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Nanoscience and Nanotechnology

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Nanoscience and nanotechnology offer means to assemble and study superstructures, composed of nanocomponents such as nanocrystals and biomolecules, exhibiting interesting unique properties. Also, nanoscience and nanotechnology enable ways to make and explore design-based artificial structures that do not exist in nature such as metamaterials and metasurfaces. Furthermore, nanoscience and nanotechnology allow us to make and understand tightly confined quasi-zero-dimensional to two-dimensional quantum structures such as nanoplatelets and graphene with unique electronic structures. For example, today by using a biomolecular linker, one can assemble crystalline nanoparticles and nanowires into complex surfaces or composite structures with new electronic and optical properties. The unique properties of these superstructures result from the chemical composition and physical arrangement of such nanocomponents (e.g., semiconductor nanocrystals, metal nanoparticles, and biomolecules). Interactions between these elements (donor and acceptor) may further enhance such properties of the resulting hybrid superstructures. One of the important mechanisms is excitonics (enabled through energy transfer of exciton-exciton coupling) and another one is plasmonics (enabled by plasmon-exciton coupling). Also, in such nanoengineered structures, the light-material interactions at the nanoscale can be modified and enhanced, giving rise to nanophotonic effects.

These emerging topics of energy transfer, plasmonics, metastructuring and the like have now reached a level of wide-scale use and popularity that they are no longer the topics of a specialist, but now span the interests of all “end-users” of the new findings in these topics including those parties in biology, medicine, materials science and engineering. Many technical books and reports have been published on individual topics in the specialized fields, and the existing literature have been typically written in a specialized manner for those in the field of interest (e.g., for only the physicists, only the chemists, etc.). However, currently there is no brief series available, which covers these topics in a way uniting all fields of interest including physics, chemistry, material science, biology, medicine, engineering, and the others.

The proposed new series in “Nanoscience and Nanotechnology” uniquely supports this cross-sectional platform spanning all of these fields. The proposed briefs series is intended to target a diverse readership and to serve as an important reference for both the specialized and general audience. This is not possible to achieve under the series of an engineering field (for example, electrical engineering) or under the series of a technical field (for example, physics and applied physics), which would have been very intimidating for biologists, medical doctors, materials scientists, etc.

The Briefs in NANOSCIENCE AND NANOTECHNOLOGY thus offers a great potential by itself, which will be interesting both for the specialists and the non-specialists.

More information about this series at http://www.springer.com/series/11713
Understanding and Modeling Förster-type Resonance Energy Transfer (FRET)

Introduction to FRET, Vol. 1
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Chapter 1
Short History of Energy Transfer Theory
Before Förster, At The Time of Förster, and After Förster

This chapter gives a brief introduction to the historical development of energy transfer. In this chapter, we are not dealing with a detailed review of applications, nor a review of modern theoretical development; instead, we outline some of the ideas, experiments and theories that formed the scientific background that culminated in the Förster resonance energy transfer (FRET) theory. A more detailed description of the historical events regarding to FRET can be found in a review [1] and references within.

FRET is a physical process where the excited state energy of the “donor” can be transferred to the “acceptor” in the ground state. This can take place whenever the donor and the acceptor are close enough, usually less than 10 nm at room temperature, and under certain other conditions.

FRET is one of the major experimental methods for discovering whether two interacting particles are in close proximity, or for determining the distance between two specific locations in a complex micro/nano structure. It has become a major experimental technique in the field of single particles, since the efficiency of energy transfer is measured via fluorescence tools. The energy transfer is typically detected relatively easily and it is used to show interactions between two particles. It is a powerful technique since FRET measures dynamics on a spatial scale that is unique (in nanometers range). It is fairly simple and can be studied in most of the laboratories. FRET has been used since early 1950s, however, its use has been exploded in the last decades mainly because of instrumentation improvements and innovations and the great number of commercially available synthetic fluorophores, which can be featured with particular chemical groups for specific purposes.

In the following section we briefly discuss the historical events that led to the understanding and modeling of FRET. First, the concept of electromagnetism and quantum mechanics as well as the concept of energy transfer previous to Förster are discussed. Next, we shortly review the experiments and concept of energy transfer
during the Förster time. Finally, we summarize the concept of energy transfer after Förster.

1.1 Brief Review of Scientific Achievements Before Förster Theory

The notion that electricity and magnetism are related were suspected before 1800 because of the formal similarities between static electricity and magnetism. Hans Christian Oersted in 1820 was the first to demonstrate the interrelationship of electricity and magnetism. He reported that a magnet’s needle held next to a current-carrying wire was deflected and oriented itself perpendicular to the line of current. This discovery, easy to reproduce, was repeated by André-Marie Ampère and others (e.g., Jean-Baptiste Biot and Félix Savart). In 1822, Ampère published a theory of electromagnetic interactions involving currents. He found that current-carrying wires attract or repel each other depending on whether the currents are in the same direction or opposite.

Faraday who discovered that changing magnetic fields produce circulating electrical fields, known as “Faraday induction”, introduced in 1821 an intuitive pictorial representation of lines of forces. Faraday pictured these lines of forces as the mechanism by which electrical and magnetic objects interact with themselves and with each other, where these lines of forces serve as “the carries” of forces through space. The first field theory was introduced by James Clerk Maxwell in 1864. His equations describe electromagnetic fields where the objects (electrical or magnetic) enter only through boundary conditions. Using the ideas and experiments of Faraday, Maxwell created a complete mathematical representation of Faraday’s descriptions of electricity and magnetism. He understood Faraday’s lines of force as a line passing through any point of space representing the direction of the force exerted giving the vector representation of the electromagnetic field. In addition to Faraday’s ideas, Maxwell introduced the notion of displacement current, that is, the circulatory magnetic field caused by a time-varying electric field. Maxwell’s equations describe all classical electrodynamic phenomena and settled the theoretical basis to predict electromagnetic radiation, which is the starting point for describing the classical theory of energy transfer.

Maxwell’s equations predicted the identity of electromagnetism and light and the quantitative properties of light (interference, refrangibility and polarization as well as the speed of light). This was confirmed by the experiment of Heinrich Hertz with his famous Hertzian oscillating dipole. Hertz carried out the experiments in 1888 and in 1889 he published the theory to explain the electromagnetic fields surrounding this electric oscillator. These theory was derived from Maxwell’s equations. Hertz experiments were performed by producing high frequency repetitive sparks in an air gap of a primary oscillating circuit. The electrodynamics disturbance was detected at a distance by a secondary circuit, resonance with the first,
with similar air gaps. Sparks were observed in the secondary receiving circuit when it was resonant with the primary circuit. Hertz calculated a graphic field-line representation of the electromagnetic field of an oscillating dipole in the near field (shorter than a wavelength of the emitted radiation), in an intermediate zone, and in the far field (at distances farther than a wavelength) where the electromagnetic energy escapes as radiation. Hertz graphical and mathematical descriptions of the oscillating electric field emanating from his Hertzian dipole, in particular in the near field, played a critical role in understanding of the energy transfer theory.

The first recorded measurements of energy transfer over distances larger than collision radii were made by Cairo and Franck in 1922 [2–4]. Cairo observed emission from thallium in a mixture of mercury and thallium vapor, when the vapor mixture was excited at wavelength of 253.6 nm, which can only excite the mercury atoms. This fluorescence emission from thallium was named “sensitized fluorescence”. The importance of resonance between energy levels of the sensitizer (the donor) and the sensitize (the acceptor) atoms was explicitly shown by further experiments, especially by the experiments of Beutler and Josephi [5, 6], who studied the sensitized fluorescence of sodium vapor in the presence of mercury vapor. The sensitized fluorescence increased in intensity when the energy differences are smaller between the states of the two participating atoms. Many of these experiments were interpreted in terms of collision theory. The number of collisions per time could be calculated from gas theory and the fraction of collision that was effective could be determined. If the rate of collisions is smaller than the calculated one, then only a certain percentage of the collisions are effective. If the rate of collisions is larger than the calculated, then there are interactions between the two collision partners that extend beyond their encounter radius. This discovery that energy transfer could take place over distances longer than the encounter radii showed that hard physical collisions were not required for atoms to interchange energy.

In 1928, Kallmann and London [7] proposed a quantum mechanical theory to explain the transfer of energy between atoms at longer distances compared to the collisional radii. This theory assumed almost resonance between the energy levels of the interacting atoms. They found that, provided that the corresponding transitions between the energy states of the two atoms were dipole-allowed, the effective cross-section $q$ of the two interacting atoms increases as $\sigma^{-2/3}$, where $\sigma$ is the difference between the excitation energies of the two interacting systems. As $\sigma \to 0$, the cross-section approaches a limiting value much larger than the collisional radii.

The Perrins (the father and the son) were the first to attempt a quantitative description of nonradiative energy transfer in solution between an excited molecule and a neighboring molecule in the ground state. The Perrins reasoned that the depolarization decrease that occurs in a fluorophore solution of at higher concentrations resulted from the transfer of excitation energy between molecules with different orientations before a photon was emitted. The Perrins’ model involved a near-field energy interaction between the oscillating dipoles of two identical molecules, i.e., the oscillating dipoles are in resonance. Initially, J. Perrin (the
father) developed a classical model to explain the depolarization decrease in a solution of a single chemical species of the fluorophore [8, 9]. He hypothesized that the transfer of the excitation energy could hop from one molecule to the other through interaction between oscillating dipoles of closely spaced molecules. J. Perrin modeled the participating molecules classically as Hertzian dipoles under the assumption that, if the molecules were separated by a sufficiently small distance, the energy could be transferred to the acceptor molecule nonradiatively. He named this process “transfert d’activation” (transfer of activation). He calculated that the distance for this process to take place is approximately $\lambda/(2\pi)$, where $\lambda$ is the wavelength of the free electric field oscillating at the frequency of the atomic electric field, $v = c/\lambda$ ($c$ is the speed of light). However, this value was 20-fold greater than the experimental results. Later, F. Perrin (J. Perrin’s son) extended J. Perrin’s theory of energy transfer by developing a quantum mechanical model [10, 11], similar to what had been suggested for the energy transfer between atoms in gases [7]. He estimated that the rate of transfer is proportional to $1/R^3$. This results in energy transfer at much longer distances than those found experimentally. Also later, F. Perrin considered collisions between the chromophores and the solvent molecules as well as Doppler effects. These reduced the distances to about 20–25 nm, which were still too long. Because of this discrepancy, the Perrin’s theory of energy transfer lay dormant for about 20 years.

1.2 Förster Energy Transfer Theory

Förster’s theory and his accompanying experimental work on the energy transfer are the most widely known, and most influential, of all energy transfer publications. His major papers are listed here [12–22]. T. Förster provided an accessible theory in a form that was practical for experimenters, commonly referred to as the Förster Resonance Energy Transfer (FRET) today. Because of this reason, FRET has been widely used in physics, engineering, chemistry, biology, and medicine.

T. Förster became interested in the energy transfer process because of the known effectiveness of photosynthesis. Experiments had shown that the capture and utilization of light energy by the plant’s leaves was much more effective than was expected if it were required that photons exactly hit the reaction centers. He reasoned that an efficient transfer of energy between the chlorophyll molecules must be responsible for the eventual diffusion of the energy, which was absorbed over the whole surface of the leaf, into the relatively sparse reaction centers. Förster assumed that this diffusion is because of the energy being rapidly hopping (resonating) between molecules.

In his first paper on FRET [12], he correctly developed the basic theoretical background of FRET. First, he reviewed the mechanisms proposed by the Perrins. Then, he proceeded to take three critical, important steps that allowed him to derive a quantitative theory of nonradiative energy transfer [14]: (1) Förster took into
account the broad spectral dispersion of the donor fluorescence and the acceptor absorption, i.e., the overlapping oscillation frequencies of the donor in the excited state and the acceptor molecules in the ground state. In his first paper [12], Förster treated this frequency overlap semi-classically and semi-quantitatively. However, shortly after [13, 14], he gave a full quantum mechanical treatment. (2) Förster was able to develop a quantitative theory of the rate of energy transfer from an excited donor molecule to a ground state acceptor molecule in terms of the overlap integral. The overlap integral represents the probability that the two molecular transition dipoles will have the same frequency. This was a major conceptual step because these spectroscopic transitions can be measured experimentally, independent of the FRET measurement, opening a way to quantitative interpretation of the experimental data. Förster also introduced helpful expressions for the orientation factor, $\kappa^2$, and included the effect of the index of refraction, which affects all electric interactions in condensed media at high optical frequencies. (3) Förster’s model included quantitatively the $1/R^6$ distance dependence of the dipole-dipole interaction. He calculated the distance $R_0$ (known as the Förster radius) where the rate of the energy transfer was equal to the rate of fluorescence emission in terms of the overlap integral, the quantum yield of the acceptor, the lifetime of the donor in the absence of an acceptor and the effective index of refraction.

Förster’s original theoretical description of energy transfer set the stage for all subsequent applications of FRET in many fields of research, and his theory is still used to interpret experimental results. His insight and great contribution were to provide the quantitatively correct and very practical description of the FRET process in terms of experimentally accessible parameters. By relating the rate of energy transfer to purely experimentally available parameters, he provided the general theoretical framework for all FRET applications.

It is worth mentioning that, before T. Förster, J.R. Oppenheimer reported the theory of FRET in 1941 at the American Physical Society meeting in a paper entitled “Internal Conversion in Photosynthesis” [23]. However, the full contribution of J.R. Oppenheimer and W. Arnold was published in 1950 [24]. In the 1941 abstract, Oppenheimer discussed that the high efficiency of the energy transfer from certain dyes to chlorophyll cannot happen due to light emission and re-absorption because the probability of this process is too small. However, the energy transfer can be enhanced if the chlorophyll molecules are much closer than the wavelength of chlorophyll fluorescence, that is, in the near field of a Hertzian dipole. In the 1950 publication, Arnold and Oppenheimer proposed a mechanism of the energy transfer from phycocyanin to chlorophyll in the blue-green algae. Here, they considered three ways for the energy transfer: (1) by direct collision, (2) by emission and re-absorption, and (3) by “internal conversion”. They found that the probability for energy transfer by the first two mechanisms was too small. Therefore, they focused on the energy transfer in the near field zone of Hertzian dipole radiation, that is, “internal conversion”. They calculated that the total energy transfer from phycocyanin to a randomly localized chlorophyll is proportional to $1/d^3$, which was the result of integrating $1/r^6$ from $d$ to infinity.
1.3 Developments After Förster

Following the pioneering studies of the Perrins and Förster, there have been many reports and reviews on FRET, both theoretical and experimental. A long literature list is available in several recent reviews [25–33]. There have been several extensions of the theory of energy transfer to other experimental conditions, by T. Förster, D. Dexter, and others. Dexter [34] made a very important contribution by generalizing and extending Förster’s energy transfer model to include the donors and acceptors with overlapping electron orbitals. This resulting energy transfer over a very small distance is called “Dexter transfer” or transfer by “electron exchange”. The distance dependence of the Dexter transfer is very different from the Förster transfer, and the rate of the Dexter process is only efficient for very short donor-acceptor separation (<1 nm).

In Ref. [28], Medintz and Mattoussi provided an overview on FRET using semiconductor quantum dots (QDs) and the application of QD-based FRET in biology. They started by discussing some of the relevant conceptual elements of FRET, the unique QD optical properties, and the advantages and limitations of using QDs as exciton donors and/or acceptors. Then, they described representative examples where QD-based FRET has been used for biological applications, including the detection of hybridation using QD-nucleic acid conjugates, pH and ion sensing, and antibody-based sensing. Overall, they provided a good understanding of the most important parameters that govern FRET for the D-A pairs of QD-QD, QD-dye, dye-QD, QD-Au-NP, and bioluminescent substrate-QD. Another review by U.O.S. Seker and H.V. Demir presented a summary on FRET based systems and applications using material binding peptides [29]. This focused on the selection process, molecular binding characterization and utilization of peptides as molecular linkers, molecular assemblies and material synthesizers for FRET applications.

Rogach et al. [30] reviewed energy transfer using semiconductor nanocrystals (NCs). This review semiconductors NC containing thin films, solution-based complexes, and bioconjugates. Here, the energy transfer involving metal nanoantennae and metal nanoparticles were discussed. In this review, it was concluded that energy transfer involving semiconductor NCs coupled to metal nanoparticles or dyes can be used for bio-imaging and sensing. And, the use of directional energy transfer in semiconductor NCs can provide a new approach for hybrid photovoltaics. Agranovich et al. [31] presented a review on FRET in hybrid organic-inorganic nanostructures. They reported several theoretical aspects of energy transfer and discussed how hybrid organic-inorganic nanostructures can be used for optoelectronic applications. A perspective on the recent understanding of the excitonic dynamics in the organic-inorganic composites of semiconductor NCs is given by Guzelturk and Demir [35]. In another review, Guzelturk et al. [32] discussed the use of colloidal quantum dots and quantum wires in FRET for the light generation and harvesting applications.
This chapter has covered mostly the work relevant to the understanding of energy transfer prior to Förster, leading up to the final, practical expression for FRET. In the following chapters we will discuss the process of energy transfer in detail.

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Chapter 2
Energy Transfer Review

In this chapter, we discuss the basic concepts of excitation energy transfer, making the distinction between radiative and nonradiative, and giving a brief overview on the classical and quantum mechanical description of energy transfer [1].

2.1 Introduction

Excitation energy transfer of an excited state energy of the donor (D) to the ground state of the acceptor (A) is possible provided that the emission spectrum of the donor partially overlaps the absorption spectrum of the acceptor. This is a very important process, which occurs in a variety of situations. Excitation energy transfer can be grouped into heterotransfer versus homotransfer and radiative versus nonradiative transfer.

Energy transfer from an excited donor (D*) to another that is chemically different, ground acceptor A, is called heterotransfer.

\[(D^*,A) \rightarrow (D,A^*)\] (2.1)

If the donor and the acceptor are identical, then the energy transfer is homotransfer.

\[(D^*,D) \rightarrow (D,D^*)\] (2.2)

In homotransfer, excitation transport or energy migration can occur. In such case, the process of energy transfer repeats itself such that the excitation migrates over several molecules.
In radiative transfer, a photon emitted by the donor is absorbed by the acceptor, whereas nonradiative transfer occurs without emission of “real” photons; it is mediated by the so-called “virtual” photons. In the following we briefly discuss the classical and quantum mechanical description for the energy transfer.

2.2 Classical Description of Energy Transfer

In classical terms, the electronic energy transfer between the donor and the acceptor is viewed as the interaction of two oscillating electric dipoles. The donor’s dipole is initially in oscillation, and the acceptor’s dipole is initially at rest. Because of the resonance condition, the excitation is transferred from the first dipole to the second one.

The electric field of a dipole oscillating in vacuum is given by

$$ E(r, t) = \frac{p(t)}{4\pi \varepsilon_0} \left\{ 3(\mathbf{n} \cdot \mathbf{d})\mathbf{n} - \mathbf{d} \left[ \frac{1}{r^3} - \frac{ik}{r^2} \right] + \left[ (\mathbf{n} \cdot \mathbf{d})\mathbf{n} - \mathbf{d} \right] \frac{k^2}{r} \right\} $$

(2.3)

where $p(t) = p_0 \cos(\omega t)$ is the time-dependent electric dipole moment, with amplitude $p_0$, $t' = t - r/c$, $\mathbf{n}$ and $\mathbf{d}$ are the unit vectors in the donor to acceptor direction and the donor’s dipole moment, respectively, $k = \omega/c$ and $r$ is the distance from the dipole [2]. The distance dependence of the electric field defines two different zones: (1) for $r \ll \lambda$ (near zone) the $r^{-3}$ term dominates, and the angular dependence is identical to that of a static dipole, with transversal and longitudinal components; and (2) for $r \ll \lambda$ (radiative or far zone, also known as wave zone), the $r^{-1}$ term dominates, the electric field is always perpendicular to $\mathbf{n}$ (transversal field), and the radiation corresponds to a spherical wave.

The power radiated by the dipole is [2]

$$ P^0 = \frac{p_0^2 \omega^4}{12\pi \varepsilon_0 c^3} $$

(2.4)

For simplicity, the acceptor can be considered as a passive absorber characterized by an absorption cross-section. Therefore, the power it absorbs, when placed at a distance $r$ from the dipole is

$$ P' = \frac{1}{2} c \varepsilon_0 E_0^2 \sigma $$

(2.5)

where $\sigma$ is the acceptor’s cross-section and $E_0^2$ is the amplitude of the dipole’s electric field given by (2.3). After orientation averaging, $E_0^2$ takes the form of
\[ E_0^2 = 2 \left( \frac{p_0}{4 \pi \varepsilon_0} \right)^2 \left( \frac{k^4}{3 r^2} + \frac{k^2}{3 r^4} + \frac{1}{r^6} \right) \] (2.6)

Substitution of (2.6) into (2.5) gives

\[ P' = \frac{\sigma}{4 \pi r^2} \left[ 1 + \left( \frac{k}{r} \right)^2 + 3 \left( \frac{k}{r} \right)^4 \right] P^0 \] (2.7)

where \( k = \lambda/(2\pi) \) For large distances \( r \gg \lambda \), (2.7) reduces to

\[ P' = \frac{\sigma}{4 \pi r^2} P^0 \] (2.8)

This equation has a simple geometric interpretation and corresponds to the radiative transfer. Equation (2.8) implies that the power emitted by the donor in the presence of an acceptor is

\[ P = \left\{ 1 + \frac{\sigma}{4 \pi r^2} \left[ \left( \frac{k}{r} \right)^2 + 3 \left( \frac{k}{r} \right)^4 \right] \right\} P^0 \] (2.9)

When the acceptor is located in the near zone \( r \gg \lambda \), \( P \) exceeds \( P^0 \). The reason for this lies in Eq. (2.3), which allows us to see that energy is stored in the near field. Energy periodically flows out of the source and returns without being lost. This energy does not appear in the net radiative balance, which only accounts for the small amount of energy leaked as radiation. When an acceptor is located in the near zone, the donor decay rate increases because the acceptor feeds on energy temporally deposited in the field by the donor.

On the other hand, from Eq. (2.7), the absorbed power of the acceptor, when it is in the near zone, is

\[ P' = \frac{3 \sigma}{64 \pi^5} \left( \frac{\lambda^3}{r^6} \right) P^0 \] (2.10)

This equation can be written in terms of the transfer rates \( k_T \) and the radiative rate \( k_r \), by dividing both sides by \( h\nu \), and relating \( \sigma \) to the molar absorption coefficient \( \varepsilon_A \), which gives

\[ k_T = k_r \left( \frac{3 \ln 10 \varepsilon_A \lambda^3}{64 \pi^5 N_A n^4} \right) \left( \frac{1}{r^6} \right) \] (2.11)

where \( N_A \) is the Avogadro’s number and \( n \) is the medium refractive index, which is assumed to be non-absorbing. \( k_r = Q_D/\tau_0 \), here \( \tau_0 \) is the donor’s lifetime in the absence of acceptors and \( Q_D \) is the donor’s quantum yield. Moreover, if we assume a spectral distribution for the emission wavelength, then Eq. (2.11) becomes
where $R_0$ is the Förster radius, named after Theodor Förster, who first derived Eq. (2.12) from quantum mechanical [3] and classical [4] treatments of the dipole-dipole interaction of the donor and acceptor.

2.3 Quantum Mechanical Description of Energy Transfer

The quantum mechanical treatment of the energy transfer considers that only two electrons are involved in the D-A transition, one from the donor and one from the acceptor. In such case, the properly anti-symmetrized wave-functions for the initial excited state $\Psi_i$ (D excited, A unexcited) and the final excited state $\Psi_f$ (D unexcited, A excited) can be written as

$$\Psi_i = \frac{1}{\sqrt{2}} [\Psi_{D'}(1)\Psi_A(2) - \Psi_{D'}(2)\Psi_A(1)]$$

$$\Psi_f = \frac{1}{\sqrt{2}} [\Psi_{D}(1)\Psi_{A'}(2) - \Psi_{D}(2)\Psi_{A'}(1)]$$

(2.13)

where the number 1 and 2 refer to the two electrons involved.

The interaction matrix element describing the coupling between the initial and final state is given by

$$U = \langle \Psi_i | \hat{V} | \Psi_f \rangle$$

(2.14)

where $\hat{V}$ is the perturbation part of the total Hamiltonian $\hat{H} = \hat{H}_D + \hat{H}_A + \hat{V}$. $U$ can be written as a sum of two terms

$$U = \langle \Psi_{D'}(1)\Psi_A(2) | \hat{V} | \Psi_D(1)\Psi_{A'}(2) \rangle - \langle \Psi_{D'}(1)\Psi_A(2) | \hat{V} | \Psi_D(2)\Psi_{A'}(1) \rangle$$

(2.15)

The first term in Eq. (2.15) is called the Coulombic term, $U_C$, where the initially excited electron on D returns the ground state while an electron on A is simultaneously promoted to the excited state. The second term in (2.15) is called the exchange term, $U_{ex}$, here there is an exchange of electrons on D and A. The exchange interaction is a quantum mechanical effect arising from the symmetry properties of the wave-functions with respect to the exchange of spin and space coordinates of two electrons.

The Coulombic term can be expanded into a sum of multipole-multipole terms, however, it is generally approximated by the first predominant term representing the dipole-dipole interaction between the transition dipoles moments $\mathbf{M}_D$ and $\mathbf{M}_A$ of the donor and acceptor.
transitions $D \rightarrow D^*$ and $A \rightarrow A^*$. It is worth mentioning that the squares of the transition dipole moments are proportional to the oscillator strengths of these transitions. Thus, the Coulombic term can be written as

$$U_{d-d} = \frac{M_D \cdot M_A}{r^3} - \frac{(M_A \cdot r)(M_D \cdot r)}{r^5}$$  \hspace{1cm} (2.16)$$

where $r$ is the donor-acceptor separation distance. This expression can be simplified into

$$U_{d-d} = 5.04 \frac{|M_D| |M_A|}{r^3} (\cos \theta_{DA} - 3 \cos \theta_D \cos \theta_A)$$  \hspace{1cm} (2.17)$$

$U_{d-d}$ is expressed in cm$^{-1}$, the transition moments in Debye units, and $r$ in nanometers. $\theta_{DA}$ is the angle between the two transition moments and $\theta_D$ and $\theta_A$ are the angles between each transition moment and the vector connecting them. Note that 1 Debye unit is equal to $3.33 \times 10^{-30}$ C m.

The dipole approximation is valid only for point-like dipoles, i.e., when the D-A separation is much larger than the donor and acceptor dimensions. At the short distances or when the dipole moments are large, higher multipole terms should be included in the calculations.

The exchange term represents the electrostatic interaction between the charge clouds. The transfer occurs via the overlap of the electron clouds and requires physical contact between the donor and the acceptor. The interaction is short range because the electron density decays exponentially outside the boundaries. For two electrons separated by the distance $r_{12}$ in the D-A pair, the space part of the exchange interaction can be written as

$$U_{ex} = \left\langle \Phi_{D'}(1) \Phi_A(2) \left| \frac{e^2}{r_{12}} \Phi_D(2) \Phi_{A'}(1) \right. \right\rangle$$  \hspace{1cm} (2.18)$$

where $\Phi_D$ and $\Phi_A$ are the contributions of the spatial wave-functions to the total wave-function $\Psi_D$ and $\Psi_A$ that include the spin functions. The spin selection rules (Wigner’s rule) for allowed energy transfer are obtained by integration over the spin coordinates.

The transfer rate $k_T$ is given by the Fermi’s Golden rule

$$k_T = \frac{2 \pi}{\hbar} |U|^2 \rho$$  \hspace{1cm} (2.19)$$

where $\rho$ is a measure of the density of the interacting initial and final states, as determined by Franck-Gordon factors, and is related to the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor.