The strong influence of intrinsic local fields on intermolecular energy transfer: Dipoles and surface potentials

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Abstract

A general theory is developed to identify the influence of local electric fields on intermolecular electronic excitation transfer processes. The analysis, based on fundamental electrodynamics, assists the interpretation and quantification of static field effects including those originating from polar chromophores, strongly polar environments and surface field gradients. The results have significant applications to fluorescence resonance energy transfer (FRET) measurements in cell biology.

1. Introduction

In the broad field of resonance energy transfer, RET, and its fluorescence measurement, FRET, the theory for the fundamental process of energy migration between individual molecules or chromophore components is well established [1-3]. Commonly, the distance between the energy donor and energy acceptor is sufficiently small for near-field electrodynamics to operate. As such, the efficiency of transfer between any particular pair of chromophores is conveniently characterised by a Förster distance, quantitatively signifying the typically nanoscale range over which resonance energy transfer to the acceptor dominates over spontaneous emission by the donor. However, the exact calculation of such a parameter is computationally demanding [4], and Förster distances are most often considered essentially pragmatic measures of transfer efficiency. Moreover, wide-ranging experimental and theoretical studies show that these efficiencies can be highly sensitive to the electronic and chemical environment of the participating chromophores, and also to the influence of any external fields. The effects of an applied static electric field were indeed first identified more than twenty years ago [5].

FRET measurements now constitute an important tool for the investigation of complex biological media, especially for measurements of inter-site displacements and dynamical motions – as for example in the mechanisms of protein folding [6], viral genome ejection, and trans-membrane ion transport [7]. Numerous sensor applications have also emerged [8]. Given this increasingly sophisticated sphere of application, it is timely to closely consider the significant involvement of strong local fields that exist within or at the surfaces of key structures. It is known, for example, that such local fields can significantly modify the absorption and fluorescence characteristics of key chromophores [9]. They may also substantially modify multipole moments [10]. Often, these local fields are associated with electrical potential gradients, or surface potentials, but they may also originate from locally ordered dipoles. Moreover, the molecules responsible for such dipoles may be either the donor or acceptor species, or other species in the surrounding medium. It is the purpose of this paper to develop a theory to comprehensively account for all such systems.

2. Foundation theory: two chromophores

The unified theory of energy transfer is the most widely familiar application of quantum electrodynamics in chemistry, biophysics and materials science, whose molecular formulation has also been extensively applied to inter-particle interactions that range from dispersion forces to optical binding. It is therefore expedient to base this new investigation on the emergent precepts, without laborious recourse to the underlying quantum formulation of Maxwell's equations and time-dependent perturbation theory. Those principles are mentioned here, with supporting references [11-16], only as a reminder of the solid foundations upon which the new constructs are to be based.

To approach a variety of more intricate systems, we first begin with a straightforward analysis of theory for a two-particle system comprising the energy donor and acceptor particles alone. In the near-zone approximation that generally applies across the range of measurably significant RET, the standard Förster rate equation emerges from a quantum amplitude that can be represented by an effective time-ordered diagram shown in Fig. 1(*a*). Since the donor-acceptor coupling is not discernibly different from an instantaneous interaction over the distances involved, (the *near-zone*, where the distance $R << \hbar$ and E is the transfer energy), the diagram simply comprises a region representing an initial state $|I\rangle$ of the system below the dotted line, and above it another region for the final state $|F\rangle$. In the former, initial state donor D is in an excited electronic state *e* and the acceptor A is in its ground state labelled *g*; the converse applies for the final state. In the figure, the dotted line represents an effective coupling interaction operator $\mathbf{W}_{\mathrm{DA}}$ which delivers the state sequence $|e\rangle_{\mathrm{D}}|g\rangle_{\mathrm{A}} \rightarrow |g\rangle_{\mathrm{D}}|e\rangle_{\mathrm{A}}$, given by:

$$\mathbf{W}_{\mathrm{DA}} = \frac{\mu_i^D \mu_j^A}{4\pi\varepsilon_0 R^3}\left(\delta_{ij} - 3\hat{R}_i\hat{R}_j\right) \equiv \frac{1}{4\pi\varepsilon_0 R^5}\left[\left(\boldsymbol{\mu}^{\mathrm{D}}.\boldsymbol{\mu}^{\mathrm{A}}\right)R^2 - 3\left(\boldsymbol{\mu}^{\mathrm{D}}.\mathbf{R}\right)\left(\boldsymbol{\mu}^{\mathrm{A}}.\mathbf{R}\right)\right] \quad . \tag{1}$$

Here, each $\boldsymbol{\mu}^{\xi}$ is a dipole moment operator on the quantum electronic states of either molecule ξ, and **R** is the intermolecular separation vector $\overrightarrow{DA}$ of magnitude *R*; in the more succinct first expression on the right, there is implied summation over repeated Cartesian indices *i* and *j*. The matrix element form of quantum amplitude, M_{FI}, is thus secured using (1) as an operator for a first-order perturbation, giving

$$M_{FI} = \langle F|\mathbf{W}_{\mathrm{DA}}|I\rangle = \frac{\mu_i^{\mathrm{D}\downarrow}\mu_j^{\mathrm{A}\uparrow}}{4\pi\varepsilon_0 R^3}\left(\delta_{ij} - 3\hat{R}_i\hat{R}_j\right) \equiv \mu_i^{\mathrm{D}\downarrow}\mu_j^{\mathrm{A}\uparrow}V_{ij}\left(0,\mathbf{R}\right) \,, \tag{2}$$

where $\boldsymbol{\mu}^{\mathrm{D}\downarrow}$ denotes the transition electric dipole moment for the $g \leftarrow e$ excited state decay of the donor, and $\boldsymbol{\mu}^{\mathrm{A}\uparrow}$ is the corresponding transition dipole for the $e \leftarrow g$ excitation of the donor. In the second expression on the right, further compaction of the result is achieved by writing it in terms of the short-range limit of the standard tensor for retarded dipole-dipole coupling [17-19]. The expression (2) may then be cast into the Fermi Rule to give the Förster rate by standard methods [20].

The above result clearly entails no involvement of permanent dipoles. To entertain their possible influence we now move up to second order perturbation theory, introducing an additional coupling of the same operator form (1). The corresponding matrix element is now given by the following expression;

$$M'_{FI} = \frac{\langle F|\mathbf{W}_{\mathrm{DA}}|II\rangle\langle II|\mathbf{W}_{\mathrm{DA}}|I\rangle}{E-E_{II}} , \tag{3}$$

summing over all possible states $|II\rangle$ that can fulfil the role of a virtual intermediate between the initial and final system states. In equation (3), E denotes the transfer energy and E_{II} is the summed energy of the two participant chromophores in state $|II\rangle$. This simple modification provides for any such effect to be brought into play is to develop the time-ordering into the form exhibited in Fig. 1, (*b*) and (*c*), introducing a second coupling that specifically entails static dipoles.

For each of the chromophores, the energy transfer process involves directly only the ground and one specific upper electronic state, and there is a better than usual case for the adopting the expedient of a two-level approximation. As such, the state of each entity within the intermediate time interval – the region bounded by the upper and lower dotted lines in Fig.s 1(*b*) and (*c*) – in principle allows four possibilities: each chromophore may be either in the ground or electronic excited state, *g* or *e*. However, it is important to note that an intermediate region where chromophores are either both in their initial states or both in their final states can play no part in the calculation, since these would introduce system intermediate states identical to one of other of system states, $|I\rangle$ and $|F\rangle$; these are explicitly precluded in the perturbation theory. Accordingly, the figure shows only the two allowed state combinations. Although it might then appear that further simplification could be effected by implementing an algorithm that specifically applies to the electrodynamics of two-state systems [21, 22], careful analysis reveals that, because two (or more) separate optical centers are involved, such an approach does not provide a short-cut to the correct result. Therefore we proceed to resolve equation (3) on the basis of interpreting Fig.s 1(*b*) and (*c*), thus securing the following result for the two state sequences $|e\rangle_{\mathrm{D}}|g\rangle_{\mathrm{A}} \rightarrow |g\rangle_{\mathrm{D}}|g\rangle_{\mathrm{A}} \rightarrow |g\rangle_{\mathrm{D}}|e\rangle_{\mathrm{A}}$; $|e\rangle_{\mathrm{D}}|g\rangle_{\mathrm{A}} \rightarrow |e\rangle_{\mathrm{D}}|e\rangle_{\mathrm{A}} \rightarrow |g\rangle_{\mathrm{D}}|e\rangle_{\mathrm{A}}$:

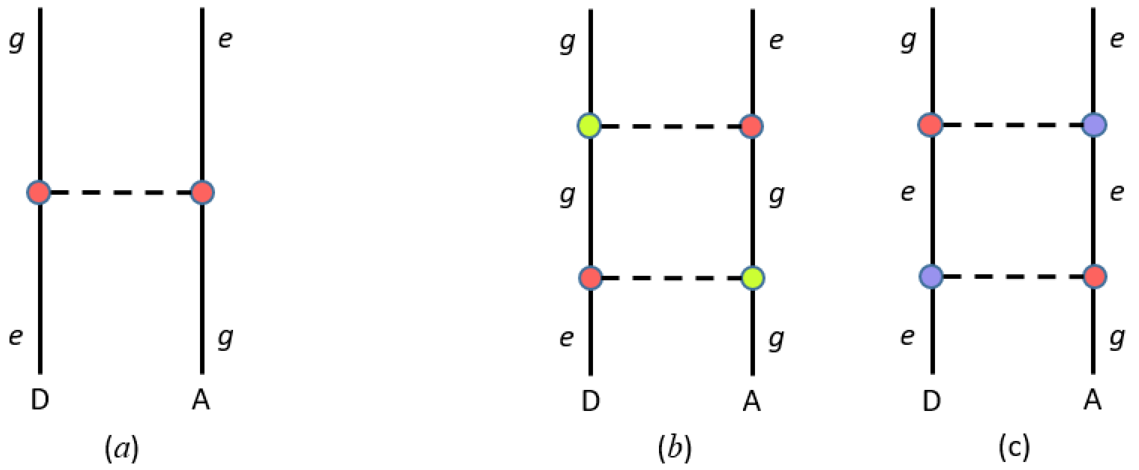


Figure 1. (*a*) First-order, and (*b*), (*c*) second-order perturbation representations of energy transfer with near-zone coupling, time progressing upwards. The red dot signifies an interaction involving a transition dipole interaction ($\boldsymbol{\mu}^{\downarrow}$ or $\boldsymbol{\mu}^{\uparrow}$); the green dot signifies a ground state dipole and the purple dot an excited state dipole.

$$M'_{FI} = \frac{1}{16\pi^2\varepsilon_0^2 R^{10} E}\Big[\Big\{\big(\boldsymbol{\mu}^{\mathrm{D}g}.\boldsymbol{\mu}^{\mathrm{A}\uparrow}\big)R^2 - 3\big(\boldsymbol{\mu}^{\mathrm{D}g}.\mathbf{R}\big)\big(\mathbf{d}^{\mathrm{A}\uparrow}.\mathbf{R}\big)\Big\}\Big\{\big(\mathbf{d}^{\mathrm{D}\downarrow}.\boldsymbol{\mu}^{\mathrm{A}g}\big)R^2 - 3\big(\mathbf{d}^{\mathrm{D}\downarrow}.\mathbf{R}\big)\big(\boldsymbol{\mu}^{\mathrm{A}g}.\mathbf{R}\big)\Big\}$$
$$-\Big\{\big(\boldsymbol{\mu}^{\mathrm{D}\downarrow}.\boldsymbol{\mu}^{\mathrm{A}e}\big)R^2 - 3\big(\boldsymbol{\mu}^{\mathrm{D}\downarrow}.\mathbf{R}\big)\big(\mathbf{d}^{\mathrm{A}e}.\mathbf{R}\big)\Big\}\Big\{\big(\mathbf{d}^{\mathrm{D}e}.\boldsymbol{\mu}^{\mathrm{A}\uparrow}\big)R^2 - 3\big(\mathbf{d}^{\mathrm{D}e}.\mathbf{R}\big)\big(\boldsymbol{\mu}^{\mathrm{A}\uparrow}.\mathbf{R}\big)\Big\}\Big] \tag{4}$$

Much more succinctly, using the earlier forms of expression including implied index summation, the same result can be cast as

$$M'_{FI} = \boldsymbol{\mu}^{\mathrm{D}\downarrow}\boldsymbol{\mu}^{\mathrm{A}\uparrow}V\,(0,\mathbf{R})V\,(0,\mathbf{R})\big(\boldsymbol{\mu}^{\mathrm{D}g}\boldsymbol{\mu}^{\mathrm{A}g} - \boldsymbol{\mu}^{\mathrm{D}u}\boldsymbol{\mu}^{\mathrm{A}u}\big)E^{-1}$$

In both forms of expression it is interesting to deduce that the possession of a static dipole moment by the donor or the acceptor is not sufficient to contribute a non-zero second-order correction; both molecules need to have a static dipole that differs between the ground and electronically excited states. Such effects are common, and they may arise from structural differences associated with displacements in the associated potential energy surfaces, or major shifts of charge distribution on excitation. The former effect is often manifest in substantial Stokes shifts in the fluorescence spectrum; the latter is commonly exhibited in large solvatochromic effects in polar solvents.

, the dependence on static moments can emerge only in terms of the vector difference $\Delta\boldsymbol{\mu}$ between the ground and excited state values, $\boldsymbol{\mu}^g$ and $\boldsymbol{\mu}^u$ respectively, i.e. the vector shift in static dipole that accompanies the transition.

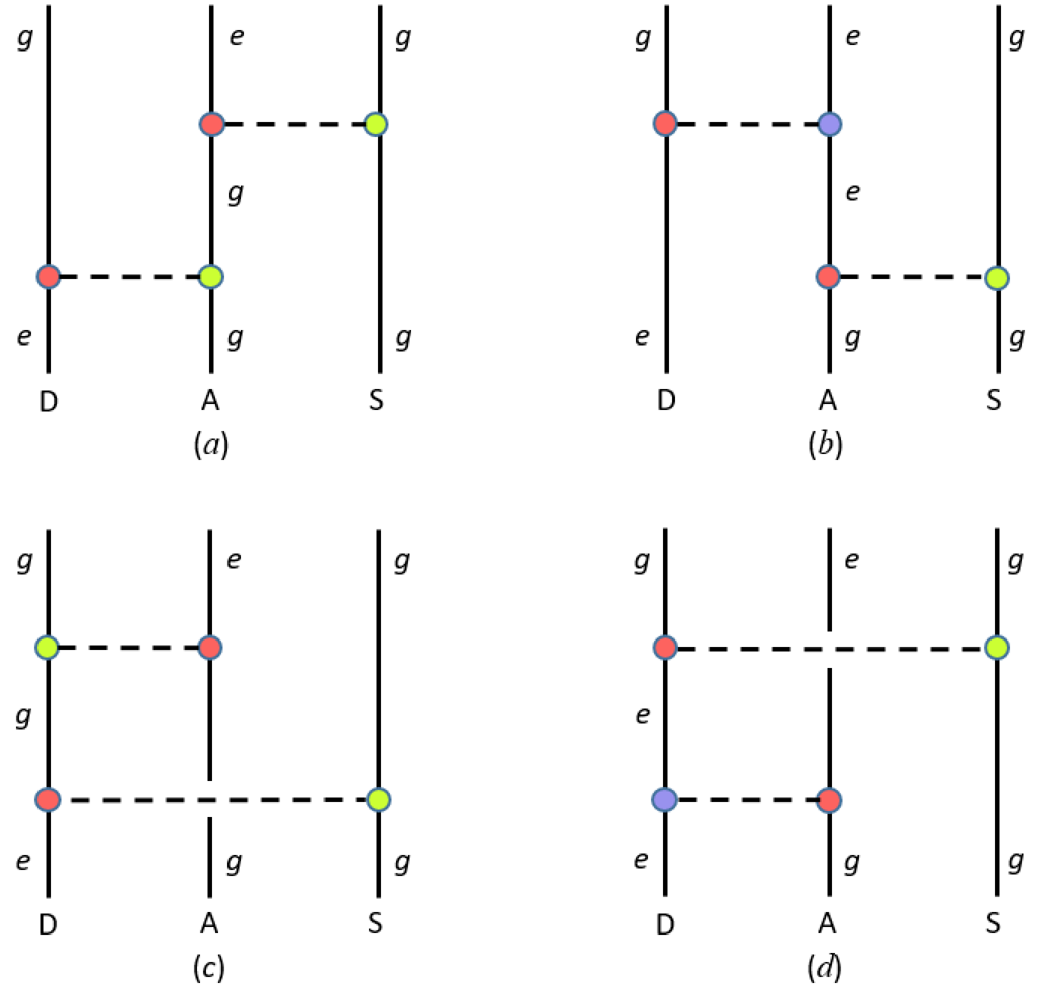
If the two-level approximation is dropped, the result for M'_{FI} naturally acquires a more intricate representation, which is most neatly expressible in summed-index tensorial form as;

$$M'_{FI} = -\frac{1}{16\pi^2\varepsilon_0^2 R^6}\sum_{r(\mathrm{D})}\sum_{s(\mathrm{A})}\mu_i^{0r(\mathrm{D})}\mu_k^{ru(\mathrm{D})}\mu_j^{us(\mathrm{A})}\mu_l^{s0(\mathrm{A})}\left(\delta_{ij}-3\hat{R}_i\hat{R}_j\right)\left(\delta_{kl}-3\hat{R}_k\hat{R}_l\right)\Big/\left(E-E_{r(\mathrm{D})}-E_{s(\mathrm{A})}\right) \tag{5}$$

where r and s are virtual intermediate states summed over all eigenstates of the molecular Hamiltonians for D and A, respectively; $\boldsymbol{\mu}^{ab}$ is a generic transition electric dipole moment for the transition $a \leftarrow b$, E_a is the energy of state a, and the double sum once again excludes the case where the sum of the two intermediate state energies given by $E_r(\mathrm{D}) + E_s(\mathrm{A})$ equals E. Here, terms that associate either r or s with the respective ground states engender contributions that more directly relate to the normal ground state dipoles of the donor and acceptor.

3. Foundation theory: surface dipole array

Based on the simple exploration of the last Section, we can now move on to consider the broader implications of local static dipoles. In general, of course, these need not be associated with either the donor or acceptor; other molecules in their vicinity may play a larger role in producing significant local fields. These neighbours may, for example, be chemically the same as the individual donor, for



(*a*) (*b*)

(*c*) (*d*)

Experimental determinations of excited states dipoles are commonly estimates based on a theoretical connection to solvatochromic shifts, exhibited in the absorption and fluorescence bands of the substance of interest when dissolved in polar solvents [23]. Although vector difference features in the excited and ground states feature in work by Suppan [24], it is relatively rare that the theory is used to support vector determinations – and clearly if the ground and excited state dipoles differ in orientation then the magnitude of $\Delta\boldsymbol{\mu}$ is not simply the difference in values $\mu^e - \mu^g$. A good example of securing information on the relative orientations as well as values is a recent analysis of Suman et al. [25].

4. Conclusion

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