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Excitation energy transfer in condensed media

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We derive an expression for resonance energy transfer between a pair of chromophores embedded in a condensed medium by considering the energy splitting of the chromophores from their resonant excited states. We employ time-dependent density functional response theory in our derivation. The linear response theory treatment is rigorous within the framework of time-dependent density functional theory, while in obtaining the energy transfer coupling, the standard first-order approximation is used. The density response function for the medium, which can be replaced by the macroscopic dielectric susceptibility, enables the inclusion of the medium influence on the energy transfer coupling between the donor and acceptor. We consider the Coulomb coupling, and determine that our result is isomorphic to the Coulomb interaction between two charge densities inside a dielectric medium. The isomorphism we found not only provides a general and useful expression for applications, but additionally offers a basis for the extension of the dielectric response model to energy transfer coupling, which has been implicitly used earlier. An illustrative model shows that for two separated molecules, the medium adds a dielectric screening effect to the Coulomb coupling of their transitions. However, if the two molecules are so closely spaced that they effectively reside in a single cavity, the medium can enhance or reduce the strength of the coupling depending on the orientation and the alignment of the two chromophores. © 2001 American Institute of Physics. [DOI: 10.1063/1.1338531]

I. INTRODUCTION

Electronic excitation energy transfer (EET) is a process in which the excitation energy of one chromophore is passed to another through an interaction between the two. EET is of fundamental importance in keeping and utilizing the energy of absorbed photons. The best illustrative example of this process is the photosynthetic light harvesting event, in which 200–300 molecules serve as solar collectors whose function is to transfer excitation energy to the reaction center where charge separation occurs. Most, but not all,^{1–3} of the theoretical studies of such systems model the pigments in vacuum, without considering any influence of the surrounding medium. This is not because the effects of the medium on EET are known to be minor, but rather due to the lack of comprehensive and yet solvable expressions for such applications. The present work develops such an expression in the framework of time-dependent density response theory, which will help us to understand the role of the surrounding solvent or medium (e.g., the protein matrix in the case of photosynthetic light harvesting) in the EET process.

Energy transfer coupling is traditionally described by two different mechanisms: Förster dipole–dipole coupling and the Dexter exchange coupling.^{4,5} The former has an R^{-6} distance dependence and the latter has an exponential dependence. The limit of Förster theory and its generalization have often been discussed (in Refs. 3 and 6–10, for example). The dipole–dipole coupling scheme is not a good approximation for chromophores that are closely spaced in a protein matrix or other media, or when one (or both) of the transitions involved is dipole forbidden. The overall Coulomb interaction between the two transition densities must be calculated explicitly in these cases, and this seems to provide a satisfactory description of the systems studied.^{7–9} However, it is often assumed in such calculations that the donor and acceptor chromophores are in vacuum, and thus the role of the surrounding medium (protein matrix) in EET is not clear.

EET has been treated with a classical formulation in situations in which planar dielectric interfaces are nearby.^{11–13} Chance *et al.*^{11,12} treated the transition dipole as a harmonic oscillating dipole with damping (to properly account for the lifetime). In this case, the dielectric medium interacts with the oscillating transition dipoles, and the ef-

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fects of the medium are described using classical dielectric theory.

Quantum electrodynamics (QED) theory offers another means by which to describe EET with the inclusion of the medium influence. The Hamiltonian for the interaction between the transition dipoles and the quantized displacement field can be properly written within QED, and dipole–dipole resonant energy transfer can be derived from first principles.^{14–19} Juzeliūnas and Andrews^{14,15} used this approach to consider transition dipoles embedded in a dielectric medium. The result in the near-zone limit (where molecules are separated by a much smaller distance than the wavelength of the photon) is essentially Förster's dipole–dipole coupling scaled by a prefactor. This prefactor consists of a screening contribution (ϵ_r^{-1}), multiplied by the square of the local field factor $\{[(\epsilon_r + 2)/3]^2\}$, where ϵ_r is the optical dielectric constant of the medium. The prefactor is defined in this way regardless of the orientation and alignment of the two transition dipoles. Agranovich and Galanin obtained the same prefactor in 1982 from basically the same considerations in a classical theory.¹³ Effects due to higher transition multipoles have also been treated within the QED framework.¹⁶ These works assumed that the chromophores were small and could therefore be treated as point sources of multipoles embedded in a dielectric medium. QED was also recently applied to dipole–dipole energy transfer coupling and van der Waals interaction near one or two planar dielectric interfaces.^{17–19} The authors found that, depending on the orientation and molecular alignment, the interaction could either be enhanced or suppressed from that of interaction in free space. However, the complexity of the boundary-value problem in this approach has made further investigation of more general cases (different geometries) rather challenging.

The classical theory and QED near-zone limit approaches are similar in that the effect of the surrounding medium on the energy transfer coupling is equivalent to the interaction energy between the two oscillating dipoles mediated by a dielectric description of the surrounding matrix. Since the classical theory approach starts by describing the transition dipoles (densities) as oscillating dipoles (densities), it is reasonable to wonder if the same method would hold for a quantum mechanical description of the transitions. Limited by technical complexity, the QED approach does not provide such a solution generally.

We have developed a general theory for resonant energy transfer coupling without explicitly treating the transition dipole moments as oscillating dipoles. We obtain the EET coupling for a pair of chromophores with resonant excited states by finding the energy splitting when the interaction is turned on, using time-dependent density functional theory (TDDFT).^{20–23} TDDFT is a formally exact theory within nonrelativistic quantum mechanics and it allows us to incorporate the effect of the surrounding medium without any additional assumptions. Our result corresponds to the near-zone limit of the QED result, and is not limited to the dipole approximation for transition densities. Moreover, since we do not explicitly use a multipole expansion in the present work, and the need for specific boundary conditions is not

necessary in the formulation, the general expression we obtain should be useful in a variety of applications.

II. EXCITATION ENERGIES IN TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY

One useful application of TDDFT is to calculate the excitation energies of a system by solving for the poles of the density response function (susceptibility).^{22,24} This approach is formally exact except for the use of approximate time-dependent exchange-correlation functionals in the calculation. The TDDFT linear density response $\delta\rho^{(1)}(\mathbf{r}, t)$ [i.e., first order changes to the diagonal elements of density matrix $\rho(\mathbf{r}, \mathbf{r}', t)$ of the electrons] to the perturbation $v(\mathbf{r}, t)$ is given by²⁴

$$\delta\rho^{(1)}(\mathbf{r}, t) = \int dt' \int d^3\mathbf{r}' \chi(\mathbf{r}, t, \mathbf{r}', t') v(\mathbf{r}', t'), \quad (1)$$

where $\chi(\mathbf{r}, t, \mathbf{r}', t')$ is the response function of the system. Using the particle–hole and hole–particle transitions (in the Kohn–Sham *noninteracting* reference system) as a basis, one can write the matrix equation equivalent to Eq. (1) within the frequency domain:²²

$$\left\{ \begin{bmatrix} A(\omega) & B(\omega) \\ B(\omega) & A(\omega) \end{bmatrix} - \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \right\} \begin{bmatrix} \delta\rho^{(1)}(\omega) \\ \delta\rho^{(1)*}(\omega) \end{bmatrix} = \begin{bmatrix} \delta\mathbf{v}(\omega) \\ \delta\mathbf{v}(\omega) \end{bmatrix}, \quad (2)$$

where

$$A_{ia\alpha, jb\beta} = \delta_{\alpha\beta} \delta_{ij} \delta_{ab} (\epsilon_{a\alpha} - \epsilon_{i\alpha}) - K_{ia\alpha, jb\beta}(\omega), \quad (3)$$

$$B_{ia\alpha, jb\beta} = -K_{ia\alpha, jb\beta}(\omega), \quad (4)$$

and $K_{ia\alpha, jb\beta}(\omega)$ is the Fourier transform to $(t - t')$,

$$K_{ia\alpha, jb\beta}(t, t') = \int d\mathbf{r} \int d\mathbf{r}' \phi_{i\alpha}^*(\mathbf{r}) \phi_{a\alpha}(\mathbf{r}) \times \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + g_{XC}(\mathbf{r}, t; \mathbf{r}', t') \right) \times \phi_{j\beta}(\mathbf{r}') \phi_{b\beta}^*(\mathbf{r}'), \quad (5)$$

where $\{\phi_{i\sigma}, \phi_{a\sigma}\}$ are the Kohn–Sham molecular orbitals of the system, (indices i, j, \dots , are used for occupied orbitals; a, b, \dots , are for virtual orbitals, while Greek letters indicate spin states), and $g_{XC}(\mathbf{r}, t; \mathbf{r}', t')$ is the exchange-correlation kernel:

$$g_{XC}(\mathbf{r}, t; \mathbf{r}', t') = \frac{\delta^2 AXC[\rho]}{\delta\rho_a(\mathbf{r}, t) \delta\rho_b(\mathbf{r}', t')}. \quad (6)$$

The terms inside the curly braces in Eq. (2) constitute the matrix representation of $\chi^{-1}(\mathbf{r}, \mathbf{r}', \omega)$, the inverse of the density–density response function $\chi(\mathbf{r}, \mathbf{r}', \omega)$. One can show with the time-dependent Schrödinger equation that the response function χ has poles at the excitation frequencies.²² In application we simply solve for the frequencies that lead to zero in the inverse response function χ^{-1} of the system, i.e., solve the following non-Hermitian eigenvalue problem:

$$\begin{pmatrix} A(\omega) & B(\omega) \\ B(\omega) & A(\omega) \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}, \quad (7)$$

where X and Y are vectors representing the change in the density matrix $\delta\rho^{(1)}$. The solution to Eq. (7) is a set of eigenvalues and eigenvectors. The eigenvalues are the excitation frequencies and the eigenvectors describe, to first order, the transition density of this excitation. The adiabatic approximation is often used in application, (in Refs. 22 and 25, for example), which ignores the memory in the response of electrons. The matrices A and B are no longer functions of ω within the adiabatic approximation. Our result does *not* rely on such an approximation. However, for simplicity of notation we drop explicit dependence on ω in the following derivation.

III. EXCITATION ENERGY TRANSFER IN VACUUM

We require an expression for energy transfer coupling in the framework of TDDFT, so let us consider a pair of donor (D) and acceptor (A) molecules having resonant excitation frequencies when there is no interaction between them. This condition can be fulfilled by the high density of nuclear states created by intra- or intermolecular vibrations in either condensed phase systems or systems of large molecules in the gas phase. We can adapt the Condon approximation to separate such nuclear coordinates from our electronic degrees of freedom.

The coupling strength between two such resonant states is half of the energy splitting when the interaction between the two molecules is turned on. We rewrite Eq. (7), for simplicity of notation, as

$$AX = \omega IX, \quad (8)$$

where

$$A = \begin{pmatrix} A & B \\ B & A \end{pmatrix}; \quad X = \begin{pmatrix} X \\ Y \end{pmatrix}; \quad I = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (9)$$

The orbitals of A generally overlap with those of D and the overlap matrix is denoted as S_{DA} . Equation (8) then becomes

$$\begin{pmatrix} A_{DD} & A_{DA} \\ A_{AD} & A_{AA} \end{pmatrix} \begin{pmatrix} X_D \\ X_A \end{pmatrix} = \omega \begin{pmatrix} I & S_{DA} \\ S_{AD} & I \end{pmatrix} \begin{pmatrix} X_D \\ X_A \end{pmatrix}. \quad (10)$$

Consider a pair of transitions, one for D (transition frequency ω_0 , with eigenvector X_D) and the other for A (ω_0, X_A), that are resonant in excitation energy when the two molecules are isolated. The transition frequencies when the interaction between the two molecules is turned on may be determined by considering such an interaction as a perturbation. The two transition frequencies then become ω_+, ω_- after including the perturbation, with zeroth-order eigenvectors X_+, X_- that are, up to a normalization factor, due to the overlap of the (unperturbed) Kohn–Sham orbitals between the two molecules,

$$X_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} X_D \\ \pm X_A \end{pmatrix}. \quad (11)$$

The (first-order) perturbed transition frequencies are then

$$\omega_{\pm} = \frac{(\mathbf{X}_D^T, \pm \mathbf{X}_A^T) \begin{pmatrix} A_{DD} & A_{DA} \\ A_{AD} & A_{AA} \end{pmatrix} \begin{pmatrix} X_D \\ \pm X_A \end{pmatrix}}{(\mathbf{X}_D^T, \pm \mathbf{X}_A^T) \begin{pmatrix} I & S_{DA} \\ S_{AD} & I \end{pmatrix} \begin{pmatrix} X_D \\ \pm X_A \end{pmatrix}}. \quad (12)$$

The energy transfer coupling (half of the energy splitting) is therefore obtained to first order as

$$J_{DA}^0 [\equiv \frac{1}{2}(\omega_+ - \omega_-)] = \mathbf{X}_D^T A_{DA} \mathbf{X}_A - \omega_0 \mathbf{X}_D^T S_{DA} \mathbf{X}_A. \quad (13)$$

The first term in Eq. (13), according to Eq. (3), contains only terms involving the coupling matrix K that couples transitions in D to those in A :

$$K_{ia\alpha,jb\beta} = \int d\mathbf{r} \int d\mathbf{r}' \phi_{i\alpha}^{*D}(\mathbf{r}) \phi_{a\alpha}^D(\mathbf{r}) \times \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + g_{XC}(\mathbf{r}, \mathbf{r}', \omega) \right) \phi_{j\beta}^A(\mathbf{r}') \phi_{b\beta}^{*A}(\mathbf{r}'), \quad (14)$$

where $\{\phi_{i\alpha}^{D(A)}\}$ are the Kohn–Sham molecular orbitals of D (or A) and $g_{XC}(\mathbf{r}, \mathbf{r}', \omega)$ is the Fourier transform of $g_{XC}(\mathbf{r}, \mathbf{r}', t')$ defined in Eq. (6). Contracting the matrix A_{DA} with vector X_M (X and Y of system M), we can rewrite the terms in Eq. (13) using (diagonal) transition densities $[\rho_M^T(\mathbf{r}), M=D, A]$. Such transition densities are linear combinations of products of molecular orbitals $\phi_{i\alpha}^{*M}(\mathbf{r}) \phi_{a\alpha}^M(\mathbf{r})$, with the coefficients given by the vector X_M (X and Y vectors of system M). Transition densities are in general one particle density matrices that should be denoted as $\tilde{\rho}_M^T(\mathbf{r}, \mathbf{r}')$. We use the term “transition densities” in the present work to denote the diagonal element of the one particle transition density matrices $\rho_M^T(\mathbf{r}) \equiv \tilde{\rho}_M^T(\mathbf{r}, \mathbf{r})$. The energy transfer coupling in vacuum is therefore

$$J_{DA}^0 = \int d\mathbf{r} \int d\mathbf{r}' \rho_D^{T*}(\mathbf{r}) \times \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + g_{XC}(\mathbf{r}, \mathbf{r}', \omega_0) \right) \rho_A^T(\mathbf{r}') - \omega_0 \int d\mathbf{r} \rho_D^{T*}(\mathbf{r}) \rho_A^T(\mathbf{r}). \quad (15)$$

Equation (15) is a density functional version of the energy transfer coupling expression, which is usually derived from the configuration interaction with single substitution (CIS) wave functions, based on a Hartree–Fock (HF) ground state result.²⁶ To make a comparison, the first term on the right-hand side (rhs) of Eq. (15) is divided into two contributions: the integration term with $1/|\mathbf{r} - \mathbf{r}'|$ is the *Coulomb* interaction, while the other term with g_{XC} arises from the *exchange-correlation* effect between the transition density of D and A . The former resembles the Förster coupling mechanism if the dipole approximation is used for the transition densities, and the latter is similar to the Dexter exchange mechanism, except that the correlation of the electrons is now effectively included by the exchange-correlation kernel. Such correlation effects on EET are not available from the HF-CIS approach. In addition, the second term of Eq. (15) shows how the orbital overlap of the two molecules contrib-

utes to the energy transfer coupling. This overlap contribution to the EET coupling has exponential distance dependence and has been suggested to be a more important contribution than exchange coupling.²⁷

IV. EXCITATION ENERGY TRANSFER IN A CONDENSED MEDIUM

We next consider the effect of a condensed medium on energy transfer coupling between two solute molecules. We rewrite Eq. (10) with additional solvent transitions, treating D and A as the system S , and calling the surrounding medium bath, B .

$$\begin{pmatrix} \mathcal{A}_{SS} & \mathcal{A}_{SB} \\ \mathcal{A}_{BS} & \mathcal{A}_{BB} \end{pmatrix} \begin{pmatrix} \mathbf{X}_S \\ \mathbf{X}_B \end{pmatrix} = \omega \begin{pmatrix} \mathcal{I}_S & \mathcal{O} \\ \mathcal{O} & \mathcal{I}_B \end{pmatrix} \begin{pmatrix} \mathbf{X}_S \\ \mathbf{X}_B \end{pmatrix}, \quad (16)$$

where \mathcal{O} is a zero rectangular matrix with appropriate dimensions.

We ignore the effects caused by the overlap of the Kohn–Sham orbitals of the medium and the system in writing Eq. (16), and focus on the solvent influence on EET coupling through the Coulomb and exchange–correlation interactions between the solvent and the medium. Equation (16) can be transformed into an effective equation for the system dimensions only by the standard partition technique.²⁸ The effective equation for the system transitions is

$$[\mathcal{A}_{SS} + \mathcal{A}_{SB}(\omega\mathcal{I}_B - \mathcal{A}_{BB})^{-1}\mathcal{A}_{BS}]\mathbf{X}_S = \omega\mathcal{I}_S\mathbf{X}_S. \quad (17)$$

The transition frequency of the solute molecules is usually far removed from those of the solvent in cases where the absorption of the system can be observed and assigned. The inversion of the matrix $\omega\mathcal{I}_B - \mathcal{A}_{BB}$ should therefore exist and be well defined for virtually all applicable cases. Equation (17) is then an effective equation to solve for the excitation energies of a solvated system. The major result in the present work is obtained, as described below, by realizing that the term $(\omega\mathcal{I}_B - \mathcal{A}_{BB})^{-1}$ in Eq. (17) is actually the charge density response function of the bath, $\chi_B(\mathbf{r}, \mathbf{r}', \omega)$, in its matrix representation, according to Eq. (2). We can substitute this quantity by the bulk susceptibility function of the solvent, for purposes of calculation, in applications in which the molecular details of the surrounding environment are not important.

The energy transfer coupling in the presence of the solvent is

$$J_{DA} = \mathbf{X}_D^T \mathcal{A}_{DA} \mathbf{X}_A - \omega_0 \mathbf{X}_D^T \mathcal{S}_{DA} \mathbf{X}_A + \mathbf{X}_D^T \mathcal{A}_{DB} (\omega\mathcal{I}_B - \mathcal{A}_{BB})^{-1} \mathcal{A}_{BA} \mathbf{X}_A. \quad (18)$$

We have included the contribution arising from the overlap of the Kohn–Sham orbitals between the donor and acceptor, which can be obtained by replacing \mathcal{I}_S in Eq. (17) as the corresponding matrix in Eq. (10):

$$\mathcal{I}_S \equiv \begin{pmatrix} \mathcal{I} & \mathcal{S}_{DA} \\ \mathcal{S}_{AD} & \mathcal{I} \end{pmatrix}. \quad (19)$$

The solvent modifies the coupling through all three terms in Eq. (18). The solvent modifies the electronic densities of the two molecules in the first two terms of Eq. (18), leading to a

change in the EET coupling which consists of Coulomb, exchange–correlation, and overlap terms, as discussed above. One can perform the electronic structure calculation with a model Hamiltonian for the solvent to account for such an effect. We have proposed such a model in earlier work,^{29,30} and there are a number of similar approaches discussed in the literature (see, e.g., Refs. 31–33). We focus on the contribution arising from the third term in Eq. (18) in the present work. This term is an additional contribution, with no corresponding term for the coupling in vacuum. Let us call the third term of Eq. (18) $J_{DA}^{(m)}$ and, for purposes of discussion, regard it as the solvent modification term.

$$J_{DA}^{(m)} \equiv \mathbf{X}_D^T \mathcal{A}_{DB} (\omega\mathcal{I}_B - \mathcal{A}_{BB})^{-1} \mathcal{A}_{BA} \mathbf{X}_A. \quad (20)$$

Therefore, in terms of transition densities, the above expression for coupling becomes

$$\begin{aligned} J_{DA}^{(m)} &= \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{r}'' \int d\mathbf{r}''' \rho_D^{T*}(\mathbf{r}) \\ &\quad \times \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + g_{XC}(\mathbf{r}, \mathbf{r}') \right) \\ &\quad \times \left[\sum_B \rho_B^T(\mathbf{r}') \frac{1}{\omega - \omega_B} \rho_B^{T*}(\mathbf{r}'') \right] \\ &\quad \times \left(\frac{1}{|\mathbf{r}'' - \mathbf{r}'''} + g_{XC}(\mathbf{r}'', \mathbf{r}''') \right) \rho_A^T(\mathbf{r}''') \rho_A^T(\mathbf{r}''') \\ &= \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{r}'' \int d\mathbf{r}''' \rho_D^{T*}(\mathbf{r}) \\ &\quad \times \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + g_{XC}(\mathbf{r}, \mathbf{r}') \right) \chi_B^*(\mathbf{r}', \mathbf{r}'', \omega) \\ &\quad \times \left(\frac{1}{|\mathbf{r}'' - \mathbf{r}'''} + g_{XC}(\mathbf{r}'', \mathbf{r}''') \right) \rho_A^T(\mathbf{r}'''), \end{aligned} \quad (21)$$

where $\chi_B(\mathbf{r}', \mathbf{r}'', \omega)$ is exactly the density–density response function for the bath. The density–density response function describes the first-order response of the charge density of the bath (at \mathbf{r}') when a time-dependent external perturbation (oscillating at the solute transition frequency ω) is applied (at \mathbf{r}''). Macroscopically, this response function for a condensed medium can be described exactly by the dielectric response. Such an approach is similar to continuum models for solvents in electronic structure calculations (see Refs. 29–34, for example). The functional form of the dielectric susceptibility is known for many cases and numerical solutions are available for general situations.^{34–37}

Equation (21) can be viewed as an expression of the transition density of the donor, $\rho_D^T(\mathbf{r})$, and the operator, $1/|\mathbf{r} - \mathbf{r}'| + g_{XC}(\mathbf{r}, \mathbf{r}')$, creating an electric potential as an external perturbation for the solvent, B . Further, the density response arising from the solvent, due to the perturbation, is then coupled with the transition density of the acceptor, (ρ_A^T) , to yield a modification in the donor–acceptor coupling. This result is similar to two real charge distributions interacting with each other in the presence of a solvent. Thus we have now transformed the problem into a more familiar situation in which the transition densities interact with the sol-

vent through the Coulomb and exchange-correlation potentials. However, instead of using the static response properties of the solvent, the optical dielectric response at the transition frequency is used. To the best of our knowledge, this is the first time such a general isomorphism between EET coupling and interaction between real charge densities has been established without explicitly using oscillating charges or dipoles for the transition, and without the limitation of a particular geometry.

The results in Eq. (21) can be divided into four contributions as a result of the two interaction kernels (Coulomb or exchange-correlation) coupling the medium and donor or acceptor. Coulomb coupling is much larger than exchange-correlation couplings in many cases^{7,8,27} (for example) and is an important feature of the reaction field models we have developed in Refs. 29 and 30. The term with the Coulomb–Coulomb kernel is thus expected to be the most important among the four contributions:

$$J_{DA}^{(m)}(\text{Coul}) = \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{r}'' \int d\mathbf{r}''' \rho_D^{T*}(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \times \left[\sum_B \rho_B^T(\mathbf{r}') \frac{1}{\omega - \omega_B} \rho_B^{T*}(\mathbf{r}'') \right] \times \frac{1}{|\mathbf{r}'' - \mathbf{r}''|} \rho_A^T(\mathbf{r}'''). \quad (22)$$

We present two illustrative examples below in order to further understand the physical implication of our result. We solve for the Coulomb coupling and the Coulomb–Coulomb contribution [Eq. (22)] in medium modified EET coupling for each example.

A. Two molecules separated by solvent

Let us first consider the situation where the donor and acceptor are embedded in and separated by solvent molecules. Each chromophore has created a cavity in the bulk continuum of solvent. For simplicity, spherical cavities are assumed. The response of a dielectric medium can be obtained by solving for the reaction field, $\Phi_{rxn}(\mathbf{r})$, arising from the multipoles (q_{lm}^D) of the transition density of the donor:^{38–40}

$$\Phi_{rxn}(\mathbf{r}; r > a) = - \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{(l+1)[\epsilon(\omega) - 1]}{\epsilon(\omega)l + \epsilon(\omega) + 1} \times q_{lm}^D r^{-(l+1)} Y_{lm}(\theta, \phi), \quad (23)$$

where a denotes the radius of the spherical cavity, and the multipole moment q_{lm}^D is defined as³⁹

$$q_{lm}^D = \int Y_{lm}^*(\theta, \phi) r^l \rho_D^T(\mathbf{r}) d\mathbf{r}, \quad (24)$$

and $\epsilon(\omega)$ is the dielectric response of the solvent at the frequency of transition (ω). The solvent modification to the Coulomb coupling is

$$J_{DA}^{(m)}(\text{Coul}) = \int d\mathbf{r} \rho_A^T(\mathbf{r}) \Phi_{rxn}(\mathbf{r}) = - \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{(l+1)(\epsilon(\omega) - 1)}{\epsilon(\omega)l + \epsilon(\omega) + 1} q_{lm}^D \times \int_{r>a} d\mathbf{r} \rho_A^T(\mathbf{r}) r^{-(l+1)} Y_{lm}(\theta, \phi). \quad (25)$$

The direct Coulomb coupling (*in vacuum*) between $\rho_D^T(\mathbf{r})$ and $\rho_A^T(\mathbf{r})$ is, using the same multipole expansion technique,

$$J_{DA}^0(\text{Coul}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} q_{lm}^D \times \int d\mathbf{r} \rho_A^T(\mathbf{r}) r^{-(l+1)} Y_{lm}(\theta, \phi). \quad (26)$$

Comparing expressions in Eqs. (25) and (26), and assuming that transition densities $\rho_{D(A)}^T$ are not affected by the solvent, we find that the different integration regions in these equations do not make a significant difference since we focus on the case where the donor and acceptor molecules are separated by some solvent. In this case

$$J_{DA}^{\text{total}}(\text{Coul}) = J_{DA}^0(\text{Coul}) + J_{DA}^{(m)}(\text{Coul}). \quad (27)$$

So for each l , there is a reduction (negative) factor of $(l+1)[\epsilon(\omega) - 1]/[\epsilon(\omega)l + \epsilon(\omega) + 1]$ multiplying to the corresponding terms in the summation for the solvent modification component ($J_{DA}^{(m)}$) of the coupling, reducing the magnitude of the overall coupling in the medium. The screening factor for the final coupling strengths ranges in general from $3/[2\epsilon(\omega) + 1]$ for $l=1$ to $2/[\epsilon(\omega) + 1]$ as l approaches infinity. (For transition densities there is no monopole.) For a solvent with $\epsilon(\omega)=2$, for example, such a factor ranges from $3/5(l=1)$ to $2/3(l \rightarrow \infty)$. In comparison, the Förster expression carries a factor of $1/n^2 [= 1/\epsilon(\omega)]$ to account for the medium screening effect, which is $1/2$ in this case. This rather simple screening factor of $1/n^2$ not only overestimates the effect of a dielectric medium, but it is also not consistent in its formulation, since the proper dielectric screening of a dipole source is usually written as $3/[2\epsilon(\omega) + 1]$ instead of $1/\epsilon(\omega)$.

B. Two molecules in a cavity

We now consider a second example, the case where the two molecules are placed sufficiently close to each other in the medium such that the cavities created by the two molecules are merged into a single cavity.

A charge–charge response function $\chi(\mathbf{r}, \mathbf{r}', \omega)$ can generally be obtained from dielectric solvation theory.⁴¹ The dipole–dipole response function has been studied extensively in Refs. 42 and 43, for example for solvents composed of neutral species, and a general solution for a spherical cavity in a dielectric continuum medium is available.^{35,44} The

interaction energy between two charges, q_1 and q_2 , located at \mathbf{r}_1 and \mathbf{r}_2 inside a spherical cavity is, according to Refs. 35 and 44,

$$E_{\text{int}} = \frac{q_1 q_2}{|\mathbf{r}_1 - \mathbf{r}_2|} + q_1 q_2 f(\mathbf{r}_1, \mathbf{r}_2), \quad (28)$$

where

$$f(\mathbf{r}_1, \mathbf{r}_2) = - \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{(\epsilon-1)(l+1)}{(l+1)\epsilon+l} \frac{r_1^l r_2^l}{a^{2l+1}} \times Y_{lm}^*(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2); \quad (29)$$

a in Eq. (29) denotes the radius of the cavity, ϵ is the dielectric constant of the medium, and the origin of the coordinates is the center of the spherical cavity.

The solvent-mediated energy transfer coupling of two chromophore is

$$J_{DA}^{(m)}(\text{Coul}) = \int d\mathbf{r} \int d\mathbf{r}' \rho_D^T(\mathbf{r}) \rho_A^T(\mathbf{r}') f(\mathbf{r}, \mathbf{r}', \omega), \quad (30)$$

where $f(\mathbf{r}, \mathbf{r}', \omega)$ is defined similarly as in Eq. (29) except the dielectric constant ϵ is replaced by the dielectric response at the frequency of transition $\epsilon(\omega)$.

A simple model that provides some insight is a system with two transition dipoles inside a spherical cavity. Suppose the two transition dipoles $\boldsymbol{\mu}_D^T, \boldsymbol{\mu}_A^T$ for the donor and acceptor are located at \mathbf{r}_D and \mathbf{r}_A , respectively. The expression in Eq. (30) is modified for interactions between two point dipoles, and the solvent modification component is

$$J_{DA}^{(m)}(\text{Coul}) = \boldsymbol{\mu}_D^T \nabla_D \nabla_A f(\mathbf{r}_D, \mathbf{r}_A, \omega) \boldsymbol{\mu}_A^T. \quad (31)$$

The interaction between the two dipoles in vacuum, for comparison, is (assuming the transition dipole moments are not changed significantly by solvation, for simplicity)

$$J_{DA}^0(\text{Coul}) = \boldsymbol{\mu}_D^T \nabla_D \nabla_A \frac{1}{|\mathbf{r}_D - \mathbf{r}_A|} \boldsymbol{\mu}_A^T, \quad (32)$$

where ∇_D (or ∇_A) is the gradient operator for \mathbf{r}_D (\mathbf{r}_A). We have assumed that the transition dipoles are the same for the molecules in vacuum as in solution so that Eq. (27) is applicable. The tensor $\nabla_D \nabla_A f(\mathbf{r}_D, \mathbf{r}_A, \omega)$ in Eq. (31) can be calculated using Eq. (29) in spherical coordinates. Similarly, the Coulomb potential $1/|\mathbf{r}_D - \mathbf{r}_A|$ can be expanded in spherical coordinates:

$$\frac{1}{|\mathbf{r}_D - \mathbf{r}_A|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}^*(\theta_D, \phi_D) \times Y_{lm}(\theta_A, \phi_A). \quad (33)$$

Let us assume, without a loss of generality, that $r_D > r_A$. (For the case where $r_D < r_A$ we can simply switch the donor and acceptor in the discussion below.) We first note that for the two functions listed above in Eqs. (29) and (33), all of the angular dependence and the radial dependence for r_A ($r_{<}$) are the same but for r_D ($r_{>}$) the dependence has the opposite slope. So if the transition dipole of the donor (or the one that is closer to the cavity boundary), $\boldsymbol{\mu}_D^T$, is parallel to the radial direction, then the dielectric medium modifies the Coulomb coupling by adding a term of the *same* sign to the

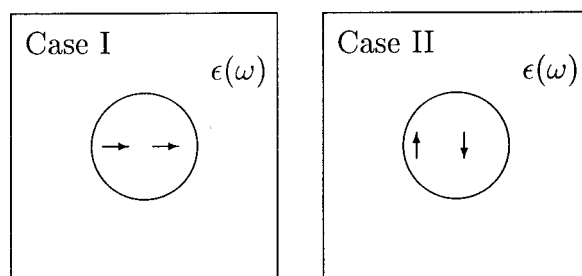


FIG. 1. Sketch for the models used in obtaining results plotted in Fig. 2. The two point dipoles are located at $(-0.8, 0, 0)$ and $(0.1, 0, 0)$ in Cartesian coordinates and the radius of the cavity is set to unity. The dipole moments are of the same magnitude. For case I, the dipole moments are pointing along the x axis. For case II, the dipoles are pointing along the z axis, in the opposite direction.

direct coupling J_{DA}^0 , *enhancing* the overall coupling strength. On the other hand, if $\boldsymbol{\mu}_D^T$ lies parallel to the boundary surface, the modification has the opposite sign, *screening* down the Coulomb coupling strength.

Using Eqs. (31) and (32), we can calculate the ratio of interaction energies in a dielectric medium to that in vacuum. We illustrate this ratio with a pair of dipoles of the same magnitude located at distances $0.8a$ and $0.1a$ from the center of a spherical cavity, respectively, oriented either in the same or opposite directions. Sketches of the models employed are plotted in Fig. 1.

A simple model calculation indicates that coupling in a medium is not always a screened Coulomb coupling, as shown in Fig. 2. We can explain the trends in Fig. 2 using the image charge approximation.⁴⁴ Replacing the source dipole with two closely spaced point charges, one realizes that the image dipole moment generated by a source dipole is in the same direction if the source dipole is perpendicular to the boundary surface, and the overall interaction of the system is *enhanced*. On the other hand, if the source dipole lies parallel to the surface, the image dipole is then in the opposite direction, reducing the interaction of the source dipole with

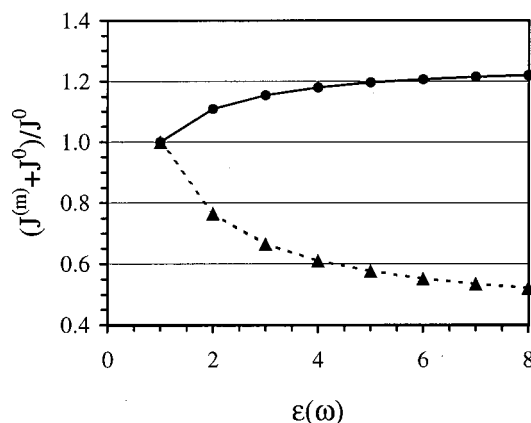


FIG. 2. Ratio of the overall Coulomb coupling ($J^0 + J^{(m)}$) in the medium to the Coulomb coupling in vacuum (J^0) for two fixed transition dipoles as a function of the dielectric constant. The Coulomb couplings are calculated using Eqs. (31) and (32). The two cases presented are for the dipole arrangements shown in Fig. 1. The solid line connecting the dots represents results for case I, while the dotted line with triangles is for case II.

other charges in the system. The same effect has been calculated and observed for planar dielectric interfaces by Cho¹⁹ and by Cho and Silbey.^{17,18} We believe that this enhancement/suppression effect can be examined in experiments and may explain the excellent agreement of some quantum chemistry calculations to experimental results without considering the effects of the medium,^{7,8,45,46} perhaps due to cancellation of enhancement and suppression effects created by different parts of the chromophores.

We note that one may want to simulate an inhomogeneous solvent environment. A protein matrix, for example, may be considered by using a model with a larger optical dielectric response in the region where more polarizable groups reside. Equation (21) is capable of accounting for such effects in numerical calculations. An example of this type of approach can be found in Ref. 47, in which the spectral density for solvation is calculated as a function of frequency.³⁵ In the calculation several models are employed using different assumptions on the dielectric response of the protein and the water, with boundaries defined as molecular shaped cavities surrounding the chromophore. A calculation for the medium effect with the Coulomb–Coulomb term in Eq. (21) can be performed in the same way except that in this case we only need to calculate the interaction for one frequency (ω), which is the frequency of the excitation energy.

V. CONCLUSION

We have derived a general approach for the effect of the medium on EET coupling using time-dependent density functional theory as shown in Eq. (21). This result is isomorphic to the interaction of two groups of electronic densities under the influence of a condensed medium except that in EET the transition densities for the donor and acceptor and the dynamic response function (at the frequency of the transition) of the medium are used. Our result does not rely on the multipole expansion of the transition densities, nor is it limited by a specific boundary condition. Therefore it provides a basis for future detailed investigations on the effects of the surrounding environment (both homogeneous and inhomogeneous media) on EET.

For specific applications, the exchange and correlation effects on the direct coupling and the influence of the medium can be calculated using approximate exchange-correlation functionals. A unique consequence of our approach using density functional theory is the inclusion of correlation effects on the EET coupling, which are unavailable in HF-CIS theory.^{26,27}

A simple model calculation of Coulombic coupling shows that the medium modification of EET coupling depends on the geometry and the arrangement of the donor, the acceptor, and the medium. The overall coupling may be enhanced or suppressed by the coupling strength in vacuum.

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