Resonance Energy Transfer: From Fundamental Theory to Recent Applications

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Abstract
Resonance energy transfer (RET), the transport of electronic energy from one atom or molecule to another, has significant importance to a number of diverse areas of science. Since the pioneering experiments on RET by Cario and Franck in 1922, the theoretical understanding of the process has been continually refined. This review presents a historical account of the post-Förster outlook on RET, based on quantum electrodynamics, up to the present-day viewpoint. It is through this quantum framework that the short-range, \( R^{-6} \) distance dependence of Förster theory was unified with the long-range, radiative transfer governed by the inverse-square law. Crucial to the theoretical knowledge of RET is the electric dipole-electric dipole coupling tensor; we outline its mathematical derivation with a view to explaining some key physical concepts of RET. The higher order interactions that involve magnetic dipoles and electric quadrupoles are also discussed. To conclude, a survey is provided on the latest research, which includes transfer between nanomaterials, enhancement due to surface plasmons, possibilities outside the usual ultraviolet or visible range and RET within a cavity.

1 Introduction and the early years of RET

Resonance energy transfer (RET, also known as fluorescence resonance energy transfer, FRET, or electronic energy transfer, EET) is an optical process, in which the excess energy of an excited molecule – usually called the donor – is transferred to an acceptor molecule [1-4]; as depicted
schematically in Figure 1. Fundamentally, RET involves two types of elementary particles: electrons and photons. In RET, all the electrons (including the dynamically active electrons) are bound to the nuclei of the molecules, and typically reside in their valence molecular orbitals. As such, the individual electrons do not migrate between molecules during the transfer process, since the molecular orbitals (the wavefunctions) do not overlap, but instead move between individual electronic states within the molecules. This is fundamentally different to the ultra-short-range Dexter energy transfer, where electrons do in fact migrate between molecules via covalent chemical bonds [5]. In RET, on relaxation of the electron to a lower energy electronic state in the donor, the excess energy is transported to the acceptor in the form of the emitted *virtual* photon – this transfer is facilitated by dipole-dipole couplings between the molecules. In fact, photons play two distinct roles towards the process: one as the mediator of donor-acceptor transfer, and the other as an external energy source that promotes donor valence electrons into an electronic excited state, via an absorption process prior to RET.

In 1922, the pioneering work of Cario and Franck enabled the earliest observation of RET [6-8]. Their spectroscopy experiment involved the illumination of a mixture of mercury and thallium vapours at a wavelength absorbed only by the mercury; the fluorescence spectra that results show frequencies lines that can only be due to thallium. In 1927, the Nobel laureate J. Perrin provided the first theoretical explanation [9]: he recognized that energy could be transferred from an excited molecule to a nearby-unexcited molecule via dipole interactions. Five years later, his son F. Perrin developed a more accurate theory of RET [10] based on Kallman and London’s results [11]. Extending the works of both Perrins, Förster developed an improved theoretical treatment of RET [12-14]. Förster found that energy transfer, through dipole coupling between molecules, mostly depends on two important quantities: spectral overlap and intermolecular distance. He discovered the now famous $R^{-6}$ distance-dependence law for the rate of resonance energy transfer in the short-range. Much later, in 1965, this distance dependence predicted by Förster was verified [15]. This led to the ‘spectroscopic ruler’ by Stryer and Haugland [16,17], a useful technique to measure the proximity of chromophores and conformational change in macromolecules using RET. The next section, which is more technical than the rest of the article, details the history of RET based on quantum electrodynamics (QED); it can be safely skipped by readers more interested in the current understanding of RET.
2 Historical role of quantum electrodynamics in RET

2.1 The success of QED

Quantum electrodynamics is a rigorous and accurate theory – which is completely verifiable by experiment [18] – that describes the interaction of electromagnetic radiation with matter. This quantum field approach differs to other theories in that the whole system is quantised, i.e. both matter and radiation are treated quantum mechanically. QED provides additional physical insights compared to classical and semi-classical electrodynamics, which treats electromagnetic radiation only as a non-quantised wave. For example, the wave-particle duality of light is uniquely portrayed within QED but not semi-classical theories. However, despite their deficiencies, classical and semi-classical theories can still be useful since, often, they are easier to implement analytically and more economic computationally.

The first major QED publication is credited to Dirac who, in 1927, wrote a description of light emission and absorption that incorporated both quantum theory and special relativity [19]; this depiction later became known as the relativistic form of QED, which is used in systems that contain fast moving electrons. Three years later Dirac completed his classic book ‘The Principles of Quantum Mechanics’ [20] in which, among other exceptional works, he derived a relativistic generalisation of the Schrödinger equation. However, for elementary physical quantities such as the mass and charge of particles, calculations using this early form of QED produce diverging results. In the late 1940s, this problem was resolved (by renormalisation) leading to a complete form of QED developed independently by Feynman [21-25], Schwinger [26-29] and Tomonaga [30,31] – all three procedures were unified by Dyson [32].

The ability of QED to provide novel predictions is monumental, but its quantitative successes are even more impressive. In particular, the theory accurately predicts the electronic $g$-factor of the free electron to 12 decimal places. In Bohr magneton units, the most precise measurement of $g/2$ is $1.00115965218073(28)$ [33]; QED has a predicted value of $1.00115965218203(27)$ [34]. In addition, there are other staggering quantitative successes. For example, the numerical calculation of Lamb shift splitting of the $2S_{1/2}$ and $2P_{1/2}$ energy levels in molecular hydrogen predicts $1,057,838(6)$ kHz [35], which is highly accurate compared to the experimental value of $1,057,839(12)$ kHz [36]. QED also provides a number of predictions that are unobtainable by semi-classical theory. These include
forecasts of spontaneous decay and the Casimir-Polder forces, a deviation from London forces for long-range intermolecular interactions [37-41].

2.2 Non-relativistic QED: a theoretical framework for RET

An individual RET process, which arises after excitation of the donor, involves light emission at one molecule and light absorption at the other. Such light-molecule interactions are best described by QED. This means that the quantum properties and the retardation effects of the mediating light, which leads to the concept of a photon, is directly incorporated into the calculations. Therefore, in terms of this framework, it is natural to describe RET in terms of photon creation and annihilation events. Namely, the creation of a photon at the excited donor and a photon annihilation at the unexcited acceptor. Mathematically, these couplings are represented as off-diagonal matrix elements of the interaction Hamiltonian. A full quantum description is usually necessary to describe the RET process over all distances, this is because the electronic energy is not transferred instantaneously as assumed by the classical and semi-classical descriptions (although retardation effects are sometimes provided in such frameworks [42]). The transfer of energy between molecules occurs via the exchange of a virtual photon, which has increasingly real (transverse) characteristics as the intermolecular separation grows; this is discussed, in more detail, in Section 3.2. The term virtual being indicative of the fact that the photon is reabsorbed before its properties, such as wavelength, take on physical significance. The dipole of each molecule is also correctly described as a transition dipole moment, connecting two non-degenerate energy states of the molecule.

Since RET involves slow moving electrons, bound within the valence states of the molecules, the non-relativistic variant of QED (as opposed to relativistic or Lorenz gauge QED) is used. The theory that underpins the quantum description of RET is the Power-Zienau-Woolley formalism of molecular (or non-relativistic) QED [43-48], which utilises the Coulomb gauge, \( \nabla \cdot \vec{A} = 0 \), where \( \vec{A} \) is the vector potential and the fields of the mediating photons can be naturally deconstructed into longitudinal and transverse components. The longitudinal components, with respect to the displacement vector \( \vec{R} \), are associated with the scalar potential and have a particular affinity for coupling molecular transition moments in the near-zone, where the donor-acceptor pair are close together. In regions far from the source (i.e. distant from the donor) the wave-vector \( \vec{k} \) and \( \vec{R} \) are essentially collinear and the scalar potential approaches zero. In this case, the transverse part of the
field dominates the coupling of the transition dipole moments of individual molecules [49]. This has important implications for the spatial and temporal dynamics of excitons within molecular aggregates [50,51]; namely, transition dipole moment pairs that are collinear to each other and collinear to the displacement vector are coupled by the longitudinal components of the field only.

The QED model of RET is traceable to the 1966 paper by Avery, which extended the Perrin and Förster theory of RET by replacing the Coulomb interaction with the relativistic Breit interaction [52]. Although Avery did not explicitly include the effects of the mediating photon, in terms of the creation and annihilation field operators, he nevertheless made a direct connection between RET and spontaneous emission. Moreover, he determined the $R^{-2}$ dependence on the transfer rate in the far-zone. He concluded that investigating RET from the point-of-view of the ‘direct action’ formulation of QED, devised by Wheeler and Feynman [53], would be ‘extremely interesting’. Soon afterwards, in the same year, the Avery work was enhanced by a more formal and rigorous quantum theoretical outlook provided by Gomberoff and Power [54].

### 2.3 RET coupling tensor: the quest for its correct form

In the early 1980s there were a number of RET studies by Thirunamachandran, in collaboration with Power and Craig, which give valuable insights into the physical connections between the near- and far-zone mechanisms of RET. In 1983, Power and Thirunamachandran published three seminal papers on QED theory [55-57]. Here they consider the problem within the Heisenberg formalism, via the time evolution of operators associated with both electron fields and Maxwell fields. In the third paper of the series, they derive an expression for the time dependent evolution of the RET quantum amplitude as:

$$
\langle \mathcal{A}_\mathbf{i} | \mathcal{D}_\mathbf{p} \rangle(t) = \frac{1}{\hbar e} \langle \mathcal{A}_\mathbf{i} | \mathcal{D}_\mathbf{p} \rangle \langle \mathcal{A}_\mathbf{j} | -\nabla^2 \delta \mathbf{d} + \nabla_i \nabla_j \rangle
\times \frac{1}{\pi R} \int_{\infty}^{\infty} \sin(kR) \left[ \frac{e^{i\mathbf{r} \cdot \mathbf{d}} - 1}{(k_A - k_D)(k_A - k_D)} + \frac{e^{i\mathbf{r} \cdot \mathbf{d}} - 1}{(k_A - k_D)(k_A - k_D)} \right] \, dk ,
$$

where $\mu_k(X)$ is the transition dipole moment of molecule $X$ along the $k$th canonical coordinate and $R$ is the distance between the two molecules. The transfer occurs from an excited molecule $D$ to molecule $A$, initially in its ground state. Subscripts $i$ and $j$ represent Cartesian components with the
usual tensor summation convention being employed [58]. The transition dipole moments elements
are \( \mu^{\delta_p} (D) \) and \( \mu^{\delta_q} (A) \); where molecule \( D \) is initially in state \( p \), and the final state of molecule \( A \) is
\( q \). Integration is over all possible wave-vectors (denoted by \( k \)) of the mediating photon. In this work,
the rapidly oscillating terms were dropped, to leave only two terms instead of the usual four; *vide infra*, equation (2.6). The terms \( k_D \) and \( k_A \) represent the wave-vectors resonant with a transition of
molecules \( D \) and \( A \), respectively. Power and Thirunamachandran did not explicitly describe how the
singularities in (2.1) were dealt with mathematically, but they show that the final expression
conforms to the correct distance dependencies in the appropriate limits.

Around the same time, Thirunamachandran and Craig considered resonance coupling between
molecules ‘where one was in an excited state’, within the dipole approximation (the term ‘resonance
energy transfer’ was not used in this work). They initially published the work as an extended paper
[59], and expanded upon it in their widely known book [45]. They consider two identical molecules
and calculate the interaction of the excited system \( D \) with the unexcited system \( A \). Firstly, they
considered calculations that ignored retardation effects and any time explicit dependencies. The
calculated electric field at \( A \), produced by the oscillating dipole at \( D \), produces an energy change of;

\[
\Delta E = \left( 4\pi \varepsilon_0 \right)^{-1} R^{-3} \mu^{\delta_p} (D) \mu^{\delta_0} (A) \left( \delta_{ij} - 3 R_j \cdot R_i \right). \tag{2.2}
\]

The final term is an orientational factor that modulates the magnitude of the energy difference based
on the relative dipole orientations of the molecules. Through the inclusion of retardation effects,
equation (2.2) becomes;

\[
\Delta E = \left( 4\pi \varepsilon_0 \right)^{-1} \mu^{\delta_p} (D) \mu^{\delta_0} (A) e^{i \vec{k} \cdot \vec{R}}
\times \left\{ k^2 R^{-1} \left( \cos kR / R \right) \left( \delta_{ij} - \hat{R}_j \cdot \hat{R}_i \right) - \left( \cos kR / R^3 + k \sin kR / R^2 \right) \left( \delta_{ij} - 3 \hat{R}_j \cdot \hat{R}_i \right) \right\}. \tag{2.3}
\]

Retardation effects give rise to the appearance of a phase factor, \( e^{i \vec{k} \cdot \vec{R}} \), as well as two other distance
dependencies, namely, \( R^{-1} \) and \( R^{-2} \).
The authors then calculated the fully retarded \textit{matrix element} in tensor-form and show that it is the same as expression (2.3). The calculation formally involves summing over all photon wave-vectors connecting the initial and final states. In practice, this summation involves using a box quantization technique to transform the problem to an integral in momentum space. The solution can be found by contour integration, in a way analogous to that in which Green’s functions solutions are found in quantum scattering problems [60]. For identical molecules, the final matrix element (or quantum amplitude) in tensorial form is:

\begin{equation}
M_{bi} = \mu_i^0 (D) V_{ij}(k, \bar{R}) \mu_j^m (A),
\end{equation}

where:

\begin{equation}
V_{ij}(k, \bar{R}) = \frac{1}{4\pi\varepsilon_0 R^3} \left[ (\delta_{ij} - 3\bar{R}_i\bar{R}_j)(\cos kR + kR \sin kR) - (\delta_{ij} - \bar{R}_i\bar{R}_j)(k^2 R^2 \cos kR) \right].
\end{equation}

In light of the subsequent analysis shown later, it is important to note that the interaction tensor $V_{ij}$, derived in this early work, is purely the real part of the full expression. In deriving equation (2.4), four different contours could be chosen around the two poles (the singularities), leading to different results. The contour they chose ensures a correct outgoing-wave solution, although there is no \textit{a priori} mathematical basis for this choice.

Further advances were achieved by Andrews and co-workers who proved a direct relationship between \textit{radiationless} and \textit{radiative} RET [61-63]. Although all three regimes of RET – i.e. the $R^{-2}$, $R^{-4}$ and $R^{-6}$ dependencies on the rate – were mathematically predicted in the original derivations, Andrews et al. were the first to comment upon the relevance of the \textit{intermediate-zone} contribution, which has a $R^{-4}$ dependence. This term dominates at critical distances; that is, when the distance separating the molecules is in the order of the reduced wavelength, $\lambda = \lambda / 2\pi$, of the mediating photon (i.e. $R \sim \lambda$). Inclusion of all three distance-dependencies in one rate equation is known as the \textit{unified theory} of RET. The particulars of which are provided in Section 3.2.
Initially Andrews and Sherborne in 1987, reconsidered the problem in the Schrödinger representation, where they derived the electric dipole-electric dipole tensor without the need of ‘outgoing wave’ arguments of scattering theory [59]. Starting from the second-order expression for the time-dependent probability amplitude for energy transfer, they inserted all intermediate states to obtain a rather complicated looking expression (not reproduced here). As detailed in the original paper, the integral of the expression gives rise to four different Green’s functions, and hence four choices of contour. The fact that four terms arise is attributed to the forward and reverse transfer processes. They showed that the choice of contour was not unique, with each giving different expressions for $V_{ij}(k, \hat{R})$. Interestingly, they found that these new contours introduced imaginary terms into $V_{ij}(k, \hat{R})$, i.e. those not included in the derivations of the earlier work by Thirunamachandran and Craig. By choosing the contour that appeared to be the ‘most acceptable’, they derived the coupling matrix element to be of the form (corrected later by Daniels et al. [63] and modifying the indexing here for better comparison with the expressions above):

$$V_{ij}(k, \hat{R}) = \sigma_{ij}(k, \hat{R}) + i \tau_{ij}(k, \hat{R}), \quad (2.5)$$

where,

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

$$\tau_{ij}(k, \hat{R}) = \frac{1}{4\pi \varepsilon_0 R^3} \left[ \left( \delta_{ij} - 3 \hat{R}_i \hat{R}_j \right)(\sin kR - kR \cos kR) - \left( \delta_{ij} - \hat{R}_i \hat{R}_j \right) k^2 R^2 \sin kR \right],$$

in which $\sigma_{ij}$ is the expression given in (2.4). This derivation eliminates the need for physical arguments based on quantum scattering theory used in the earlier work. It, nevertheless, did require careful consideration of the correct contour with which to apply Cauchy’s residue theorem for solving the integral. In later work, Andrews and Juzeliūnas applied an alternative method of contour integration, whereby they infinitesimally displaced the problematic poles away from the real axis [64]. The idea being that the imaginary addenda shifted the poles to enable integration around a closed contour along the real axis. The approach gave results in agreement with those of Andrews and Sherborne’s favoured choice of contour. Thus, this study removes the need to choose a contour;
however, artificial displacements of the poles, including the choice of direction of displacement on the complex plane, must be made.

In 2003, Daniels et al. re-examined the problem and avoided the uncertainties of the contour integration entirely by solving the Green’s function using judicious substitutions within the integrals. Namely, when the Green’s function is expressed as a sum of two integrals, so that:

\[
G(k, R) = \int_0^\infty \frac{\sin pR}{R(k-p)} dp + \int_0^\infty \frac{\sin pR}{R(-k-p)} dp ,
\]

(2.6)

substitutions of the form \( t = pR - kR \) and \( s = pR + kR \) for the first and second integral, respectively, give an expression in which terms are oscillatory, but convergent. The authors solved these integrals by expressing them as series expansions (in the form of special functions) to get a result, analogous to equation (2.5), in the form:

\[
\sigma_\gamma(k, \tilde{R}) = \frac{1}{4\pi e_0 R^3} \left\{ (\cos kR + kR \sin kR) \left[ \delta_{ij} - 3\hat{R}_i\hat{R}_j \right] - k^2 R^2 \cos kR \left[ \delta_{ij} - \hat{R}_i\hat{R}_j \right] \right\}
\]

\[
\tau_\gamma(k, \tilde{R}) = \frac{1}{4\pi e_0 R^3} \left\{ \mp (\sin kR - kR \cos kR) \left[ \delta_{ij} - 3\hat{R}_i\hat{R}_j \right] \pm k^2 R^2 \sin kR \left[ \delta_{ij} - \hat{R}_i\hat{R}_j \right] \right\} .
\]

(2.7)

Here, on comparing with the earlier expressions, the only difference is a choice of sign for the imaginary term \( \tau_\gamma \). The authors suggested that the ambiguity of sign for this term signifies that \( V_{ij}^\pm(k, \tilde{R}) \) describes both incoming and outgoing waves, accommodating thereby both time-ordered (Feynman) diagrams, as a complete quantum description should. However, the authors stress that it is unimportant which sign to ascribe to a particular process (photon absorption or emission), as only the modulus squared of the matrix element is physically measureable and, hence, using either sign on \( \tau_\gamma \) provides an identical result for all calculations relevant to experiment. Jenkins et al. wrote a follow-up paper that analysed the importance of each Feynman diagram, called time-ordered pathways, to the overall RET rate. They discovered that both pathways have equal contribution when the two molecules are close together; however, one pathway begins to dominate as the molecules are moved further apart [65].
In 2016, Grinter and Jones re-derived expression (2.7) using a spherical wave description of the mediating photon, via vector spherical harmonics [66]. All previous derivations employed a plane-wave description of the mediating photon. One advantage of the spherical wave approach is that multipole contributions are more concretely defined in terms of the angular momentum quantum numbers $l$ and $m$. Furthermore, the work involved the development of an approach complementary to the plane wave methods, giving additional insight into orientational aspects of RET and forming a natural setting for the decomposition of fields into transverse and longitudinal components. In 2018, a comprehensive review of the spherical wave approach was published [67]. In the plane-wave method, defined in terms of the position vector $\vec{r}$, the oscillating part of the field is expanded as;

\[
\hat{\vec{e}}_n e^{i\vec{k}\cdot\vec{r}} = \hat{\vec{e}}_n \left[ 1 + ik \cdot \vec{r} + \frac{(ik \cdot \vec{r})^2}{2!} + \frac{(ik \cdot \vec{r})^3}{3!} + \cdots \right].
\] (2.8)

where the first term relates to the electric dipole, the second to the magnetic dipole and the electric quadrupole, and so on. In the spherical wave description, the expansion is written as;

\[
e^{i\vec{k}\cdot\vec{r}} = \sum_l j_l(2l+1)j_l(kr)P_l(\cos \theta) .
\] (2.9)

where $j_l(kr)$ are Bessel functions and $P_l(\cos \theta)$ are Legendre polynomials. The spherical wave description consequently attributes radiation emerging from specific pure multipole sources to specific angular momentum quantum numbers, thereby separating different multipole contributions that are of the same order.

Additionally, derivation of the RET matrix element using spherical waves eliminates the need to perform contour integration and, therefore, select the physically correct solutions. The arbitrary choice of sign, which can be seen in the imaginary part ($\tau_{ij}$) of equation (2.7), does not appear in the spherical wave analysis. The $R$ dependence can be expressed in terms of Hankel functions of the first kind, i.e. $h^{(1)}(kR) = j_l(kR) + in_l(kR)$ for outgoing waves, while Hankel functions of the second kind, i.e. $h^{(2)}_l(kR) = j_l(kR) - in_l(kR)$ describe incoming waves. The ambiguous sign in equation (2.7) was interpreted to mean that both incoming and outgoing waves are required to calculate the quantum
amplitude of the process (i.e. photon absorption and emission). In the spherical wave approach, the incoming and outgoing waves emerge naturally and can be linked directly to one or other of the signs in the imaginary part of equation (2.7), up to the phase factor $\exp(\pm i\omega t)$.

In a separate study, Grinter and Jones also analysed the transfer of angular momentum between multipoles using a spherical description of the mediating photon [68]. Although it has been known for some time that coupling between multipoles of different order can be non-zero [69-74], this work showed that RET between multipoles of different order is formally allowed. This is because the isotropy of space is broken during an individual transfer event, even though one may expect the process to be forbidden on the grounds of the violation of the conservation of angular momentum. For example, in the case of electric dipole-electric quadruple (E1-E2) transfer, two units of angular momentum are lost from the electronic state of a quadrupole emitter (the donor), whereas the dipole acceptor only takes up one quantum of electronic angular momentum. The above analyses indicate that treating the mediating photon of an RET process in terms of spherical waves may be valuable in some applications, particularly in the case of multipolar QED. A discussion on higher-order considerations, such as these, is found in Section 3.3

3 RET based on quantum electrodynamics

3.1 Derivation of the RET coupling tensor

In order to understand any optical process within the framework of QED, a matrix element (or quantum amplitude) that links the initial and final states is required. In the case of RET between two molecules, the initial state is the donor, $D$, in an excited state and an acceptor, $A$, in the ground state. In the final state, the acceptor molecule is in an excited state and the donor molecule is in its ground state. Photophysically, this can be simply understood as;

$$D^* + A \rightarrow D + A^*$$  \hspace{1cm} (3.1)

where, in this type of chemical expression, the asterisk denotes the molecule in an electronically excited state.
The usual starting point for any QED analysis is the illustration of the process by Feynman diagrams [23], thereby aiding construction of the matrix element by defining all of the intermediate system states. Feynman diagrams are graphical descriptions of electronic and photonic processes with a time frame that moves upwards. Resonance energy transfer between two molecules, in isolation, involves two Feynman diagrams – as shown in Figure 2. Here, examining the left-hand diagram, the initial system state has the donor in excited state \( n \) and the acceptor in the ground state, labelled 0 (the red section). Moving up the time axis, a photon is created from the excited donor to provide an intermediate system state, in which both molecules are in the ground state and a photon is present (the black section). Higher up the diagram this photon is annihilated at the donor and, thus, excites it to state \( m \) (the blue section). The diagram on the right-hand side is legitimate, albeit counter-intuitive. In this case, the intermediate system state represents both molecules simultaneously in their excited states in the presence of the mediating photon – meaning that conservation of energy is clearly violated. However, this is fully justifiable within the constraints of the energy-time uncertainty principles.

These diagrams (which represent the two pathways of RET) involve two light-molecule interactions: one at the donor and the other at the acceptor. This is indicative of second-order perturbation theory, which we examine below, as the minimal level of theory necessary to describe RET. The total Hamiltonian for RET between neutral molecules, in multipolar form, is written as:

\[
H = H_{\text{mol}}(D) + H_{\text{mol}}(A) + H_{\text{rad}} + H_{\text{int}}(D) + H_{\text{int}}(A).
\]  

(3.2)

Here, the first two terms correspond to the molecular Hamiltonians of the donor and acceptor \( H_{\text{mol}}(X) \); \( X = D, A \), which are usually the non-relativistic Born-Oppenheimer molecular Hamiltonian. The third term is the radiation Hamiltonian, \( H_{\text{rad}} \), not seen in semi-classical theory; this is typically defined in terms of the electric and magnetic field operators and/or the auxiliary field operator, \( \vec{a}(\vec{R}, t) \) [45,75]. Although these three Hamiltonians are important for describing the light-matter system in its entirety, they play no explicit role in the derivation of the matrix element for RET. The key parts of the Hamiltonian for RET are the interaction terms \( H_{\text{int}}(X) \); \( X = D, A \). These two terms represent the interaction between each molecule and the electromagnetic field; they are perturbative in nature because the light-molecule interactions of RET is weak compared to the large
Coulombic energies of the molecules. The eigenstates of the interaction Hamiltonian are constructed with the tensor product of molecule and radiation states. Of particular note is that no interaction term between the donor and acceptor exists in equation (3.2), unlike in semi-classical formalisms. The QED description of RET is, therefore, a genuinely full quantum theory, whereby the transfer of energy between an excited donor to an unexcited acceptor is via the electromagnetic field; direct Coulombic interactions between the two molecules do not arise in this multipolar form of the Hamiltonian [55].

Using the electric dipole approximation, in which only the transition electric dipole (E1) of each molecule are considered, the interaction Hamiltonian is written as:

\[ H_{\text{int}} = -\varepsilon_0^{-1} \hat{\mu}(D) \cdot \hat{\mathbf{d}} \left( \mathbf{R}_D \right) - \varepsilon_0^{-1} \hat{\mu}(A) \cdot \hat{\mathbf{d}} \left( \mathbf{R}_A \right) \], \hspace{1cm} (3.3)

where \( \hat{\mu}(X) \) is the dipole operator of molecule \( X \) at position \( \mathbf{R}_X \) (it is usually presumed that the donor is positioned at the origin); \( \varepsilon_0 \) is the permittivity of free space. The displacement electric field operator, \( \hat{\mathbf{d}} \left( \mathbf{R}_X \right) \), can be written in terms of a mode expansion;

\[ \hat{\mathbf{d}} \left( \mathbf{R}_X \right) = i \sum_{\lambda, \lambda'} \left( \frac{\hbar c \varepsilon_0}{2V} \right)^{1/2} \left\{ \hat{e}^{(\lambda) \star} \left( \mathbf{p} \right) \hat{a}^{(\lambda)} \left( \mathbf{p} \right) e^{i \mathbf{p} \cdot \mathbf{R}_X} - e^{-i \mathbf{p} \cdot \mathbf{R}_X} \hat{a}^{(\lambda) \star} \left( \mathbf{p} \right) \hat{e}^{(\lambda)} \left( \mathbf{p} \right) \right\} . \] \hspace{1cm} (3.4)

Here, \( c \) is the speed of light in a vacuum, \( \hat{e}^{(\lambda) \star} \left( \mathbf{p} \right) \) defines the polarisation of the mediating photon (the asterisk denoting its complex conjugate), \( \hat{a}^{(\lambda)} \left( \mathbf{p} \right) \) and \( \hat{a}^{(\lambda) \star} \left( \mathbf{p} \right) \) are the annihilation and creation operators, respectively, for a photon of wave-vector \( \mathbf{p} \) and polarisation \( \lambda \). In the pre-exponential factor, \( V \) represents the volume used in the box quantisation procedure that enables fields to be defined in terms of operators, as required by QED. The second-order perturbative term, which is the leading term in the matrix element for RET, is explicitly written (in terms of Dirac brackets) as;

\[ M_{\beta} = \frac{\left\langle f | H_{\text{int}} | l_1 \right\rangle \left\langle l_1 | H_{\text{int}} | i \right\rangle}{E_i - E_{l_1}} + \frac{\left\langle f | H_{\text{int}} | l_2 \right\rangle \left\langle l_2 | H_{\text{int}} | i \right\rangle}{E_i - E_{l_2}} . \] \hspace{1cm} (3.5)
From Figure 2, we easily identify the key system states (which is a combination of the two molecular states and the radiation state). These are the initial state \( |i\rangle = |E_D^0, E_A^\infty; 0(p, \lambda)\rangle \) (donor excited, acceptor unexcited and no photon), the final state \( |f\rangle = |E_D^0, E_A^\infty; 0(p, \lambda)\rangle \) (donor unexcited, acceptor excited and no photon) and the two possible intermediate states, \( |I_1\rangle = |E_D^0, E_A^\infty; 1(p, \lambda)\rangle \) (donor and acceptor unexcited and one photon) and \( |I_2\rangle = |E_D^0, E_A^\infty; 1(p, \lambda)\rangle \) (donor and acceptor excited and one photon). The radiation states, often referred to as number or Fock states, have eigenvalues that are occupation numbers of the quantized electromagnetic field, i.e. the number of photons in the system.

The creation and annihilation operators act on the relevant radiation states via \( a^{\dagger}(p)|0(p, \lambda)\rangle = |1(p, \lambda)\rangle \) and \( a(p)|1(p, \lambda)\rangle = |0(p, \lambda)\rangle \). The commutator involving these two operators is given by the relationship \( [a^{\dagger}(p), a(p)] = (8\pi V)^{-1} \delta'(p - p') \delta_{\lambda\lambda'} \), where \( \delta'(p - p') \) is a Dirac delta function and \( \delta_{\lambda\lambda'} \) is a Kronecker delta [76].

Equipped with these state expressions, the interaction Hamiltonian of equation (3.3) and the energies of each state in Table 1 (note that the initial and final states have the same energy, since conservation of energy has to be restored after a miniscule amount of time), an expression for the RET matrix element can be found. For illustrative purposes, we explicitly calculate just one of the Dirac brackets, namely \( \langle I_1 | \hat{H}_{\text{int}} | i \rangle \); which is the initial bracket, since it is convention to move from right to left in these equations. Explicitly, it is written as:

\[
\langle I_1 | \hat{H}_{\text{int}} | i \rangle = \langle E_D^0, E_A^0; 1(p, \lambda) \rangle - \epsilon_0 \hat{\mu}(D) \cdot d \langle R_D \rangle - \epsilon_0 \hat{\mu}(A) \cdot d \langle R_A \rangle |E_D^0, E_A^\infty; 0(p, \lambda)\rangle .
\] (3.6)

This represents the creation of a photon when the excited donor relaxes (the acceptor is unchanged, as denoted by the superscript on either \( E_A \)) and, hence, dipole operators acting on the acceptor molecular state and the annihilation operator (within \( d \hat{\mu} \)) on the radiation state are zero due to orthonormality. Therefore, equation (3.6) is simplified to:

\[
\langle I_1 | \hat{H}_{\text{int}} | i \rangle = -\epsilon_0 \langle E_D^0 | \hat{\mu}(D) | E_D^0 \rangle \langle 1(p, \lambda) | d \langle R_D \rangle | 0(p, \lambda) \rangle .
\] (3.7)

The solution of which, on insertion of equation (3.4), is expressed concisely as;
\[
\langle I_1 | H_{\text{int}} | i \rangle = i \sum_{p,A} \left( \frac{\hbar c p e_u}{2 V} \right)^{\frac{1}{2}} e_i^{(A)}(\vec{p}) \mu_i^{0n}(D) e^{-i \vec{k} \cdot \vec{R}_i} ,
\]
(3.8)

with the \( i^{\text{th}} \) component of the \textit{transition} dipole moment written as;

\[
\mu_i^{0n}(D) = \langle E_D^0 | \mu_i(D) | E_D^n \rangle .
\]
(3.9)

Following a similar procedure for the other three Dirac brackets, and finding the energy denominators for each term of (3.5), the full expression for the RET process is given as;

\[
M_\beta = \sum_{p,A} \left( \frac{\hbar c p}{2 e_0 V} \right)^{\frac{1}{2}} e_i^{(A)}(\vec{p}) e_j^{(A)}(\vec{p}) \left\{ \mu_i^{0n}(D) \mu_j^{w0}(A) \frac{e^{i \vec{k} \cdot \vec{R}}}{E_{n0} - \hbar c p} + \mu_j^{0n}(D) \mu_i^{w0}(A) \frac{e^{-i \vec{k} \cdot \vec{R}}}{-E_{n0} - \hbar c p} \right\} .
\]
(3.10)

In order to determine a final result for the RET matrix element, we use the cosine rule to rewrite the summation over of polarizations as;

\[
\sum_{A} e_i^{(A)}(\vec{p}) e_j^{(A)}(\vec{p}) = \delta_{ij} - \hat{p}_i \hat{p}_j ,
\]
(3.11)

where \( \delta_{ij} \) is the Kronecker delta and a caret denotes a unit vector, and convert the inverse of the quantization volume to an integral in momentum space;

\[
\frac{1}{V} \sum_p \to \int \frac{d^3 \vec{p}}{(2\pi)^3} .
\]
(3.12)

The quantum amplitude then becomes an integral of the form;

\[
M_\beta = \frac{1}{2 e_0} \mu_i^{0n}(D) \mu_j^{w0}(A) \left\{ \frac{p^z}{k^z - p^z} \left( \delta_{ij} - \hat{p}_i \hat{p}_j \right) \times \left\{ k \left( e^{i \vec{k} \cdot \vec{R}} - e^{-i \vec{k} \cdot \vec{R}} \right) + p \left( e^{i \vec{k} \cdot \vec{R}} + e^{-i \vec{k} \cdot \vec{R}} \right) \right\} \frac{d^3 \vec{p}}{(2\pi)^3} ,
\]
(3.13)
where $\hbar \epsilon$ is the energy transferred from $D$ to $A$. As outlined in the subsequent section, this integral has been solved analytically using various vector calculus techniques. Omitting the long and intricate derivation based on special functions [63], the matrix element for RET – including the retarded electric dipole-electric dipole (E1-E1) coupling tensor, denoted as $V_{ij}$ – is obtained as:

$$M_{ji} = \mu_0 (D) V_j (k, \bar{R}) \mu_0^* (A),$$

(3.14)

$$V_j (k, \bar{R}) = \frac{e^{ikR}}{4\pi \varepsilon R^3} \left\{ \left( 1 - ikR \right) \left( \delta_j - 3\hat{R} \cdot \hat{R}_j \right) - (kR)^2 \left( \delta_j - \hat{R} \cdot \hat{R}_j \right) \right\}. \quad (3.15)$$

A more in-depth analysis of the derivation of the E1-E1 coupling tensor, $V_{ij}$, and the transfer rate of RET (an outline of which follows) – without providing all of the intricate specifics – is delivered by Salam in his recent review [77].

### 3.2 Physical interpretation of the RET coupling tensor

The physical observable derived from the $V_{ij}$ tensor, via the matrix element, is the transfer rate of RET, symbolised by $\Gamma$. This rate is demined from the Fermi rule [78]: $\Gamma = \frac{2\pi}{\hbar} |M_{ji}|^2 \rho_f$, where $\rho_f$ is the density of acceptor final states. Assuming a system of two freely tumbling molecules, meaning that a rotational average is applied [79], the following is found:

$$\Gamma = \frac{1}{9} |\hat{\mu}(D)|^2 |\hat{\mu}(A)|^2 A(k, R). \quad (3.16)$$

where the E1-E1 transfer function, $A(k, R)$, is defined by [62];

$$A(k, R) = V_j (k, \bar{R}) V_j^* (k, \bar{R}) = \frac{2}{(4\pi \varepsilon R^3)^2} \left\{ 3 + (kR)^2 + (kR)^4 \right\}. \quad (3.17)$$

In contrast to Förster coupling, the QED form of the electronic coupling has a complicated distance dependence, which underscores the unification of the radiationless and radiative transfer mechanisms. Whereas the semi-classical Förster theory predicts only an $R^{-6}$ dependence [80], the
QED rate expression of (3.17) contains three distance dependencies: $R^{-2}$, $R^{-4}$ and $R^{-6}$. This signifies three distinct regimes that dominate in the long-, intermediate- and short-range, respectively.

The different regimes of RET are most readily understood in terms of the mediating photon [49]. As outlined in Section 2.2, the photon is said to have real characteristics – i.e. it has a large transverse component w.r.t. $\tilde{R}$ – when the separation of the donor and acceptor exceeds its reduced wavelength (i.e. $R \gg \lambda$). Meaning that, since the mediating photon is always transverse w.r.t. its wave-vector $\tilde{p}$, the photons (emitted in all directions by $D$) that are annihilated at $A$ in the long-range are the ones where $\tilde{p}$ is essentially co-linear with $\tilde{R}$. Conversely, if $R$ is significantly less than the reduced wavelength the photon is fully virtual, meaning that retardation effects are not present. That is, it does not have well defined physical characteristics, such as momentum. This arises because, due to the uncertainty principle, the position of the mediating photon is ‘smeared out’ in the short-range so that $\tilde{p}$ may no longer be co-linear with $\tilde{R}$ – therefore, there is a longitudinal component to the photon w.r.t. $\tilde{R}$. The two limiting cases of RET are, hence, often referred to as radiationless (virtual photon) and radiative (real) transfer – in the past, until the unified theory, they were usually considered to be two completely separate and distinct mechanisms. Since all three terms of equation (3.17) are non-zero in RET (or, at least, the short-range term always exists), it is justifiable to say that all photons are virtual in nature [49,81]. This means that a notional ‘real’ photon – which is transverse w.r.t both $\tilde{p}$ and $\tilde{R}$ – does not exist, because these two vectors are never exactly collinear due to the uncertainty principle.

To summarise, long-range (or far-zone) energy transfer has an inverse-square, $R^{-2}$, dependence on the rate, and short-range (or near-zone or Förster) transfer has the well-known $R^{-6}$ dependence. That leaves the intermediate zone, which was not previously identified until Andrews’s work [62], where the distance separating the molecules is of the same order as the reduced wavelength of the mediating photon; this region has an $R^{-4}$ dependence. Our expressions have assumed dynamic coupling between the transition dipole moments of the donor and acceptor, for cases of static dipole couplings (in which $k = 0$) only the first term of equation (3.17) applies.
3.3 Higher order RET

Often the electric dipole approximation is employed for studies on RET, which means that only E1-E1 coupling is considered. However, the coupling of the electric dipole of a molecule with the magnetic dipole (M1) or electric quadrupole (E2) of the other can be important [82], for example, in chirality-sensitive RET [77,83-86]. E1-M1 and E1-E2 couplings are, in general, of similar magnitude but are roughly 150 times smaller than E1-E1 interactions; other multipoles are even smaller and almost never utilised in RET analyses.

The derivation of the matrix element for E1-M1 coupling, with use of special functions, is provided elsewhere [63]. The final result is given by:

$$M_{ji}^{E1-M1} = \left\{ \mu_{j}^{0m} (D) \frac{m_{j}^{00} (A)}{c} + \frac{m_{j}^{0m} (D)}{c} \mu_{i}^{00} (A) \right\} U_{ij} (k, \vec{R}) , \quad (3.18)$$

which features the transition magnetic dipole, $m_{j}$, and the E1-M1 tensor, $U_{ij} (k, \vec{R})$, with the latter explicitly expressed as:

$$U_{ij} (k, \vec{R}) = \frac{e^{-ikR}}{4\pi \varepsilon_0} \frac{\hat{R}}{R^3} \varepsilon_{ijk} \left( -ikR + k^2 R^2 \right) , \quad (3.19)$$

where $\varepsilon_{ijk}$ is the Levi-Civita symbol. Following a rotational average [79], the rate of RET based on this type of coupling is:

$$\Gamma' \sim \frac{B(k,R)}{9c^2} \left\{ |\vec{\mu} (D)|^2 |\vec{m} (A)|^2 + |\vec{\mu} (A)|^2 |\vec{m} (D)|^2 - 2 \text{Re} [\vec{\mu} (D) \cdot \vec{m}^* (D)] [\vec{\mu}^* (A) \cdot \vec{m} (A)] \right\} . \quad (3.20)$$

where the E1-M1 transfer function, $B(k,R)$, is written as:

$$B(k,R) = U_{ij} (k, \vec{R}) U_{ij}^* (k, \vec{R}) = \frac{2}{(4\pi \varepsilon_0 R^3)^2} \left( k^2 R^2 + k^4 R^4 \right) . \quad (3.21)$$
Comparing equations (3.17) with (3.21), i.e. the A and B functions, it is clear that the first term (the $R^{-6}$ dependent term) is missing in E1-M1 coupling. Physically, this means that the photons that mediate E1-M1 interactions have real characteristics, i.e. they are never fully virtual. However, in contrast to a commonly held view, E1-M1 coupling is not exclusively related to radiative energy transfer since a short-range $R^{-4}$ term also exists. The lack of the $R^{-6}$ term also tells us that static electric and magnetic dipoles (in which $k = 0$) do not interact, since all the other terms involve $k$.

The matrix element for E1-E2 interactions is determined as [69,71];

$$M_{fi}^{E1-E2} = \{\mu_i(D)Q_{jk}(A) - Q_{jk}(D)\mu_i(A)\}V_{(ijk)}^{\pm}(k, \vec{R}), \quad (3.22)$$

where the E1-E2 tensor, $V_{(ijk)}^{\pm}(k, \vec{R})$, is expressed by;

$$V_{(ijk)}^{\pm}(k, \vec{R}) = \frac{e^{ikR}}{4\pi\varepsilon_0 R^4} \left\{ (-3 + 3ikR + k^2 R^2) \left( \delta_{ij}\hat{R}_k + \delta_{jk}\hat{R}_i + \delta_{ki}\hat{R}_j - 5\hat{R}_i\hat{R}_j\hat{R}_k \right) 
+ \left( k^2 R^2 - ik^3 R^3 \right) \left( \frac{1}{2} \left( \delta_{ij}\hat{R}_k + \delta_{jk}\hat{R}_i - \hat{R}_i\hat{R}_j\hat{R}_k \right) \right) \right\}. \quad (3.23)$$

This expression is the $-jk$ index symmetry form of the tensor, which is justified since it contracts with the index-symmetric electric quadrupole, $Q_{jk}^\pm$. After a rotational average, the corresponding rate is obtained as;

$$\Gamma^\sigma = \frac{C(k, R)}{15} \left\{ [\tilde{\mu}(D)]^\sigma Q_{\lambda\mu}(A)Q_{\lambda\mu}^*(A) + [\tilde{\mu}(A)]^\sigma Q_{\lambda\mu}(D)Q_{\lambda\mu}^*(D) \right\}, \quad (3.24)$$

where $C(k, R)$ is found as;

$$C(k, R) = V_{(ijk)}(k, \vec{R})V_{(ijk)}^*(k, \vec{R}) = \frac{1}{(4\pi\varepsilon_0 R^4)^2} \left\{ 90 + 18k^2 R^2 + 3k^4 R^4 + k^6 R^6 \right\}. \quad (3.25)$$
Examining this expression, we see that E1-E2 coupling has four terms with the distance dependencies $R^2$, $R^4$, $R^6$ and $R^8$ (rather than the three of E1-E1 interactions). The new radiationless ($R^8$) term dominates in the near-zone, as predicted by Dexter [5], while the usual inverse-square distance dependence of radiative transfer dictates the far-zone. The presence of these terms (and the distinctive middle terms) in a single expression again signifies that they are the two extremes of a unified theory. Since the first term does not depend on $k$, we determine that static electric dipole and quadrupoles can interact.

3.4 Effects of a bridging molecule

Recent theoretical work, based on QED in the electric dipole approximation, is an analysis on the effects of a third molecule, $M$, on RET [87-91]. In this sub-section, we touch upon the case where $M$ bridges the energy transfer between $D$ and $A$ – a Feynman diagram of which is provided in Figure 3. This is the DMA configuration; the other cases (DAM and MDA), in which the molecules are interchanged, have also been investigated. The matrix element for DMA, delivered from fourth-order perturbation theory, is given by:

$$M^p_{fi} = \mu^{0n}_i (D)V_{ij}(k,\vec{R}_{DM})\alpha_{jk}^{00}(M)V_{kl}(k,\vec{R}_{MA})\mu_{nk}^{m0}(A), \quad (3.26)$$

where $\alpha_{jk}^{00}(M)$ is the polarisability tensor that arises because two light-molecule interactions occur at the third molecule (which begins and ends in its ground state, as denoted by the superscript 00) and two couplings tensors are used since two energy transfer steps occur. Using the Fermi rule, the leading term in the physically observable rate (that includes the third body) is the quantum interference, i.e. the cross-term, that involves multiplication of equations (3.14) and (3.26) so that [88];

$$M^p_{fi}M^{n+}_{fi} = \mu^{0n}_i (D)V_{ij}(k,\vec{R}_{DM})\alpha_{jk}^{00}(M)V_{kl}(k,\vec{R}_{MA})\mu_{nk}^{m0}(A)\mu^{0n}_p (D)V_{pq}^*(k,\vec{R})\mu_{q}^{m0}(A). \quad (3.27)$$

This is the rate that dominates if energy transfer between $D$ and $A$ is forbidden, for example, due to symmetry selection rules or when the dipole moments of $D$ and $A$ are both orthogonal with each other and their displacement vector, $\vec{R}$. In this scenario, the mediator $M$ facilitates the RET that
would not occur otherwise [89]. A recent review by Salam provides a more comprehensive analysis on the role of a third body in RET [77].

4 Recent RET research

4.1 Nanomaterials for energy transfer

While the generic term ‘molecule’ has been used throughout this manuscript, other materials can be used in RET such as atoms, chromophores, particles and, more recently, carbon nanotubes [92-96] and quantum dots (QDs). In 1996, first observation of energy transfer between the latter was achieved with cadmium selenide (CdSe) QDs [97] and similar compounds followed; for example, cadmium telluride (CdTe) [98] and lead sulfide (PbS) [99] QDs. In experiments, quantum dots are attractive because they can be much brighter, and contain greater photostability, than typical organic chromophores [100,101]. Hence, QDs have become important in bio-inspired RET-based applications [102,103], such as nanosensors [104-111] and photodynamic therapy [112,113]. In terms of theory, it has been determined that RET between quantum dots and nanotubes can be modelled using dipole-dipole couplings [90,114-119]. For more on the experiments and theory of RET in nanomaterials, Liu and Qiu provide an excellent review on recent advances [120].

While quantum dots are suggested as artificial antennas in synthetic light-harvesting materials [111,121], research on such systems usually involve multi-chromophore macromolecules. One type of which are known as dendrimers; from its periphery to core, these branch-like structures comprise decreasing number of chromophores [122-130]. They work on the principle that photons are absorbed at the periphery and the excitation energy is funneled to a central reaction centre via multiple RET steps; an example of this is shown in Figure 4. A significant amount of theory has been published on this multi-chromophore transfer mechanism [131-140]. Towards the centre of the dendrimer, where the number of chromophores is decreased, there is a possibility that two excited donors will be in the vicinity of an acceptor. In this case, another RET mechanism, known as energy pooling [141-143], becomes possible. This process is illustrated in Figure 5 and can be written, in terms of photophysics, as:

\[ D^* + D^* + A \rightarrow D + D + A^{**} \]
where the double asterisk denotes that the acceptor is doubly excited, i.e. the acceptor is promoted to an excited state that requires the excitation energies of the sum of the two donors. This contrasts to the process known as energy transfer up-conversion [144,145], which has the same initial condition but excitation is transferred from one donor to the other – so that one of the donors is doubly excited – and the third molecule is not involved. The matrix element for energy pooling has an analogous form to equation (3.26); the only difference is that the superscript $m0$ on $A$ (which is now a donor) becomes $0n$ and the superscript $00$ on $M$ (now the acceptor) becomes $s0$, where $s$ signifies a doubly excited molecule. In recent years, Lusk and co-workers have demonstrated energy pooling experimentally [146] and discovered, among other advances, that the efficiency of energy pooling can be improved within a cavity [147-149]. Lately, moreover, they have studied the time-inverse mechanism of energy pooling, known as quantum cutting, which involves the excitation on $A$ transferring to both $D$ molecules [150].

Another double-excitation mechanism is two-photon RET [151,152], which involves the absorption of two photons at the donor and the transfer of the resulting excitation to the acceptor. The matrix element of this process is identical to equation (3.14), except the superscript on $D$ is $0s$ rather than $0n$. Since the incident light in two-photon RET is lower in energy compared to RET, photo-destruction of living tissue can be circumvented. Therefore, biological applications of this process have arisen, including photodynamic therapy [153-160] and bioimaging [155,160-163].

### 4.2 Plasmon-based RET

The quest for control of light-energy at the nanoscale has led to some very interesting studies, from both an experimental and a theoretical point-of-view, that often involve RET coupling between molecules near a surface plasmon [164-194] – the latter, basically, acting as a bridging material for the energy transfer. Plasmons are the collective excitations of conduction electrons by light, which generally reside in a confined metallic structure. By coupling plasmonic materials to RET chromophores, a substantial amount of energy transfer can occur over significantly larger separations than the RET between conventional materials – up to distances approaching the optical wavelength. The effects of a surrounding nanophotonic environment, such as a surface plasmon, on RET is an ongoing debate [189,195].
In 2011, Pustovit and Shahbazyan developed a classical theory of plasmon-assisted RET that involves an isotropic complex polarizability [196]. Their model, which maintains an energy balance between transfer, dissipation and radiation, analyses the geometry of a plasmon-RET system – with a focus on distance and orientational effects – by providing numerical results. This mechanism shows that plasmon-assisted RET will dominate the usual non-radiative (Förster) transfer, even in the near-zone. While a comparable study predicts, over hundreds of nanometres, an enhanced rate by a factor of $10^6$ [197]. These forecast improvements now have experimental verification. For example, Wenger and co-workers demonstrate enhanced transfer between donor-acceptor pairs confined to a gold ‘nanoapparatus’; they endorse a six-fold increase in the rate of RET over 13 nm [198].

In the years that followed, other innovative studies on plasmon RET have arisen. An experimental study by Zhao et al. showed that the efficiency of RET can be controlled by the plasmonic wavelength [199]. Remarkably, they discovered that RET can be turned off and on by tuning the plasmon spectrum with the donor emission and acceptor absorption peaks, respectively. Related theory develops the concept of a ‘generalised spectral overlap’, whereby the rate of plasmon RET is not just dependent on the overlap integral of the donor emission and acceptor absorption spectra (as follows from Förster theory), but includes a plasmonic contribution from an electromagnetic coupling factor [200,201]. Other experimental work, which is analogous to the effects of a bridging molecule that is discussed earlier [89], use plasmonic nanoantennas to enable E1-E1 RET that is otherwise forbidden by geometry [202].

Bershike et al. explain, by comparing model and experimental data, enhanced coupling between a nanoscale metal and a light emitting dipole [203]. They employ a complex dielectric function that indicates an $R^{-4}$ distance dependence (ranging from 0.945 to 8.25 nm) between the fluorescent molecule and the gold nanoparticle surface. Similar to this study, Bradley and co-workers provide an investigation, which employs a Green’s tensor analysis of Mie theory, that again show plasmon RET can display an $R^{-4}$ dependence [204]. These results are consistent with numerical predictions, based on QED, that intermediate-zone RET dominates at these separation distances [51].

4.3 Energy transfer at non-optical frequencies

Resonance energy transfer usually occurs in the ultraviolet or visible range of the electromagnetic spectrum, which is comparable to the energy required for electronic transitions in molecules etc.
Recently, however, energy transfer involving either a much lower or higher frequency range has gained traction. An outline on which now follows.

At the lower end, in the infrared range, transfer of vibrational energy can arise between excited (donor) and unexcited (acceptor) oscillating bonds on adjacent molecules. Applications include the observation of local orientational order in liquids [205] and, analogous to the spectroscopic ruler in RET, a measure of intermolecular distances at the sub-nanoscale in the condensed phase [206,207]. This type of transfer is especially prevalent between water molecules, due to the strong dipole-dipole interactions between the O–H stretch vibrations [208-210]. It has been determined that, with some modifications, that Förster theory can be valid at these light frequencies [211]. Energy transfer at even lower frequencies, namely in the microwave range, is the subject of a very recent paper by Wenger and co-workers [212]. In this work, the energy transfer is enhanced by positioning the donor and acceptor pair within a cavity.

At the higher end is interatomic and intermolecular Coulombic decay (collectively ICD), a process that involves the x-ray range of the spectrum. First predicted in 1997 [213], and experimentally verified six years later [214], ICD is a process in which photoionization of one atom or molecule can lead to remote photoionization of another atom or molecule via the exchange of a high energy photon. In terms of fundamental theory, ICD is now understood to be equivalent to Förster transfer (although ICD involves much more complex prior and posterior processes) – since the mechanism is driven by dipole-dipole coupling with the characteristic $R^{-6}$ distance dependence. Nevertheless, there is a major fundamental difference between RET and ICD. Namely, as explained previously, the former typically involves only valence electrons whereas ICD is initiated by an intra-atomic (or intra-molecular) decay process; a high-energy transition, in which a donor valence electron relaxes to the core shell resulting in promotion of an acceptor valence electron to the continuum, i.e. acceptor ionization. This means that an ionization cross-section will feature instead of the absorption cross-section of Förster transfer.

A prototypical example is the photo-ionization of a neon dimer ($\text{Ne}_2$) via 2S-electron emission from one of its atoms. This results in the relaxation of a valence 2P-electron into the formed vacancy and, consequently, a high-energy photon is released. Following absorption of this light by the neighbouring atom, a 2P-electron is ejected from it [215,216]. The interaction of the two newly charged ions causes a Coulomb explosion, i.e. the fragmentation of the dimer. For clarity, the whole mechanism is illustrated in Figure 6. ICD is typically ultra-short-range, in which (just like Dexter
transfer) wavefunction overlap occurs; hence, terms relating to electron correlation and exchange will contribute. Moreover, since ICD involves electron relaxation from a valence shell to the core shell in the donor, account of the Auger effect is required. This competing mechanism occurs because the energy generated from this relaxation could be transferred to another electron within the donor (and, thus, ejecting it), so energy in the form of a photon would not reach the acceptor. Therefore, for an accurate theoretical description of ICD, a detailed interpretation of the Auger effect along with electron correlation and exchange is required. This is achieved by considering direct and exchange Coulomb integrals for the decay rate. An overview of this is provided by Jahnke in his recent review [217].

Since the pioneering studies on diatomic systems, there have been a number of experimental and theoretical investigations into ICD that involve different materials, including clusters of atoms and molecules [218], quantum dots [219,220] and quantum wells [221]. Although ICD has considerable theoretical interest, there is evidence of its practical importance to biological chemistry; in particular, in the understanding of a DNA repair mechanism provided by the enzymes known as photolyases [222,223]. The theoretical developments of ICD often mirror those already established in RET – such as the effects of retardation, dielectric environments, a third body and virtual photons [224,225]. Clearly, more research in this exciting emerging field is required, with much still to learn in terms of its fundamental theory and applications.

4.4 RET in cavities

It can be challenging to elucidate fundamental processes experimentally, particularly because RET often occurs in natural biological systems and ‘energy materials’ in the condensed phase. Necessarily involving a level of phenomenological modelling, their simulation can be tremendously complicated. Associated research, especially in connection to the field of biology, has been covered in a numerous recent reviews [226-246]. Cavity quantum electrodynamics (cQED) works on the principle that electronic species are restricted to small volumes (usually bounded by mirrors in one or more dimensions) so that the electromagnetic field is tuned to specific quantised modes and the quantum nature of the light becomes more apparent compared to the free field. In terms of mathematical formulation, the arbitrary quantisation volume, \( V \), of equation (3.10) is simply replaced by the dimensions of the cavity. Early applications of cQED revealed an understanding of the fundamental light-matter interactions in atoms, quantum dots and similar materials [247-252].
More recently cQED has been applied to chemical substances, such as organic dyes, and connected to phenomena such as RET [253]. The main advantage of studying these cavity-based schemes is that experimentalists are able to control the electromagnetic radiation at the quantum level, while simultaneously reducing interference with the surroundings to a significant extent. This allows for the explicit study of polariton modes (sometimes called hybrid states in this context), which is typically difficult in the condensed phase because of the rapid decoherence that derives from system coupling with a continuum of environmental modes. For example, in 2012, Ebbesen and co-workers experimentally showed that the photophysical properties of light-induced chemical reactions can be influenced by cavity fields, which can modify the chemical reaction landscape [254]. In another study, the same research group cleverly showed how to alter the reaction rates of chemical reactions by coupling molecular vibrations to infrared cavity modes [255]. Since experiments with negligible amount of decoherence are now conceivable, there is increasing interest in the effects of polariton modes on energy transfer within a cavity. In 2015, for instance, a couple of theoretical studies indicated that ‘exciton conductance’ could be considerably enhanced, by orders of magnitude, when organic materials are coupled to cavity modes [256,257]. Experimental verification of this amplified energy transfer soon followed [258-260]. Attempts to better understand polariton-assisted RET are increasingly prevalent. In 2018, Du et al. developed a ‘polariton-assisted remote energy transfer’ model to explain how enhanced RET is mediated by vibrational relaxation in an optical microcavity [261]. While earlier this year, Schäfer et al. proposed that energy transfer could be drastically affected by a modification of the vacuum fluctuations in the cavity. In this research, they make a connection to Förster and Dexter transfer, and account for the often-disregarded Coulomb and self-polarisation interactions. Interestingly, they predict that photonic degrees of freedom give rise to electron-electron correlations over large distances in the cavity [262]. What we do know for sure is that cavity RET is a representative example of the strong coupling regime; an excellent recent review on such strong light-matter interactions is provided by Börjesson and co-workers [263].

5 Discussion

Today it is nearly 100 years since the discovery of RET and, remarkably, the 71 year-old Förster theory that describes this transfer is still widely utilised. This model has provided us with the famous $R^{-6}$ distance dependence on the rate between donor and acceptor molecules. Following these earlier
times, from the 1960s until the late 1980s, significant theoretical developments based on fundamental quantum electrodynamics has been applied to two-centre RET. This has culminated into the unified theory of RET, which links the short-range (near-zone) process of Förster with a long-range (far-zone), $R^{-2}$ dependent transfer consistent with Coulomb’s Law. It also predicts a $R^{-4}$ dependence in the intermediate region, where the distance between the molecules approximately equals the reduced wavelength of the mediating virtual photon. The latter could be said to have increasingly real characteristics in this range. Although not detailed in this review, further work in the 1990s predicted that optically active molecules in the condensed phase could also have a $R^{-3}$ and a $R^{-5}$ distance dependence, which become significant when the imaginary part of the refractive index is especially large [264,265]. Soon afterwards, a QED description for the rate of RET in the presence of dispersing and absorbing material bodies of arbitrary shapes was provided [266]. In the 21st century, among other advances, quantum theory has helped us understand the role of mediators in energy transfer (i.e. 3- and 4-body RET) and the rederivations of the RET coupling tensor has provided new physical insights.

In the last ten years, research into RET has moved into many exciting directions – too numerous to cover in detail in a single review. For example, the enhancement and control of long-range, super-Coulombic RET in hyperbolic metamaterials is shown [267,268] and the influence of epsilon-and-mu-near-zero waveguide super-coupling on RET is considered [269]. Moreover, many research groups continue to unravel the nature of energy transfer within biological photosynthesis, with a special focus on the understanding of the roles that molecular vibrations may play in facilitating the process. There are also enormous efforts to develop ‘energy materials’ that may enable new technologies, which include those focused on solar energy harvesting. Materials based on surface plasmons have shown great promise, especially in its connection to the huge enhancements of RET efficiency. Research groups are also working on RET in both the non-optical regions of the electromagnetic spectrum and within optical cavities. In all of these exciting areas of research, new experiments and theory need continued development. The theory of QED, while the most precise theory we know for light-matter interactions, assumes non-dissipative closed systems and that the electrons are localised to the molecules. Consequently, in its current formulation, microscopic QED is not directly applicable to the investigation of surface plasmons (delocalised excitons) or the process of decoherence, which occurs because the system is open to the environment. While semiclassical theories can address these questions in a limited way, the continued development of macroscopic QED [270] is desirable for accurate portrayals of such processes.
Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Author Contributions

GJ and DB equally wrote and edited the final manuscript. The figures and table are produced by them.

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Table 1. All the system states and their associated energies for RET. The energies of the donor and acceptor are represented by superscript of $E_D$ and $E_A$, respectively. Due to conservation of energy arguments, $E^i = E^f$.

<table>
<thead>
<tr>
<th>System state</th>
<th>Dirac bracket</th>
<th>Energy</th>
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<tbody>
<tr>
<td>$</td>
<td>i\rangle$</td>
<td>$E_D^0, E_A^0, 0(p, \lambda)$</td>
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<tr>
<td>$</td>
<td>I_1\rangle$</td>
<td>$E_D^0, E_A^0, 1(p, \lambda)$</td>
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<td>$</td>
<td>I_2\rangle$</td>
<td>$E_D^m, E_A^m, 1(p, \lambda)$</td>
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<td>f\rangle$</td>
<td>$E_D^0, E_A^m, 0(p, \lambda)$</td>
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Figure 1. Representation of energy transfer, the excited donor (on the left-hand side) transfers energy, represented by the red arrow, to the acceptor (on the right).

Figure 2. Two time-orderings for RET between a donor ($D$) and an acceptor ($A$). The vertical lines denote the two molecules, wavy lines are the photons, $n$ and $m$ represents the excited state of $D$ and $A$, respectively, and $0$ is their ground state; time, $t$, increases up the graph. Red, black and blue lines represent the initial, intermediate and final system state.

Figure 3. One of 24 possible time-orderings for RET mediated by a third molecule, $M$, acting as a bridge between donor $D$ and acceptor $A$. Energy is transferred from $D$ to $A$, and $M$ begins and ends in its ground state.

Figure 4. Two-step RET in a second-generation phenylacetylene dendrimer. This schematic depicts initial electronic excitation at a peripheral phenyl group, which acts as a donor of energy to a neighbouring inner-ring chromophore; this acceptor then becomes a donor of energy to the phenaline core. Original image appeared in reference [137].
Figure 5. Representation of energy pooling, the two excited donors (on the left- and right-hand side) transfer energy, represented by the red arrows, to the acceptor (in the centre).

Figure 6. (a) Photoionization of a neon dimer, via ejection of an inner shell electron from an atom (green arrow), due to incident x-ray radiation (orange wavy line). (b) Interatomic Coulombic decay: an outer electron relaxes into the vacancy (blue arrow) and, consequently, photo-ionization of the other atom occurs due to energy transfer between the atoms (red arrow). (c) The newly charged atoms (plus signs) repel each other (yellow arrows), which results in destruction of the neon dimer.
Figure 1.

Figure 2.
Figure 3.

Figure 4.
Figure 5.

Figure 6.