbar^{-1}U_{FI}^{(2)}(\omega_{A^.})\Theta(\tau)\frac{e^{-\frac{1}{2}\gamma_{A^.}\tau} - e^{\left[-\frac{1}{2}\gamma_{D^.} + i(\omega_{A^.} - \omega_{D^.})\right]\tau}}{(\omega_{A^.} - \omega_{D^.}) + \frac{1}{2}i(\gamma_{D^.} - \gamma_{A^.})}. \qquad (2.122)$$

which takes account of damping for both species D and A. Here the two-center contributions $\Gamma_{D^.A}$ and $\Gamma'_{DA^.}$ are, for the present, omitted; the physical basis of this approximation will be clarified in due course.

It is worth noting that the radiative group velocity ν_g featured in Eqn 2.122, via the shift of the origin of time, describes the delay of the initial arrival of the excitation at acceptor A, whereas the phase velocity $\nu_\phi = c/n$, which enters the exponential factor $\exp(in\omega R/c)$ of the transition matrix element $U_{FI}^{(2)}(\omega_{A^.})$ (with $n \equiv n(\omega_{A^.})$), characterizes the changes of optical phase with distance. Note also that incorporation of the time lag in the above manner implies that the refractive index, and hence also the group velocity, takes real values. Nonetheless, the general result to follow (Eqn 2.123) for the transfer rates holds both for lossless and absorbing media.

2.6.2.1   Transfer rates

Let us consider first the case in which the spectral widths of the species participating in the transfer exceed the magnitude of the corresponding transition matrix elements. The overall migration is then incoherent, described as a multistep process involving uncorrelated events of excitation transfer between the molecules of the system. With regard to the selected pair D–A, by omitting the relaxation terms $\gamma_{D^.}$ and $\gamma_{A^.}$ in Eqn 2.122, and for times in excess of the transit time R/ν_g, the resultant rate of the excitation transfer reads

$$W_{FI} = \frac{d}{dt}|\langle F|\tilde{S}(t)|I\rangle|^2 = \frac{2\pi}{\hbar}|U_{FI}^{(2)}(\omega_{D^.})|^2\delta(\hbar\omega_{D^.} - \hbar\omega_{A^.}), \qquad (2.123)$$

This provides the Fermi Golden Rule exploited previously, subject to the replacement of $U_{FI}^{(2)}(\omega_{D^.})$ by $\langle F|T^{(2)}|I\rangle$, using the relationship of Eqn 2.118. The full pair transfer rate W_{DA} is subsequently obtained by means of the standard procedure involving averaging over initial and summing over final molecular sublevels, as in the previous sections.

A new feature that arises in the present dynamical context is that the excitation frequencies $\omega_{D^.}$ and $\omega_{A^.}$ have now been modified (renormalized) through

interaction of the transfer species D and A with the molecules of the surrounding medium. The mutual interaction of D with A may also be taken into account by retaining the omitted terms $\Gamma_{D^.A}$ and $\Gamma'_{DA^.}$ in Eqn 2.121. That alters the molecular excitation frequencies $\omega_{D^.}$ and $\omega_{A^.}$ featured in the energy conservation δ-function of Eqn 2.123, by the amounts $-\text{Im}\Gamma_{D^.A}/2$ and $-\text{Im}\Gamma'_{DA^.}/2$, respectively: these represent changes in the excitation energy of each transfer species due to its interaction with the other. The effects of such corrections decrease with distance, and over the separations of interest where R is greater than typical intermolecular distances within the medium, they contribute negligibly.

At this juncture, a remark should be made concerning some asymmetry of the formalism with regard to the initial and final states, as reflected by the prime on $\Gamma'_{DA^.}$. The rate regime generally implies the presence of a dense structure of (usually vibrational) molecular energy levels within the electronic manifolds of D and A. Hence the apparent asymmetry in question vanishes, as either inclusion or exclusion of the individual states (such as $|I\rangle$ or $|F\rangle$) in the intermediate-state summation does not significantly alter the quantities $\Gamma_{D^.A}$ and $\Gamma'_{DA^.}$. It is a different story in the case where there is no intrinsic density of molecular states for the participating species, as is to be considered next.

2.6.2.2   Nonrate regime

Suppose now that each of the ground and exited state manifolds of D and A is characterized by only one molecular sublevel, so that the subsystem D–A may be treated as a pair of two-level species. Ignoring contributions from states with two or more mediating bath excitations (polaritons), the exchange of energy between D and A now occurs exclusively through intermediate states in which both transfer species are either in their ground or excited states, the bath being in a one-polariton excited state. Under these conditions, the quantities $\Gamma_{D^.A}$ and $\Gamma'_{DA^.}$ introduced in Eqns 2.107 and 2.108 are as follows:

$$-\frac{i}{2}\Gamma_{D^.A} = \left\{\left[U_{FI}^{(2)}(\omega)\right]^2/\hbar^2\right\}\left(\omega - \omega_{A^.} + \frac{i}{2}\gamma_{A^.} + i\eta'\right)^{-1}, \qquad (2.124)$$

$$\Gamma'_{DA^.} = 0, \qquad (2.125)$$

where use has been made of Eqns 2.100 and 2.104. Substituting these results for $\Gamma'_{DA^.}$ and $\Gamma_{D^.A}$ into the general dynamical equation 2.109, the probability amplitude becomes

$$\langle F|\tilde{S}(t)|I\rangle = -\frac{1}{2\pi\hbar i}\int_{-\infty}^{+\infty}d\omega\, U_{FI}^{(2)}(\omega)e^{-i(\omega-\omega_{A^.})t}\left\{\left(\omega - \omega_{A^.} + \frac{i}{2}\gamma_{A^.} + i\eta'\right)\right.$$

$$\left.\left(\omega - \omega_{D^.} + \frac{i}{2}\gamma_{D^.} + i\eta'\right) - \left[U_{FI}^{(2)}(\omega)/\hbar\right]^2\right\}^{-1}. $$

$$(2.126)$$

To illustrate the precise form of the time evolution for one specific application, one finds for the case of identical species ($\omega_{D^*} = \omega_{A^*}, \gamma_{D^*} = \gamma_{A^*}$), and without regard to the delay time R/ν_g, the following:†

$$|\langle F|\tilde{S}(t)|I\rangle|^2 = \tfrac{1}{2}[\cosh(\gamma_{DA}t) - \cos(2\Omega_{DA}t)]e^{-\gamma_{D^*}t}, \qquad (2.127)$$

where the transfer frequency Ω_{DA} and the inverse time γ_{DA}, respectively, represent the real and imaginary parts of the transition matrix element:

$$\hbar^{-1}U_{FI}^{(2)}(\hbar\omega_{A^*}) = \Omega_{DA} - \frac{i}{2}\gamma_{DA}. \qquad (2.128)$$

Equation 2.127 has a form that is familiar from the case of energy transfer between molecules *in vacuo* [22, 32, 41], although the parameters $\gamma_{DA}, \gamma_{A^*}$, and Ω_{DA} here display the influence of the medium. Note that although in writing Eqns 2.124–2.128 the transfer species D and A have been modeled as two-level systems, the formulation still allows each of the surrounding molecules to possess an arbitrary number of energy levels, thus accommodating the cases of both absorbing and lossless media.

The result given by Eqn 2.127 represents an oscillatory, to- and-fro exchange of excitation, accompanied by damping. That type of dynamical behavior is a direct consequence of the absence of a density of final states, a feature which obviously makes the rate description inadequate. Nonetheless, a distinction should be drawn between the short-range reversible Rabi-type oscillatory behavior, which does not represent any real flow of energy from D to A, and the long-range behavior. In the latter case, the excitation energy of the donor is irreversibly passed to the acceptor. Under such circumstances it is appropriate to introduce transfer probabilities (rather than rates), as will be shown below.

In the long-range limit, the contribution $[U_{FI}^{(2)}]^2$, associated with the coupling between D and A, may legitimately be omitted in the denominator of the integrand in Eqn 2.126. The system then follows the same time evolution as described through the earlier Eqn 2.122, where in the current consideration D and A are not necessarily identical two-level species. The transfer dynamics given by Eqn 2.122 reflects both the initial arrival of excitation at the acceptor, commencing from time $t = R/\nu_g$, and subsequent decay of the resulting excited state of A. The rate of the latter decay may be considered to be the same as that for an individual acceptor in the dielectric medium (i.e. γ_{A^*}), since at large distances the remaining influence of the donor is minimal. Accordingly, the total transfer probability P may be defined as the probability for irreversible trapping of the excitation by the acceptor. Integrating the population-weighted rate of decay of the excited state of A, we obtain, for P,

† Such a time delay leading to the effects of multiple delay in to- and-fro exchange of excitation, has been investigated by Milonni and Knight [44], who analysed the transfer dynamics between a pair of species *in vacuo*.

$$P = \int_{R/\nu_g}^{\infty} |\langle F|\tilde{S}(t)|I\rangle|^2 \gamma_{A^*}\, dt \qquad (2.129)$$

$$= (\Omega_{DA}^2 + \gamma_{DA}^2)\gamma_{D^*}^{-1}\frac{(\gamma_{D^*} + \gamma_{A^*})}{(\omega_{A^*} - \omega_{D^*})^2 + (\gamma_{D^*} + \gamma_{A^*})^2/4}, \qquad (2.130)$$

which is in agreement with the previous far-zone result for the transfer of energy between a pair of molecules *in vacuo* [54]. In passing, we note that the individual rates of the excited-state decay $\gamma_{D^*} \equiv \Gamma_D$ and $\gamma_{A^*} \equiv \Gamma_A$, featured in the above equations, have been explicitly analysed in Section 2.5.2. Calling on Eqns 2.114, 2.116, 2.117 and 2.128, the long-range result of Eqn 2.130 assumes the following form in the case of a nonabsorbing medium:

$$P = \frac{9}{8\pi}\langle\sigma_A\rangle\left[(\hat{\boldsymbol{\mu}}_D \cdot \hat{\boldsymbol{\mu}}_A) - (\hat{\boldsymbol{\mu}}_D \cdot \hat{\mathbf{R}})(\hat{\boldsymbol{\mu}}_A \cdot \hat{\mathbf{R}})\right]^2/R^2, \qquad (2.131)$$

with

$$\langle\sigma_A\rangle = \frac{1}{n}\left(\frac{n^2+2}{3}\right)^2\frac{\mu_A^2\omega_{A^*}}{3\varepsilon_0\hbar c}\left[\frac{(\gamma_{D^*} + \gamma_{A^*})/2}{(\omega_{A^*} - \omega_{D^*})^2 + (\gamma_{D^*} + \gamma_{A^*})^2/4}\right] \qquad (2.132)$$

Here, in addition to the appearance of the refractive pre-factors, the influence of the medium extends to the excitation frequencies ω_{D^*} and ω_{A^*}, as well as to the decay parameters γ_{A^*} and γ_{B^*}. The above $\langle\sigma_A\rangle$ may be identified as the isotropic absorption section of the acceptor, $\sigma_A(\omega)$, averaged over the normalized emission spectrum of the donor, $I_{D^*}(\omega)$:

$$\langle\sigma_A\rangle = \int_{-\infty}^{+\infty} \sigma_A(\omega)I_{D^*}(\omega)d\omega, \qquad (2.133)$$

with $\sigma_A(\omega)$ and $I_{D^*}(\omega)$ given by

$$\sigma_A(\omega) = \frac{1}{n}\left(\frac{n^2+2}{3}\right)^2\frac{\mu_A^2\omega_{A^*}}{3\varepsilon_0\hbar c}\left[\frac{\gamma_{A^*}/2}{(\omega - \omega_{A^*})^2 + (\gamma_{A^*}/2)^2}\right] \qquad (2.134)$$

and

$$I_{D^*}(\omega) = \frac{1}{\pi}\left[\frac{\gamma_{D^*}/2}{(\omega - \omega_{D^*})^2 + (\gamma_{D^*}/2)^2}\right]. \qquad (2.135)$$

Finally, one obtains, for the orientationally averaged probability,

$$\bar{P} = \langle \sigma_A \rangle / 4\pi R^2, \tag{2.136}$$

which is the ratio of the spectrally averaged isotropic absorption cross-section to the spherical surface at distance $R, 4\pi R^2$. In the case of an absorbing medium, an exponential decay factor of the form $\exp(-2n''\omega R/c)$ would also feature in the above expression.

2.7 CONCLUSION

The unified theory of resonance energy transfer described in this chapter represents a seamless union of mechanisms that were previously considered to be entirely separate. It has resolved a number of thorny issues that were obscured or skirted by earlier theories and, in fully fledged form, it naturally accommodates all of the optical, dynamical and electronic influences of the host medium on the characteristics of donor–acceptor transfer. In particular, this theory has established the following:

- There is no competition between "radiationless" and "radiative" mechanisms for energy transfer. Both are manifestations of a single interaction which operates over the full range of distances beyond wavefunction overlap. This interaction additionally includes other, previously hidden, forms of interaction, whose distance dependence is characterized by intermediate power laws. With this theory, there is no longer any need to model systems in which energy migrates across both short- and long-range distances in terms of distinct mechanisms.
- The shift in the inverse power which is apparent as distance increases reflects a powerful interplay between the governing principles of relativistic retardation and quantum uncertainty, as they relate to the propagation of the signal mediating the energy transfer. At short distances the overwhelming quantum uncertainty is reflected in the completely virtual nature of the mediating photons; over long distances the uncertainty is small and the photons acquire unequivocally real character. The polarization of acceptor fluorescence has been shown to display a distance dependence which dramatically exhibits this behavior.
- The pair transfer rates provided by the unified theory have been integrated into the context of an ensemble treatment that is directly amenable to experimental application. The effect of spontaneous emission by donor species within an absorbing ensemble in all respects properly corresponds to the far-zone limit of unified energy transfer. Finally, the apparent rate divergence associated with transfer from a single donor within an infinite ensemble of acceptor species has been resolved by proper accommodation of the effect of the ensemble on the characteristics of (virtual) medium-

dressed photons that mediate the resonance energy transfer between the molecules.

Appendix A: Heitler–Ma method for analysis of the transition operator

Consider the following Green's operator:

$$\zeta(\varepsilon - H) = (\varepsilon - H + i\eta)^{-1}, \tag{A.1}$$

where the full Hamiltonian H is divided into the zero-order Hamiltonian H^0 and the interaction operator V as in Eqn 2.57. Let $N(\varepsilon)$ be the diagonal part of $\zeta(\varepsilon - H)$ (in the representation of the eigenvectors of H^0). Then the operator $\zeta(\varepsilon - H)$ may written as

$$\zeta(\varepsilon - H) = [1 + \zeta(\varepsilon - H_0)U(\varepsilon)]N(\varepsilon), \tag{A.2}$$

where $U(\varepsilon)$ is an off-diagonal operator. Multiplying Eqn A.2 by $\varepsilon - H$, one finds that

$$N^{-1}(\varepsilon) = \varepsilon - H + U(\varepsilon) - V\zeta(\varepsilon - H_0)U(\varepsilon). \tag{A.3}$$

The diagonal operator $N(\varepsilon)$ may be represented as

$$N(\varepsilon) = \left[\varepsilon - H_0 + \frac{i}{2}\hbar\Gamma(\varepsilon)\right]^{-1}, \tag{A.4}$$

$\Gamma(\varepsilon)$ being another diagonal matrix, so that one has

$$U(\varepsilon) - \frac{i}{2}\hbar\Gamma(\varepsilon) = V + V\zeta(\varepsilon - H_0)U(\varepsilon). \tag{A.5}$$

Calling on Eqns A.2, A.4, and A.5, one arrives at

$$\zeta(\varepsilon - H)|I\rangle = \frac{[1 + \zeta(\varepsilon - H_0)U(\varepsilon)]|I\rangle}{\varepsilon - E_I + i\hbar\Gamma_I(\varepsilon)/2 + i\eta} \tag{A.6}$$

The last two equations, together with the definition in Eqn A.1, provide the required results, Eqns 2.98 and 2.99 of the main text. Finally, the relationship A.6 can be represented in a nonrecursive format using Eqn 2.100, as

$$\zeta(\varepsilon - H)|I\rangle = \frac{[1 + P_I\zeta(\varepsilon - H_0 - P_IVP_I)P_IV]|I\rangle}{\varepsilon - E_I + i\hbar\Gamma_I(\varepsilon)/2 + i\eta}. \tag{A.7}$$

Appendix B: Modified approach to the transition operator

Using Eqn 2.100 of the main text, one finds for the transition operator that one has

$$\langle F|U(\varepsilon)|I\rangle = \langle X|P_I V|I\rangle, \tag{B.1}$$

with

$$\langle X| = \langle F|\left[1 + P_I V P_1 (\varepsilon - H_0 - P_I V P_I + i\eta)^{-1}\right]. \tag{B.2}$$

The above ket vector may be rewritten as

$$\langle X| = \langle F|(\varepsilon - H_0 + i\eta)(\varepsilon - H_0 - P_I V P_I + i\eta)^{-1},$$

giving

$$\langle X| = (\varepsilon - E_F + i\eta)\langle F|\zeta(\varepsilon - H_0 - P_I V P_I) \tag{B.3}$$

Next, in complete analogy to Eqn A.7 for the bra vectors, the above ket vector $\langle F|\zeta(\varepsilon - H_0 - P_I V P_I)$ is

$$\langle F|\zeta(\varepsilon - H_0 - P_I V P_I) = \frac{\langle F|[1 + V P_I P_F \zeta(\varepsilon - H_0 - P_F P_I V P_I P_F)]}{\varepsilon - E_F + i\hbar\Gamma'_F/2 + i\eta}, \tag{B.4}$$

with Γ'_F and P_F as in Eqns 2.104 and 2.105. Lastly, calling on Eqns B.1, B.3, and B.4, one arrives at the required result, Eqn 2.102, presented in the main text.

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