

Polariton-assisted resonance energy transfer beyond resonant dipole-dipole interaction: A transition-current-density approach

Ming-Wei Lee^{1,2} and Liang-Yan Hsu^{2,3,4,*}¹*Department of Physics, National Taiwan University, Taipei 10617, Taiwan*²*Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan*³*Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan*⁴*Physics Division, National Center for Theoretical Sciences, Taipei 10617, Taiwan*

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Using electric dipoles to describe light-matter interactions between two entities is a conventional approximation in physics, chemistry, and materials science. However, the lack of material structures makes the approximation inadequate when the size of an entity is comparable to the spatial extent of electromagnetic fields or the distance of two entities. In this study, we develop a unified theory of radiative and nonradiative resonance energy transfer based on transition current density in a theoretical framework of macroscopic quantum electrodynamics. The proposed theory allows us to describe polariton-assisted resonance energy transfer between two entities with arbitrary material structures in spatially dependent electromagnetic fields. To demonstrate the generality of the proposed theory, we rigorously prove that our theory can cover the main results of the transition density cube method and the plasmon-coupled resonance energy transfer. We believe that this study opens a promising direction for exploring light-matter interactions beyond the scope of electric dipoles and provides insights into materials physics.

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I. INTRODUCTION

Resonance energy transfer (RET) is a fundamental process in photophysics and has attracted considerable attention in a variety of fields owing to its extensive applications in biological and chemical sensing [1–9], molecular imaging [10–14], and photovoltaics [15–19]. To understand the mechanism of RET, numerous theoretical studies have been conducted based on the electric dipole approximation (EDA) [20–28]. For example, Förster developed a concept of spectral overlap for the description of RET [29,30], Andrews and co-workers established a unified theory of radiative and nonradiative RET [31–33] (which corresponds to the resonant dipole-dipole interaction in free space) from molecular quantum electrodynamics (QED) [34], and Dung *et al.* incorporated the effect of dielectric environment into the resonant dipole-dipole interaction [35,36]. These theories not only advance the understanding of RET, but also successfully capture the main features of RET.

Recently, experimental studies have shown that the RET rates between two entities (molecules [37–41], semiconductors [18], biomolecules [42,43], etc.) can be significantly influenced by the presence of polaritons, which provides a new perspective on exploring light-matter interaction in spatially dependent electromagnetic fields. It is well known that the EDA cannot be used to describe RET in the following scenarios: (i) The distance between two entities is insufficient [44–48] and (ii) the surrounding electromagnetic field of

entities varies drastically [49,50]. In the former scenario, several approaches have been successively proposed and applied to some representative systems, e.g., the transition monopole theory for chlorophyll [51], the line-dipole approximation for conjugated polymers [52], and the transition density cube (TDC) method for pigments of light-harvesting complex [53], but these approaches cannot describe the retardation effect, i.e., the mechanism of radiative RET. In the latter scenario, a straightforward improvement is to consider the quadrupolar interaction [50,54,55], but the convergence of multipolar expansion depends on material structures. Moreover, the methods used to address scenarios (i) and (ii) cannot describe the influence of polaritons (photons dressed by dielectric environments) on RET. Therefore, to address the above issues, our strategy is to start from the framework of macroscopic QED [56,57] (which enables us to incorporate the effect of dielectric environments) and derive an explicit RET-rate expression by employing a transition current density approach (which enables us to capture the retardation effects).

In this article, the main goal is to establish a generalized theory of RET beyond the EDA and allow us to study RET between two entities with material structures in spatially dependent vacuum electric fields. The structure of this article is organized as follows. In Sec. II we begin with the total Hamiltonian of polaritons and point charges with interactions introduced via the minimal coupling procedure. Next we derive the RET rate of a pair of molecules expressed by the molecular transition current density by expanding the Born series to the second order. Moreover, we adopt the Condon-like approximation in order to separate the electronic and nuclear degrees of freedom and then derive a formula which

*lyhsu@gate.sinica.edu.tw

allows us to acquire the transition current density via *ab initio* calculations. In Sec. III we demonstrate the generality of our theory by comparing them to previous works, including the TDC method [53] and plasmon-coupled RET [58]. In Sec. IV we present a brief summary of this research.

II. THEORY

A. Total Hamiltonian

In the nonrelativistic regime, we consider a collection of point charges with the quantized electromagnetic fields in the presence of linear, dispersive, and absorbing media (polaritons). Note that the formation of polaritons originates from the hybridization of photons and media, which does not include the contribution of point charges. Hence, in this context, the total Hamiltonian comprises a polariton Hamiltonian and a Hamiltonian of point charges $\hat{H}_{\text{tot}} = \hat{H}_{\text{pol}} + \hat{H}_{\text{PC}}$. To properly describe the quantum behavior of polaritons, we adopt the quantization framework of macroscopic QED [36,56,57] and express the polariton Hamiltonian as

$$\hat{H}_{\text{pol}} = \int d^3\mathbf{r} \int_0^\infty d\omega \hbar\omega \hat{\mathbf{f}}^\dagger(\mathbf{r}, \omega) \cdot \hat{\mathbf{f}}(\mathbf{r}, \omega), \quad (1)$$

where the vector bosonic operators $\hat{\mathbf{f}}^\dagger(\mathbf{r}, \omega)$ and $\hat{\mathbf{f}}(\mathbf{r}, \omega)$ are the creation and annihilation operators, respectively, that obey the commutation relations

$$[\hat{f}_k(\mathbf{r}, \omega), \hat{f}_{k'}^\dagger(\mathbf{r}', \omega')] = \delta_{kk'} \delta(\mathbf{r} - \mathbf{r}') \delta(\omega - \omega'), \quad (2a)$$

$$[\hat{f}_k(\mathbf{r}, \omega), \hat{f}_{k'}(\mathbf{r}', \omega')] = 0. \quad (2b)$$

Incidentally, the macroscopic QED can be reduced to the microscopic (or molecular) QED [34,59] in the cases of homogeneous dilute media or vacuum [60]. For the Hamiltonian of point charges, the interaction between point charges and quantized electromagnetic fields is introduced through the minimal coupling procedure in the Coulomb gauge

$$\begin{aligned} \hat{H}_{\text{PC}} = & \sum_n \frac{1}{2m_n} [\hat{\mathbf{p}}_n - q_n \hat{\mathbf{A}}(\hat{\mathbf{r}}_n)]^2 + \sum_{n < m} \hat{V}(\hat{\mathbf{r}}_n, \hat{\mathbf{r}}_m) \\ & + \sum_n q_n \hat{\phi}(\hat{\mathbf{r}}_n). \end{aligned} \quad (3)$$

The first term in \hat{H}_{PC} describes the mechanical kinetic energy of point charges in the presence of electromagnetic fields, where m_n , q_n , $\hat{\mathbf{r}}_n$, and $\hat{\mathbf{p}}_n$ are the mass, charge number, position operator, and canonical momentum operator of the n th point charge, respectively [61]. The second term $\hat{V}(\hat{\mathbf{r}}_n, \hat{\mathbf{r}}_m)$ describes the Coulomb interaction between the n th and m th point charges. The final term is the interaction between point charges and scalar potential from media. In the Coulomb gauge, the scalar potential operator $\hat{\phi}(\mathbf{r})$ is associated with the longitudinal auxiliary electric-field operator $\hat{\mathbf{E}}^\parallel(\mathbf{r}, \omega)$ [Eq. (4a)]. Similarly, the vector potential operator $\hat{\mathbf{A}}(\mathbf{r})$ is associated with the transverse auxiliary electric-field operator $\hat{\mathbf{E}}^\perp(\mathbf{r}, \omega)$ [Eq. (4b)],

$$-\nabla \hat{\phi}(\mathbf{r}) = \int_0^\infty d\omega [\hat{\mathbf{E}}^\parallel(\mathbf{r}, \omega) + \text{H.c.}], \quad (4a)$$

$$\hat{\mathbf{A}}(\mathbf{r}) = \int_0^\infty d\omega [(i\omega)^{-1} \hat{\mathbf{E}}^\perp(\mathbf{r}, \omega) + \text{H.c.}]. \quad (4b)$$

Here the longitudinal (transverse) component is defined by the auxiliary electric-field operator $\hat{\mathbf{E}}(\mathbf{r}, \omega)$,

$$\hat{\mathbf{E}}^{\parallel(\perp)}(\mathbf{r}, \omega) = \int d^3\mathbf{r}' \bar{\bar{\delta}}^{\parallel(\perp)}(\mathbf{r} - \mathbf{r}') \cdot \hat{\mathbf{E}}(\mathbf{r}', \omega), \quad (5)$$

where $\bar{\bar{\delta}}^\parallel(\mathbf{r} - \mathbf{r}')$ and $\bar{\bar{\delta}}^\perp(\mathbf{r} - \mathbf{r}')$ denote the longitudinal and transverse dyadic delta functions, respectively. Moreover, the auxiliary electric-field operator in the frequency domain is defined by [36,62]

$$\hat{\mathbf{E}}(\mathbf{r}, \omega) = i \sqrt{\frac{\hbar}{\pi \epsilon_0}} \frac{\omega^2}{c^2} \int d^3\mathbf{r}' \sqrt{\epsilon_1(\mathbf{r}', \omega)} \bar{\bar{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \hat{\mathbf{f}}(\mathbf{r}', \omega). \quad (6)$$

Here $\epsilon_1(\mathbf{r}', \omega) = \text{Im}[\epsilon(\mathbf{r}', \omega)]$ denotes the imaginary part of the relative permittivity function and $\bar{\bar{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega)$ is the dyadic Green's function of macroscopic Maxwell's equations, i.e.,

$$\left(\frac{\omega^2 \epsilon(\mathbf{r}, \omega)}{c^2} - \nabla \times \nabla \right) \times \bar{\bar{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega) = -\bar{\bar{\mathbf{I}}} \delta(\mathbf{r} - \mathbf{r}'), \quad (7)$$

where $\bar{\bar{\mathbf{I}}}$ is a 3×3 identity matrix.

On the basis of the total Hamiltonian, we further categorize the point charges according to their belonging entities because the main purpose of this study is to focus on the RET between the entities, where the entities can be atoms, molecules, two-dimensional materials, etc. Accordingly, the Hamiltonian of point charges is rewritten as

$$\hat{H}_{\text{PC}} = \sum_M \hat{H}_M + \sum_{M < M'} \hat{V}_{MM'} + \sum_M [\hat{V}_{\text{pol},M} + \hat{\Lambda}_{\text{pol},M}],$$

where M denotes the index of entities and $\xi \in M$ denotes the index of point charges (including nuclei and electrons) in the entity M . Here the Hamiltonian \hat{H}_M of the entity M and the Coulomb interaction between two entities $\hat{V}_{MM'}$ are defined by

$$\hat{H}_M = \sum_{\xi \in M} \frac{\hat{\mathbf{p}}_\xi^2}{2m_\xi} + \sum_{\xi < \zeta} \hat{V}(\hat{\mathbf{r}}_\xi, \hat{\mathbf{r}}_\zeta), \quad (8)$$

$$\hat{V}_{MM'} = \sum_{\xi \in M} \sum_{\zeta \in M'} \hat{V}(\hat{\mathbf{r}}_\xi, \hat{\mathbf{r}}_\zeta), \quad (9)$$

respectively. The interactions between polaritons and the entity M ($\hat{V}_{\text{pol},M}$ and $\hat{\Lambda}_{\text{pol},M}$) are defined as

$$\hat{V}_{\text{pol},M} = \sum_{\xi \in M} \left(q_\xi \hat{\phi}(\hat{\mathbf{r}}_\xi) - \frac{q_\xi}{m_\xi} \hat{\mathbf{A}}(\hat{\mathbf{r}}_\xi) \cdot \hat{\mathbf{p}}_\xi \right), \quad (10a)$$

$$\hat{\Lambda}_{\text{pol},M} = \sum_{\xi \in M} \frac{q_\xi^2}{2m_\xi} \hat{\mathbf{A}}^2(\hat{\mathbf{r}}_\xi). \quad (10b)$$

Note that in Eq. (10a) we use the relation $\hat{\mathbf{p}}_\xi \cdot \hat{\mathbf{A}}(\hat{\mathbf{r}}_\xi) = \hat{\mathbf{A}}(\hat{\mathbf{r}}_\xi) \cdot \hat{\mathbf{p}}_\xi$, which holds as we choose the Coulomb gauge. In

addition, it is convenient to define the charge density operator $\hat{\rho}_M(\mathbf{r})$ and the current density operator $\hat{\mathbf{j}}_M(\mathbf{r})$ of the entity M ,

$$\hat{\rho}_M(\mathbf{r}) \equiv \sum_{\xi \in M} q_\xi \delta(\mathbf{r} - \hat{\mathbf{r}}_\xi), \quad (11)$$

$$\hat{\mathbf{j}}_M(\mathbf{r}) \equiv \sum_{\xi \in M} \frac{q_\xi}{2m_\xi} [\delta(\mathbf{r} - \hat{\mathbf{r}}_\xi) \hat{\mathbf{p}}_\xi + \hat{\mathbf{p}}_\xi \delta(\mathbf{r} - \hat{\mathbf{r}}_\xi)], \quad (12)$$

so that $\hat{V}_{\text{pol},M}$ can be expressed in a continuous form

$$\hat{V}_{\text{pol},M} = \int d^3\mathbf{r} [\hat{\varphi}(\mathbf{r}) \hat{\rho}_M(\mathbf{r}) - \hat{\mathbf{A}}(\mathbf{r}) \cdot \hat{\mathbf{j}}_M(\mathbf{r})]. \quad (13)$$

Note that the order of δ functions and canonical momentum operators in Eq. (12) should be done with care because $\hat{\mathbf{r}}_\xi$ and $\hat{\mathbf{p}}_\xi$ are not commutative. The details can be found in Appendix A. In contrast to $\hat{V}_{\text{pol},M}$, which includes both scalar and vector potentials, $\hat{\Lambda}_{\text{pol},M}$ depends only on the vector potential and is associated with the diamagnetic response [63–65] of the entity M . Here we would like to emphasize that the interactions in Eqs. (10) and (10b) are the complete couplings between polaritons and molecules, i.e., the couplings beyond the commonly used EDA. In other words, the information of molecular structures is fully preserved in Eq. (10). Finally, the total Hamiltonian is reorganized as the compact form

$$\hat{H}_{\text{tot}} = \hat{H}_{\text{pol}} + \sum_M \hat{H}_M + \sum_M (\hat{V}_{\text{pol},M} + \hat{\Lambda}_{\text{pol},M}) + \sum_{M < M'} V_{MM'}. \quad (14)$$

It is worth pointing out that the above Hamiltonian is a general form for entities coupled to the quantized electromagnetic fields in the presence of dispersive and absorbing media, which can also be applied to investigate other photophysical (photochemical) topics such as spontaneous emission and electron transfer under the influence of polaritons.

B. Transfer rate of a two-entity system

Now we focus on the RET between a pair of entities with the assistance of polaritons in the incoherent limit [23,66–69], i.e., the RET processes can be described by kinetic rates. According to the definition in Eq. (14), the total Hamiltonian in the two-entity case reads

$$\hat{H} \equiv \hat{H}_{\text{tot}}(M = \{A, B\}) = \hat{H}_0 + \hat{H}_1, \quad (15)$$

with the unperturbed Hamiltonian \hat{H}_0 and interaction Hamiltonian \hat{H}_1 described by

$$\begin{aligned} \hat{H}_0 &= \hat{H}_{\text{pol}} + \hat{H}_A + \hat{H}_B, \\ \hat{H}_1 &= \hat{V}_{\text{pol},A} + \hat{\Lambda}_{\text{pol},A} + \hat{V}_{\text{pol},B} + \hat{\Lambda}_{\text{pol},B} + \hat{V}_{AB} \\ &\approx \hat{V}_{\text{pol},A} + \hat{V}_{\text{pol},B} + \hat{V}_{AB}. \end{aligned} \quad (16)$$

In the interaction Hamiltonian, we do not consider the diamagnetic effect in the RET (i.e., we neglect the contribution from the diamagnetic terms $\hat{\Lambda}_{\text{pol},A}$ and $\hat{\Lambda}_{\text{pol},B}$) because their magnitude is far less than that of the remaining terms [70,71]. In this system, we consider the initial (final) state, which is the direct product of the polaritonic vacuum state and the energy eigenstates A and B ,

$$|i\rangle = |a'\rangle \otimes |b\rangle \otimes |0\rangle, \quad E_i = E_{a'} + E_b, \quad (18a)$$

$$|f\rangle = |a\rangle \otimes |b'\rangle \otimes |0\rangle, \quad E_f = E_a + E_{b'}. \quad (18b)$$

Here $|a(a')\rangle$ and $|b(b')\rangle$ are the eigenkets of the Hamiltonians \hat{H}_A and \hat{H}_B , and their corresponding energy are $E_{a(a')}$ and $E_{b(b')}$. Also, we denote the energy of the initial (final) state by E_i (E_f) and we require that $E_{a'} > E_a$ and $E_{b'} > E_b$. By expanding Born series up to the second order in the time-dependent perturbation theory [72], the total RET rate Γ is expressed as

$$\Gamma = \sum_{f,i} P_i \Gamma_{fi}, \quad \Gamma_{fi} = \frac{2\pi}{\hbar} |\langle f | \hat{T} | i \rangle|^2 \delta(E_f - E_i), \quad (19)$$

where P_i is the probability of the initial state and the transition operator \hat{T} is given by

$$\hat{T} = \hat{T}_1 + \hat{T}_2 = \hat{H}_1 + \hat{H}_1 \hat{G}_0 \hat{H}_1. \quad (20)$$

Here \hat{G}_0 is the retarded Green's operator, which is defined by

$$\hat{G}_0 = \frac{1}{E_i - \hat{H}_0 + i\eta}, \quad \eta \rightarrow 0^+. \quad (21)$$

Now we evaluate the total transition amplitude $\langle f | \hat{T} | i \rangle$ and divide $\langle f | \hat{T} | i \rangle$ into two parts $\langle f | \hat{T}_1 | i \rangle$ and $\langle f | \hat{T}_2 | i \rangle$. First, in the transition amplitude of \mathcal{T}_1 , it is not difficult to obtain that only \hat{V}_{AB} contributes to transition amplitude,

$$\langle f | \hat{T}_1 | i \rangle = \langle f | \hat{V}_{AB} | i \rangle = \langle a; b' | \sum_{\xi \in A} \sum_{\zeta \in B} \frac{q_\xi q_\zeta}{4\pi\epsilon_0 |\hat{\mathbf{r}}_\xi - \hat{\mathbf{r}}_\zeta|} | a'; b \rangle, \quad (22)$$

where ϵ_0 denotes the vacuum permittivity. Equation (22) clearly shows that the first-order perturbation excludes the interplay of molecules and polaritons due to $\hat{V}_{\text{pol},A}$ ($\hat{V}_{\text{pol},B}$) as indirect couplings between two entities. This is the reason that the second-order perturbation is required in our theory. Second, the transition amplitude of \mathcal{T}_2 contains the nonzero terms

$$\langle f | \hat{T}_2 | i \rangle = \langle f | \hat{V}_{\text{pol},A} \hat{G}_0 \hat{V}_{\text{pol},B} | i \rangle + \langle f | \hat{V}_{\text{pol},B} \hat{G}_0 \hat{V}_{\text{pol},A} | i \rangle + \langle f | \hat{V}_{AB} \hat{G}_0 \hat{V}_{AB} | i \rangle. \quad (23)$$

It is worth noting that $\langle f | \hat{V}_{AB} \hat{G}_0 \hat{V}_{AB} | i \rangle$ can be neglected if the entities are far apart, resulting in negligible Coulomb interactions. At the present stage, we neglect the contribution of $\langle f | \hat{V}_{AB} \hat{G}_0 \hat{V}_{AB} | i \rangle$ and evaluate the second-order transition amplitude by using

the spectral representation of the retarded Green's operator

$$\begin{aligned} \langle f | \hat{\mathcal{T}}_2 | i \rangle &\approx \langle f | \hat{V}_{\text{pol},A} \hat{\mathcal{G}}_0 \hat{V}_{\text{pol},B} | i \rangle + \langle f | \hat{V}_{\text{pol},B} \hat{\mathcal{G}}_0 \hat{V}_{\text{pol},A} | i \rangle \\ &= \sum_{l=1}^3 \int d^3 \mathbf{s} \int_0^\infty d\omega \frac{\langle a; \{0\} | \hat{V}_{\text{pol},A} | a'; \{1_l(\mathbf{s}, \omega)\} \rangle \langle b'; \{1_l(\mathbf{s}, \omega)\} | \hat{V}_{\text{pol},B} | b; \{0\} \rangle}{E_b - E_{b'} - \hbar\omega + i\eta} \\ &\quad + \sum_{l=1}^3 \int d^3 \mathbf{s} \int_0^\infty d\omega \frac{\langle b'; \{0\} | \hat{V}_{\text{pol},B} | b; \{1_l(\mathbf{s}, \omega)\} \rangle \langle a; \{1_l(\mathbf{s}, \omega)\} | \hat{V}_{\text{pol},A} | a'; \{0\} \rangle}{E_{a'} - E_a - \hbar\omega + i\eta}. \end{aligned} \quad (24)$$

In $\langle f | \hat{V}_{\text{pol},A} \hat{\mathcal{G}}_0 \hat{V}_{\text{pol},B} | i \rangle$ and $\langle f | \hat{V}_{\text{pol},B} \hat{\mathcal{G}}_0 \hat{V}_{\text{pol},A} | i \rangle$, we consider the two intermediate states $|a', b'; \{1_l(\mathbf{s}, \omega)\}$ and $|a, b; \{1_l(\mathbf{s}, \omega)\}$, respectively. Recall that the single-polariton Fock state in Eq. (24) is defined by $|\{1_l(\mathbf{s}, \omega)\}\rangle = f_l^\dagger(\mathbf{s}, \omega) |\{0\}\rangle$, which is interpreted as a single-polariton density with the polarization component l at the frequency ω and at the position \mathbf{s} . Furthermore, to adequately cope with $\hat{V}_{\text{pol},M}$, one can define the auxiliary current density of the entity M ,

$$\mathcal{J}_{mm'}(\mathbf{r}; \omega) \equiv \frac{\omega}{\omega_{m'm}} \mathbf{j}_{mm'}^\parallel(\mathbf{r}) + \mathbf{j}_{mm'}^\perp(\mathbf{r}), \quad (25a)$$

$$\mathcal{J}_{m'm}(\mathbf{r}; \omega) \equiv \frac{\omega}{\omega_{m'm}} \mathbf{j}_{m'm}^\parallel(\mathbf{r}) + \mathbf{j}_{m'm}^\perp(\mathbf{r}), \quad (25b)$$

where $\omega_{m'm} = \omega_{m'} - \omega_m$ and $\mathbf{j}_{mm'}^{\parallel(\perp)}(\mathbf{r})$ is the longitudinal (transverse) part of the transition current density $\mathbf{j}_{mm'(m'm)}(\mathbf{r}) = \langle m(m') | \hat{\mathbf{j}}_M(\mathbf{r}) | m'(m) \rangle$. For convenience, we restrict the denominator $\omega_{m'm}$ in Eq. (25) to be positive and $\omega_{mm'}$ to be negative. Therefore, according to the auxiliary transition current density, each element of $\hat{V}_{\text{pol},M}$ in Eq. (24) can be expressed as

$$\langle a; \{0\} | \hat{V}_{\text{pol},A} | a'; \{1_l(\mathbf{s}, \omega)\} \rangle = - \int d^3 \mathbf{r} \int_0^\infty d\omega' (i\omega')^{-1} \langle \{0\} | \hat{\mathbf{E}}(\mathbf{r}, \omega') | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \mathcal{J}_{aa'}(\mathbf{r}; -\omega'), \quad (26a)$$

$$\langle b'; \{1_l(\mathbf{s}, \omega)\} | \hat{V}_{\text{pol},B} | b; \{0\} \rangle = \int d^3 \mathbf{r} \int_0^\infty d\omega' (i\omega')^{-1} \langle \{1_l(\mathbf{s}, \omega)\} | \hat{\mathbf{E}}^\dagger(\mathbf{r}, \omega') | \{0\} \rangle \cdot \mathcal{J}_{b'b}(\mathbf{r}; -\omega'), \quad (26b)$$

$$\langle b'; \{0\} | \hat{V}_{\text{pol},B} | b; \{1_l(\mathbf{s}, \omega)\} \rangle = - \int d^3 \mathbf{r} \int_0^\infty d\omega' (i\omega')^{-1} \langle \{0\} | \hat{\mathbf{E}}(\mathbf{r}, \omega') | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \mathcal{J}_{b'b}(\mathbf{r}; \omega'), \quad (26c)$$

$$\langle a; \{1_l(\mathbf{s}, \omega)\} | \hat{V}_{\text{pol},A} | a'; \{0\} \rangle = \int d^3 \mathbf{r} \int_0^\infty d\omega' (i\omega')^{-1} \langle \{1_l(\mathbf{s}, \omega)\} | \hat{\mathbf{E}}^\dagger(\mathbf{r}, \omega') | \{0\} \rangle \cdot \mathcal{J}_{aa'}(\mathbf{r}; \omega'). \quad (26d)$$

The details can be found in Appendix B. Note that the integral variable ω' differs from the frequency ω in the single-polariton Fock state. Substituting Eqs. (6) and (26) into Eq. (24) with mathematical operations and using the identity to contract two dyadic Green's functions

$$\text{Im} \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega) = \int d^3 \mathbf{s} \frac{\omega^2 \epsilon_1(\mathbf{s}, \omega)}{c^2} \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{s}, \omega) \cdot \overline{\overline{\mathbf{G}}}^\dagger(\mathbf{r}', \mathbf{s}, \omega), \quad (27)$$

we finally obtain that the transition amplitude of \mathcal{T}_2 becomes

$$\langle f | \hat{\mathcal{T}}_2 | i \rangle = \frac{\hbar}{\pi \epsilon_0 c^2} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \int_0^\infty d\omega \left(\frac{\mathcal{J}_{aa'}(\mathbf{r}; -\omega) \cdot \text{Im} \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathcal{J}_{b'b}(\mathbf{r}'; -\omega)}{\hbar(\omega_b - \omega_{b'} - \omega) + i\eta} + \frac{\mathcal{J}_{b'b}(\mathbf{r}; \omega) \cdot \text{Im} \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathcal{J}_{aa'}(\mathbf{r}'; \omega)}{\hbar(\omega_{a'} - \omega_a - \omega) + i\eta} \right). \quad (28)$$

To further simplify the transition amplitude in Eq. (28), we next evaluate the ω integral by contour integration in the complex domain. We evaluate the ω integral by extending the interval $[0, \infty)$ to the whole real axis through the transformation $\omega \rightarrow -\omega$ to the first term in Eq. (28) and using the identity $\text{Im} \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', -\omega) = -\text{Im} \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega)$ [36,57]. Next, by exchanging the inner product order of the dyadic Green's function (by Onsager reciprocity [57]), we extend the ω integral to the whole real axis

$$\langle f | \hat{\mathcal{T}}_2 | i \rangle = \frac{\hbar}{\pi \epsilon_0 c^2} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \int_{-\infty}^\infty d\omega \frac{\mathcal{J}_{b'b}(\mathbf{r}; \omega) \cdot \text{Im} \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathcal{J}_{aa'}(\mathbf{r}'; \omega)}{\hbar(\omega_\Gamma - \omega) + i\eta \text{sgn}(\omega)}, \quad (29)$$

where $\text{sgn}(z) \equiv z/|z|$ is a sign function. Here we assume that the transition frequencies of entities A and B are the same, $\omega_\Gamma = \omega_{a'} - \omega_a = \omega_{b'} - \omega_b$, because we focus on the process of resonance energy transfer. Moreover, because

$\text{Im} \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega)$ is not holomorphic, we rewrite Eq. (29) as

$$\langle f | \hat{\mathcal{T}}_2 | i \rangle = \frac{\hbar}{\pi \epsilon_0} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \int_{-\infty}^\infty d\omega I(\mathbf{r}, \mathbf{r}', \omega), \quad (30)$$

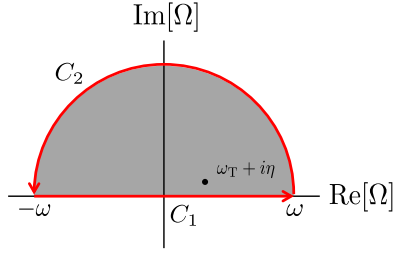


FIG. 1. Illustration of the contour adopted in the ω integral. The total closed contour C is equal to $C_1 + C_2$. A singularity at $\Omega = \omega_T + i\eta$ is located in the upper complex half plane.

where

$$I(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{2ic^2} \left(\frac{\mathcal{J}_{b'b}(\mathbf{r}; \omega) \cdot \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathcal{J}_{aa'}(\mathbf{r}'; \omega)}{\hbar(\omega_T - \omega) + i\eta \operatorname{sgn}(\omega)} - \frac{\mathcal{J}_{b'b}(\mathbf{r}; \omega) \cdot \overline{\overline{\mathbf{G}}}^*(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathcal{J}_{aa'}(\mathbf{r}'; \omega)}{\hbar(\omega_T - \omega) + i\eta \operatorname{sgn}(\omega)} \right). \quad (31)$$

By using the fact that the dyadic Green's function $\overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega)$ is holomorphic in the upper complex half plane [36], we choose the path, as shown in Fig. 1, and evaluate the ω integral. Hence, the ω integral becomes

$$\int_{-\infty}^{\infty} I(\mathbf{r}, \mathbf{r}', \omega) d\omega = \oint_C I(\mathbf{r}, \mathbf{r}', \Omega) d\Omega - \int_{C_2} I(\mathbf{r}, \mathbf{r}', \Omega) d\Omega. \quad (32)$$

According to the result derived in Appendix C, the contour integral gives the result

$$\langle f | \hat{\mathcal{T}}_2 | i \rangle|_{C_2} = \frac{1}{\epsilon_0 \omega_T^2} \int d^3 \mathbf{r} \mathbf{j}_{b'b}^{\parallel}(\mathbf{r}) \cdot \mathbf{j}_{aa'}^{\parallel}(\mathbf{r}) \quad (33)$$

$$= \langle a; b' | \hat{V}_{AB} | a'; b \rangle. \quad (34)$$

In Eq. (33) the coupling of longitudinal transition current densities between entities A and B can be further reduced to the Coulomb interaction form (the derivation details can be found in Appendix D), as a consequence of the Coulomb gauge. For the contour integral of the closed path $C = C_1 + C_2$, according to the residue theorem, we can obtain

$$\begin{aligned} \oint_C I(\mathbf{r}, \mathbf{r}', \Omega) d\Omega &= 2\pi i \operatorname{Res}[I(\mathbf{r}, \mathbf{r}', \Omega), \omega_T + i\eta/\hbar] \\ &= \frac{\pi}{\hbar c^2} \mathbf{j}_{b'b}(\mathbf{r}) \cdot \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega_T) \cdot \mathbf{j}_{aa'}(\mathbf{r}'), \end{aligned}$$

which indicates that

$$\begin{aligned} \langle f | \hat{\mathcal{T}}_2 | i \rangle|_C &= \frac{1}{\epsilon_0 c^2} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \\ &\times \mathbf{j}_{b'b}(\mathbf{r}) \cdot \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega_T) \cdot \mathbf{j}_{aa'}(\mathbf{r}'). \end{aligned} \quad (35)$$

Recall that the auxiliary current density defined in Eq. (25) gives $\mathcal{J}_{b'b}(\mathbf{r}; \omega_T) = \mathbf{j}_{b'b}(\mathbf{r})$ and $\mathcal{J}_{aa'}(\mathbf{r}'; \omega_T) = \mathbf{j}_{aa'}(\mathbf{r}')$. Finally,

according to Eqs. (22), (32), (33), and (35), we obtain the total transition amplitude

$$\langle f | \hat{\mathcal{T}} | i \rangle = \frac{1}{\epsilon_0 c^2} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \mathbf{j}_{b'b}(\mathbf{r}) \cdot \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega_T) \cdot \mathbf{j}_{aa'}(\mathbf{r}'). \quad (36)$$

Note that the transition amplitudes in Eqs. (22) and (33) mutually cancel out. Finally, we obtain the RET rate in terms of transition current density in the expression

$$\begin{aligned} \Gamma &= \frac{2\pi}{\hbar^2} \int_0^{\infty} d\omega \sum_{(a,b')} \sum_{(a',b)} P_{a'} P_b \left| \frac{1}{\epsilon_0 c^2} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \mathbf{j}_{b'b}(\mathbf{r}) \cdot \overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{j}_{aa'}(\mathbf{r}') \right|^2 \delta(\omega_{a'} - \omega_a - \omega) \\ &\times \delta(\omega_b - \omega_b - \omega), \end{aligned} \quad (37)$$

where (a', b) $[(a, b')]$ denotes the grouped indices of the initial (final) state and $P_{a'}$ (P_b) denotes the initial-state probability distribution of the entity A (B). Recall that the transition frequencies of A and B are the same, $\omega_{a'} - \omega_a = \omega_b - \omega_b$. In the current stage, we have derived an explicit form of the RET rates in terms of transition current density, as shown in Eq. (37), but this equation cannot be used to directly evaluate RET rates in material systems via *ab initio* methods. To solve this issue, we adopt a further approximation in the next section.

C. Transition current density and molecule

To evaluate the transition current density via *ab initio* methods, it is necessary to separate the electronic and nuclear degrees of freedom (approach to recapturing the vibronic effect can be found in Refs. [73–75]). In the same spirit of the Condon approximation [76,77], we approximate the transition current density to

$$\mathbf{j}_{mm'}(\mathbf{r}) = \langle m | \hat{\mathbf{j}}_M(\mathbf{r}) | m' \rangle \approx \langle \phi_{M,\gamma} | \hat{\mathbf{j}}_M(\mathbf{r}) | \phi_{M,\gamma'} \rangle_{\{\mathbf{R}\}} \langle \chi_{M,\nu} | \chi_{M,\nu'} \rangle, \quad (38)$$

where $|\phi_{M,\gamma}\rangle$ denotes the γ th electronic state and $|\chi_{M,\nu}\rangle$ is the ν th nuclear state associated with the γ th electronic state. Here the subscript $\{\mathbf{R}\}$ represents the electronic element being evaluated under a specific nuclear coordinate $\{\mathbf{R}\}$. The Condon-like approximation allows us to separate the electronic and nuclear degrees of freedoms. As a result, we can focus only on the electronic transition current density, and the contribution of the nuclear part can be attributed to the nuclear wavefunction overlap $\langle \chi_{M,\nu} | \chi_{M,\nu'} \rangle$. As a consequence, the quantum number m is now assigned to the two indices, $m \rightarrow (\gamma, \nu)$. In addition, because most *ab initio* calculations are performed in the coordinate space, the projection of the states to the position-spin coordinates is required. After taking the projection and considering the antisymmetric property of electrons, we finally get the electronic transition current density (detail derivations can be found in Appendix E)

$$\begin{aligned} \mathbf{j}_{\gamma\gamma'}^M(\mathbf{r}) &\equiv \langle \phi_{M,\gamma} | \hat{\mathbf{j}}_M(\mathbf{r}) | \phi_{M,\gamma'} \rangle_{\{\mathbf{R}\}} \\ &= \frac{-i\hbar e N_{\text{el}}}{2m_{\text{el}}} [\tilde{\phi}_{M,\gamma}^*(\mathbf{r}; \{\mathbf{R}\}) \nabla \tilde{\phi}_{M,\gamma'}(\mathbf{r}; \{\mathbf{R}\}) \\ &\quad - \tilde{\phi}_{M,\gamma'}(\mathbf{r}; \{\mathbf{R}\}) \nabla \tilde{\phi}_{M,\gamma}^*(\mathbf{r}; \{\mathbf{R}\})], \end{aligned} \quad (39)$$

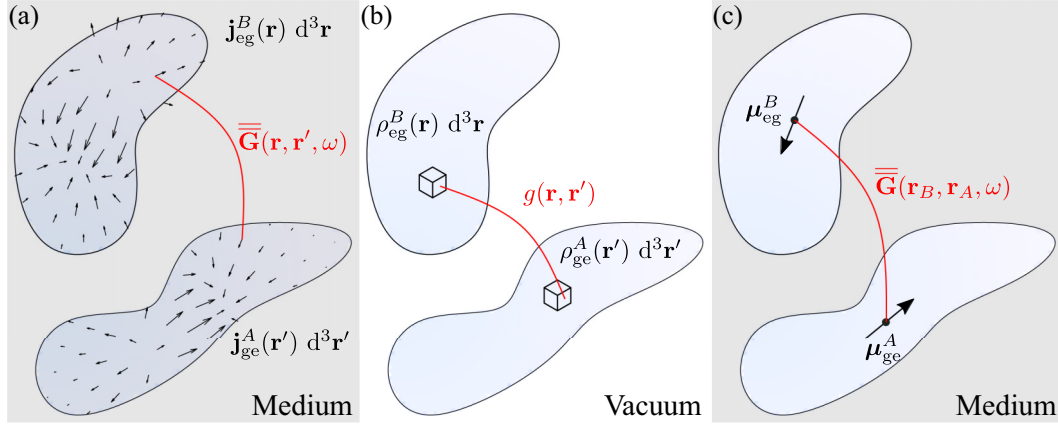


FIG. 2. Schematic diagram of how to calculate the electromagnetic coupling factors within three different theoretical approaches: (a) transition current density method $F(\omega) = |\epsilon_0^{-1} c^{-2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \mathbf{j}_{\text{eg}}^B(\mathbf{r}) \cdot \overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{j}_{\text{ge}}^A(\mathbf{r}')|^2$, (b) transition density method $F_{\text{TD}} = |(4\pi\epsilon_0)^{-1} \int d^3\mathbf{r} \int d^3\mathbf{r}' \rho_{\text{eg}}^B(\mathbf{r}) g(\mathbf{r}, \mathbf{r}') \rho_{\text{ge}}^A(\mathbf{r}')|^2$, and (c) transition dipole moment method $F_{\text{RDDI}}(\omega) = |\omega^2 \epsilon_0^{-1} c^{-2} \boldsymbol{\mu}_{\text{eg}}^B \cdot \overline{\mathbf{G}}(\mathbf{r}_B, \mathbf{r}_A, \omega) \cdot \boldsymbol{\mu}_{\text{ge}}^A|^2$.

where N_{el} is the total number of electrons in molecule M , e is the elementary charge of an electron, and m_{el} is the electron mass. Recall that the gradient operator only operates on \mathbf{r} , not $\{\mathbf{R}\}$. Moreover, $\tilde{\phi}_{M,\gamma}(\mathbf{r}; \{\mathbf{R}\})$ is the single-electron reduced wavefunction of the electronic state γ , which is defined by

$$\begin{aligned} & \tilde{\phi}_{M,\gamma}^*(\mathbf{x}_1; \{\mathbf{R}\}) \tilde{\phi}_{M,\gamma'}(\mathbf{x}_1; \{\mathbf{R}\}) \\ & \equiv \int \mathcal{D}\{\mathbf{x}_{\mu \neq 1}\} \phi_{M,\gamma}^*(\{\mathbf{x}_{\mu}\}; \{\mathbf{R}\}) \phi_{M,\gamma'}(\{\mathbf{x}_{\mu}\}; \{\mathbf{R}\}). \end{aligned} \quad (40)$$

In Eq. (40), $\{\mathbf{x}_{\mu}\}$ denotes the set of position-spin coordinates and $\phi_{M,\gamma}(\{\mathbf{x}_{\mu}\}; \{\mathbf{R}\})$ denotes the multielectron wavefunction of the electronic state γ , which is parametrized by a specific nuclear coordinate $\{\mathbf{R}\}$. The integration symbol represents a series of integrals except for \mathbf{x}_1 ,

$$\int \mathcal{D}\{\mathbf{x}_{\mu \neq 1}\} \equiv \int d\mathbf{x}_2 \cdots \int d\mathbf{x}_{N_{\text{el}}}.$$

In particular, in molecular systems, it is common to approximate the single-electron reduced wavefunctions as molecular orbitals (MOs), which can be obtained from *ab initio* calculations. If the transition between the electronic ground state and the first excited state is the most important transition, one can assume that the single-electron reduced wavefunction can be properly described by

$$\tilde{\phi}_{M,e}(\mathbf{r}; \{\mathbf{R}\}) \approx \phi_{M,\text{LUMO}}(\mathbf{r}; \{\mathbf{R}\}), \quad \gamma' \equiv e, \quad (41a)$$

$$\tilde{\phi}_{M,g}(\mathbf{r}; \{\mathbf{R}\}) \approx \phi_{M,\text{HOMO}}(\mathbf{r}; \{\mathbf{R}\}), \quad \gamma \equiv g, \quad (41b)$$

where the transition current density for the molecule M is determined by its highest occupied MO (HOMO), lowest unoccupied MO (LUMO), and the nuclear wavefunction overlap. Under the approximation in Eq. (41), the transition current density can be expressed as

$$\mathbf{j}_{mm'}(\mathbf{r}) = \langle \chi_{M,v} | \chi_{M,v'} \rangle \mathbf{j}_{\text{ge}}^M(\mathbf{r}). \quad (42)$$

According to Eqs. (39) and (41), one can obtain $\mathbf{j}_{\text{ge}}^M(\mathbf{r})$ as

$$\begin{aligned} \mathbf{j}_{\text{ge}}^M(\mathbf{r}) &= \frac{-i\hbar e N_{\text{el}}}{2m_{\text{el}}} [\phi_{M,\text{HOMO}}^*(\mathbf{r}; \{\mathbf{R}\}) \nabla \phi_{M,\text{LUMO}}(\mathbf{r}; \{\mathbf{R}\}) \\ & \quad - \phi_{M,\text{LUMO}}(\mathbf{r}; \{\mathbf{R}\}) \nabla \phi_{M,\text{HOMO}}^*(\mathbf{r}; \{\mathbf{R}\})]. \end{aligned} \quad (43)$$

Eventually, the RET rates in Eq. (37) can be expressed and interpreted as a generalized spectral overlap between two molecules and the electromagnetic coupling factor $F(\omega)$,

$$\Gamma = \frac{2\pi}{\hbar^2} \int_0^\infty d\omega \mathcal{L}_B^{\text{abs}}(\omega) F(\omega) \mathcal{L}_A^{\text{em}}(\omega), \quad (44)$$

with

$$\mathcal{L}_A^{\text{em}}(\omega) \equiv \sum_{a,a'} P_a |\langle \chi_{A,\alpha} | \chi_{A,\alpha'} \rangle|^2 \delta(\omega_{a'} - \omega_a - \omega),$$

$$\mathcal{L}_B^{\text{abs}}(\omega) \equiv \sum_{b,b'} P_b |\langle \chi_{B,\beta'} | \chi_{B,\beta} \rangle|^2 \delta(\omega_{b'} - \omega_b - \omega),$$

and

$$F(\omega) = \left| \frac{1}{\epsilon_0 c^2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \mathbf{j}_{\text{eg}}^B(\mathbf{r}) \cdot \overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{j}_{\text{ge}}^A(\mathbf{r}') \right|^2.$$

The schematic illustration of $F(\omega)$ is shown in Fig. 2(a). Note that $\mathcal{L}_B^{\text{abs}}(\omega)$ and $\mathcal{L}_A^{\text{em}}(\omega)$ are related to the absorption spectrum of B and the emission spectrum of A , respectively.

III. APPLICABILITY TO FORMER THEORIES

In Sec. II we showed how to derive the RET rate based on the transition current density approach in the framework of macroscopic QED. Furthermore, to demonstrate the generality of our theory, in this section we will prove that Eq. (44) can recover to the main results in previous studies: the TDC method [53] and the plasmon-coupled resonance energy transfer [58].

A. Transition density cube method

For the case when two entities are close, Krueger *et al.* developed the TDC method [53] in the electrostatic limit and

demonstrated how to calculate the Coulomb coupling between the pigments of the bacterial light-harvesting complex. To recover the main result given in the TDC method, we consider the free-space dyadic Green's function $\overline{\overline{\mathbf{G}}}_0(\mathbf{r}, \mathbf{r}', \omega)$ and adopt the electrostatic approximation

$$\overline{\overline{\mathbf{G}}}(\mathbf{r}, \mathbf{r}', \omega) \rightarrow \lim_{k_0 \rightarrow 0} \overline{\overline{\mathbf{G}}}_0(\mathbf{r}, \mathbf{r}', \omega) = \nabla \nabla \frac{1}{4\pi k_0^2 R}, \quad (45)$$

where $k_0 = \omega/c$, $R = |\mathbf{r} - \mathbf{r}'|$, and $\nabla \nabla$ is a dyadic operator. Thus, under the electrostatic limit, the electromagnetic coupling factor $F(\omega)$ becomes F_{TD} (TD denotes transition density) as

$$\begin{aligned} F_{\text{TD}} &\equiv \lim_{k_0 \rightarrow 0} F(\omega) \\ &= \left| \frac{1}{\epsilon_0 c^2} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \nabla \cdot \mathbf{j}_{\text{eg}}^B(\mathbf{r}) \frac{1}{4\pi k_0^2 R} \nabla' \cdot \mathbf{j}_{\text{ge}}^A(\mathbf{r}') \right|^2 \\ &= \left| \frac{1}{4\pi \epsilon_0} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \rho_{\text{eg}}^B(\mathbf{r}) g(\mathbf{r}, \mathbf{r}') \rho_{\text{ge}}^A(\mathbf{r}') \right|^2, \end{aligned} \quad (46)$$

where $\rho_{\text{ge}}^A(\mathbf{r}')$ and $\rho_{\text{eg}}^B(\mathbf{r})$ are transition densities of the entity A and the entity B , respectively, and $g(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$ is the scalar Green's function of the Poisson equation. Note that the derivation of Eq. (46) requires the continuity equation. Obviously, F_{TD} is exactly the continuous form of the electronic coupling corresponding to Eq. (5) in Ref. [53]. Incidentally, to numerically perform the integral in Eq. (46), Krueger *et al.* discretized the space into sufficiently small cubes shown in Fig. 2(b), hence the name transition density cube. Furthermore, because F_{TD} is independent of frequency, it can be taken out from the generalized spectral overlap and the RET rate becomes

$$\Gamma = \frac{2\pi}{\hbar^2} F_{\text{TD}} J, \quad J = \int_0^\infty d\omega \mathcal{L}_B^{\text{abs}}(\omega) \mathcal{L}_A^{\text{em}}(\omega), \quad (47)$$

where F_{TD} corresponds to $|V|^2$ in Eq. (8) in Ref. [53]. Note that the prefactor of Eq. (8) in Ref. [53] is slightly different from that in Eq. (47) because of their spectral overlap integrals in different units (J in Ref. [53] expressed in $\bar{v} = \omega/2\pi c$). In addition, we would like to point out that J defined in Eq. (47) is associated with the well-known spectral overlap in Förster's theory. In brief, the TDC method is the electrostatic limit of our theory in free space (i.e., neglect of the retardation effect in homogeneous, nondispersive, and nonabsorbing media).

B. Plasmon-coupled resonance energy transfer

Equation (44) is general for us to describe RET in linear, dispersive, and absorbing media. In other words, the effect of plasmon polaritons can be included in our theory, indicating that the main result of plasmon-coupled RET should be able to be recovered. The influence of plasmon polaritons on the RET rates under the EDA have been discussed in various electromagnetic environments [78–82]. To obtain the RET rate [Eq. (2)] in Ref. [58], we start from

the definition of the current density and apply the relation $\hat{\mathbf{p}}_\xi = -im_\xi \hbar^{-1} [\hat{\mathbf{r}}_\xi, \hat{H}_M]$,

$$\begin{aligned} \hat{\mathbf{j}}_M(\mathbf{r}) &= \sum_{\xi \in M} \frac{q_\xi}{2i\hbar} \{ \delta(\mathbf{r} - \hat{\mathbf{r}}_\xi) [\hat{\mathbf{r}}_\xi, \hat{H}_M] + \text{H.c.} \} \\ &\approx \sum_{\xi \in M} \frac{q_\xi}{2i\hbar} \{ \delta(\mathbf{r} - \mathbf{r}_M) [\hat{\mathbf{r}}_\xi - \mathbf{r}_M, \hat{H}_M] + \text{H.c.} \} \\ &= \frac{1}{i\hbar} [\hat{\boldsymbol{\mu}}_M, \hat{H}_M] \delta(\mathbf{r} - \mathbf{r}_M). \end{aligned} \quad (48)$$

Here we introduce the center of mass \mathbf{r}_M for the entity M and make the point-dipole approximation to get the dipole operator $\hat{\boldsymbol{\mu}}_M$. Through calculating $\langle m(m') | \hat{\mathbf{j}}_M(\mathbf{r}) | m'(m) \rangle = \mathbf{j}_{mm'(m'm)}(\mathbf{r})$ in Eq. (48), where $|m(m')\rangle$ is the m th (m' th) energy eigenstate of an entity M , we can obtain

$$\mathbf{j}_{mm'(m'm)}(\mathbf{r}) = \mp i\omega_{\text{T}} \boldsymbol{\mu}_{mm'(m'm)} \delta(\mathbf{r} - \mathbf{r}_M). \quad (49)$$

Next we take the Condon approximation to the transition dipole $\boldsymbol{\mu}_{mm'(m'm)}$, it is straightforward to obtain

$$\boldsymbol{\mu}_{mm'(m'm)} \approx \boldsymbol{\mu}_{\text{ge}(\text{eg})}^M \langle \chi_{M,v'(v')} | \chi_{M,v(v)} \rangle, \quad (50)$$

where $\boldsymbol{\mu}_{\text{ge}(\text{eg})}^M$ is the electronic transition dipole. Substituting Eqs. (49) and (50) into Eq. (37), we obtain that

$$\Gamma = \frac{2\pi}{\hbar^2} \int_0^\infty d\omega \mathcal{L}_B^{\text{abs}}(\omega) F_{\text{RDDI}}(\omega) \mathcal{L}_A^{\text{em}}(\omega), \quad (51)$$

where

$$F_{\text{RDDI}}(\omega) = \left| \frac{\omega^2}{\epsilon_0 c^2} \boldsymbol{\mu}_{\text{eg}}^B \cdot \overline{\overline{\mathbf{G}}}(\mathbf{r}_B, \mathbf{r}_A, \omega) \cdot \boldsymbol{\mu}_{\text{ge}}^A \right|^2 \quad (52)$$

is exactly the form of the resonant dipole-dipole interaction (RDDI) in Ref. [58]. Here we would like to mention that the definition of $F_{\text{RDDI}}(\omega)$ is slightly different from that of the coupling factor in Ref. [58] because the magnitudes of the transition dipoles of molecules A and B in Ref. [58] have been incorporated into the emission and absorption lineshape functions, i.e.,

$$W_A^{\text{em}}(\omega) = \frac{2\pi}{\hbar^2} |\boldsymbol{\mu}_{\text{ge}}^A|^2 \mathcal{L}_A^{\text{em}}(\omega), \quad (53a)$$

$$W_B^{\text{abs}}(\omega) = \frac{2\pi}{\hbar^2} |\boldsymbol{\mu}_{\text{eg}}^B|^2 \mathcal{L}_B^{\text{abs}}(\omega). \quad (53b)$$

According to Eq. (53), it is obvious that Eq. (44) covers the main result in Ref. [58]. Also, it is worth mentioning that $F_{\text{RDDI}}(\omega)$ in Eq. (52) is consistent with the transition tensor deduced from the framework of microscopic (or molecular) QED [33], which requires the entities in the homogeneous dilute media or in vacuum. In such a case, the electromagnetic coupling factor becomes

$$F_{\text{RDDI}}^{\text{dil}}(\omega) = \left| \frac{\omega^2}{\epsilon_0 c^2} \boldsymbol{\mu}_{\text{eg}}^B \cdot \overline{\overline{\mathbf{G}}}^{\text{dil}}(\mathbf{r}_B, \mathbf{r}_A, \omega) \cdot \boldsymbol{\mu}_{\text{ge}}^A \right|^2, \quad (54)$$

with

$$\begin{aligned} \overline{\overline{\mathbf{G}}}^{\text{dil}}(\mathbf{r}_B, \mathbf{r}_A, \omega) &= \frac{e^{ikR}}{4\pi R} \left\{ [3\hat{\mathbf{e}}_R \otimes \hat{\mathbf{e}}_R - \bar{\mathbf{I}}] \left(\frac{1}{(kR)^2} - \frac{i}{kR} \right) \right. \\ &\quad \left. + [\bar{\mathbf{I}} - \hat{\mathbf{e}}_R \otimes \hat{\mathbf{e}}_R] \right\}. \end{aligned} \quad (55)$$

TABLE I. Summary of RET theories with and without approximations. We use the following denotations: TCD, transition current density; TDM-1, transition dipole moment (macroscopic QED); TDM-2, transition dipole moment (molecular QED); FRET, Förster resonance energy transfer; and κ , orientation factor.

Method	Approximation	Rate	Coupling form
TCD		$\Gamma = \frac{2\pi}{\hbar^2} \int_0^\infty d\omega \mathcal{L}_B^{\text{abs}}(\omega) F(\omega) \mathcal{L}_A^{\text{em}}(\omega)$	$F(\omega) = \left \frac{1}{\epsilon_0 c^2} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \mathbf{j}_{\text{eg}}^B(\mathbf{r}) \cdot \overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{j}_{\text{ge}}^A(\mathbf{r}') \right ^2$
TD	Electrostatic	$\Gamma = \frac{2\pi}{\hbar^2} F_{\text{TD}} \int_0^\infty d\omega \mathcal{L}_B^{\text{abs}}(\omega) \mathcal{L}_A^{\text{em}}(\omega)$	$F_{\text{TD}} = \left \frac{1}{4\pi\epsilon_0} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \rho_{\text{eg}}^B(\mathbf{r}) g(\mathbf{r}, \mathbf{r}') \rho_{\text{ge}}^A(\mathbf{r}') \right ^2$
TDM-1	Point dipole	$\Gamma = \frac{2\pi}{\hbar^2} \int_0^\infty d\omega \mathcal{L}_B^{\text{abs}}(\omega) F_{\text{RDDI}}(\omega) \mathcal{L}_A^{\text{em}}(\omega)$	$F_{\text{RDDI}}(\omega) = \left \frac{\omega^2}{\epsilon_0 c^2} \boldsymbol{\mu}_{\text{eg}}^B \cdot \overline{\mathbf{G}}(\mathbf{r}_B, \mathbf{r}_A, \omega) \cdot \boldsymbol{\mu}_{\text{ge}}^A \right ^2$
TDM-2	Point dipole (dilute media)	$\Gamma = \frac{2\pi}{\hbar^2} \int_0^\infty d\omega \mathcal{L}_B^{\text{abs}}(\omega) F_{\text{RDDI}}^{\text{dil}}(\omega) \mathcal{L}_A^{\text{em}}(\omega)$	$F_{\text{RDDI}}^{\text{dil}}(\omega) = \left \frac{\omega^2}{\epsilon_0 c^2} \boldsymbol{\mu}_{\text{eg}}^B \cdot \overline{\mathbf{G}}^{\text{dil}}(\mathbf{r}_B, \mathbf{r}_A, \omega) \cdot \boldsymbol{\mu}_{\text{ge}}^A \right ^2$
FRET	Electrostatic & point dipole	$\Gamma = \frac{2\pi}{\hbar^2} F_{\text{FRET}} \int_0^\infty d\omega \mathcal{L}_B^{\text{abs}}(\omega) \mathcal{L}_A^{\text{em}}(\omega)$	$F_{\text{FRET}} = \frac{\kappa^2}{16\pi^2 \epsilon_0^2 R^6} \boldsymbol{\mu}_{\text{eg}}^B ^2 \boldsymbol{\mu}_{\text{ge}}^A ^2$

Note that $k = n\omega/c$, $\mathbf{r}_B - \mathbf{r}_A = R \hat{\mathbf{e}}_R$, and n is the refractive index for dilute media. Moreover, if we further impose the electrostatic limit on Eq. (51), we can obtain the famous Förster theory, as discussed in Ref. [58]. To emphasize the difference among these RET theories, we provide a schematic diagram, shown in Fig. 2, that depicts the key concepts of the three electromagnetic coupling factors in RET theories.

IV. CONCLUSION

The resonant dipole-dipole interaction has been widely used to describe light-matter interaction in physics, chemistry, and materials science; however, the RDDI is only a first-step approximation because it cannot fully contain the structural information of entities (e.g., atoms, molecules, quantum dots, and two-dimensional materials) when describing light-matter interactions. To include a spatially dependent light-matter interaction, we developed the generalized RET theory based on the concept of transition current density in the presence of linear, dispersive, and absorbing media within the framework of macroscopic QED. By expanding the Born series up to the second order in the time-dependent perturbation theory, we successfully derived the RET rate in the generalized-coupling expression of the transition dipole moment. Furthermore, by applying the Condon-like approximation to the transition current density, we separated the electronic and nuclear degrees of freedom and showed that the transition current density can be described by the HOMO and LUMO, which can be obtained from *ab initio* calculations. Moreover, we expressed the RET rates in terms of the generalized spectral overlap, as shown in Eq. (44). Finally, to demonstrate the validity and generality of Eq. (44), we proved that the present theory can be reduced to the main results in the previous studies, including TDC and plasmon-coupled RET. The comparison of several representative RET theories are summarized in Table I. In short, in the framework of macroscopic QED, the current approach provides one key step beyond the traditional RET theory based on RDDI [35,36,58] because Eq. (44) not only serves as a generalized version (i.e., containing retardation effect) of the TDC method, but also includes the influence of photonic environments, e.g., polaritons.

The generalized RET theory beyond the RDDI has been presented in this work. However, this study is just the beginning, and several issues are worth further exploration. First,

in the present theory, we do not consider the mechanism of Dexter energy transfer [20–23] (i.e., electron exchange between two entities). This mechanism becomes important when the wave-function overlap of two entities cannot be negligible. Second, the quantum dynamics of RET cannot be described in the present theory due to the limitation of Fermi's golden rule. How to generalize the theory to include quantum dynamics is an intriguing but challenging issue. In the end, we leave the numerical demonstration to the future study and hope that the present theory will inspire further investigation into the basic theory of energy transfer and its applications.

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APPENDIX A: CONTINUOUS FORM OF $\hat{\mathbf{A}}(\hat{\mathbf{r}}_\xi) \cdot \hat{\mathbf{p}}_\xi$ IN EQ. (13)

In this Appendix we prove that the order of momentum operator and Dirac δ function do not affect the result in the Coulomb gauge, i.e.,

$$\begin{aligned} & \sum_{\xi \in M} \frac{q_\xi}{2m_\xi} \int d^3 \mathbf{r} \hat{\mathbf{A}}(\mathbf{r}) \cdot \hat{\mathbf{p}}_\xi \delta(\mathbf{r} - \hat{\mathbf{r}}_\xi) \\ &= \sum_{\xi \in M} \frac{q_\xi}{2m_\xi} \int d^3 \mathbf{r} \hat{\mathbf{A}}(\mathbf{r}) \cdot \delta(\mathbf{r} - \hat{\mathbf{r}}_\xi) \hat{\mathbf{p}}_\xi. \end{aligned} \quad (\text{A1})$$

We start from the Fourier expression of Dirac δ functions,

$$\delta(\mathbf{r} - \hat{\mathbf{r}}_\xi) = \frac{1}{(2\pi\hbar)^3} \int d^3 \mathbf{p} e^{i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_\xi)/\hbar}. \quad (\text{A2})$$

According to Eq. (A2), the product of $\hat{\mathbf{p}}_\xi$ and $\delta(\mathbf{r} - \hat{\mathbf{r}}_\xi)$ becomes

$$\hat{\mathbf{p}}_\xi \delta(\mathbf{r} - \hat{\mathbf{r}}_\xi) = \frac{1}{(2\pi\hbar)^3} \int d^3 \mathbf{p} \hat{\mathbf{p}}_\xi \sum_{n=0}^{\infty} \frac{[i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_\xi)/\hbar]^n}{n!}, \quad (\text{A3})$$

where we take the Maclaurin series of the exponential function. Next we exchange the order of operators $\hat{\mathbf{p}}_\xi$ and $\hat{\mathbf{r}}_\xi$.

For the term of the n th power, we obtain the recursive relation

$$\hat{\mathbf{p}}_{\xi} [i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_{\xi})/\hbar]^n = \{[i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_{\xi})/\hbar] \hat{\mathbf{p}}_{\xi} - \mathbf{p}\} [i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_{\xi})/\hbar]^{n-1}, \quad (\text{A4})$$

with the canonical commutation relation $[\hat{r}_{\xi,j}, \hat{p}_{\xi,k}] = i\hbar\delta_{jk}$. Using Eq. (A4), we can show that

$$\hat{\mathbf{p}}_{\xi} [i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_{\xi})/\hbar]^n = [i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_{\xi})/\hbar]^n \hat{\mathbf{p}}_{\xi} - n\mathbf{p} [i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_{\xi})/\hbar]^{n-1}. \quad (\text{A5})$$

Hence, Eq. (A3) becomes

$$\hat{\mathbf{p}}_{\xi} \delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}) = \frac{1}{(2\pi\hbar)^3} \int d^3\mathbf{p} e^{i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_{\xi})/\hbar} \hat{\mathbf{p}}_{\xi} - \frac{1}{(2\pi\hbar)^3} \int d^3\mathbf{p} \mathbf{p} e^{i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_{\xi})/\hbar}. \quad (\text{A6})$$

In Eq. (A6) we convert the infinite series back to exponential functions. Note that the integrand of the second term in Eq. (A6) can be further rewritten as

$$-\mathbf{p} e^{i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_{\xi})/\hbar} = i\hbar \nabla e^{i\mathbf{p} \cdot (\mathbf{r} - \hat{\mathbf{r}}_{\xi})/\hbar}, \quad (\text{A7})$$

where the gradient operator acts on functions containing \mathbf{r} . Taking the momentum integral, we obtain the identity

$$\hat{\mathbf{p}}_{\xi} \delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}) = \delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}) \hat{\mathbf{p}}_{\xi} + i\hbar \nabla \delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}). \quad (\text{A8})$$

Finally, it is straightforward to obtain that

$$\begin{aligned} & \sum_{\xi \in M} \frac{q_{\xi}}{2m_{\xi}} \int d^3\mathbf{r} \hat{\mathbf{A}}(\mathbf{r}) \cdot \hat{\mathbf{p}}_{\xi} \delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}) \\ &= \sum_{\xi \in M} \frac{q_{\xi}}{2m_{\xi}} \int d^3\mathbf{r} \hat{\mathbf{A}}(\mathbf{r}) \cdot \delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}) \hat{\mathbf{p}}_{\xi} \\ &+ \sum_{\xi \in M} \frac{q_{\xi}}{2m_{\xi}} \int d^3\mathbf{r} (-i\hbar) \delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}) \nabla \cdot \hat{\mathbf{A}}(\mathbf{r}) \end{aligned} \quad (\text{A9})$$

$$= \sum_{\xi \in M} \frac{q_{\xi}}{2m_{\xi}} \int d^3\mathbf{r} \hat{\mathbf{A}}(\mathbf{r}) \cdot [\delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}) \hat{\mathbf{p}}_{\xi}], \quad (\text{A10})$$

where we utilize integration by parts to get $\nabla \cdot \hat{\mathbf{A}}(\mathbf{r})$. Moreover, the choice of the Coulomb gauge makes $\nabla \cdot \hat{\mathbf{A}}(\mathbf{r}) = 0$. Thus, the order of $\delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi})$ and $\hat{\mathbf{p}}_{\xi}$ does not alter the result in the Coulomb gauge.

APPENDIX B: DERIVATION OF EQ. (26)

In this Appendix we show the detailed derivation of Eq. (26). According to the definition in Eq. (13), we divide the discussion into two parts, the scalar coupling $[\hat{\varphi}(\mathbf{r}) \hat{\rho}_M(\mathbf{r})]$ and the vector coupling $[\hat{\mathbf{A}}(\mathbf{r}) \cdot \hat{\mathbf{j}}_M(\mathbf{r})]$. The key step to deriving Eq. (26) is to express the scalar coupling in terms of a currentlike operator. Because the scalar coupling is associated

with the longitudinal interaction, we begin with the quantity

$$\begin{aligned} & \int d^3\mathbf{r} \langle \{0\} | \hat{\mathbf{E}}(\mathbf{r}) | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \hat{\mathbf{j}}_{mm'(m'm)}^{\parallel}(\mathbf{r}) \\ &= \int d^3\mathbf{r} \langle \{0\} | \hat{\mathbf{E}}^{\parallel}(\mathbf{r}) | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \hat{\mathbf{j}}_{mm'(m'm)}^{\parallel}(\mathbf{r}) \\ &= \int d^3\mathbf{r} \langle \{0\} | \hat{\varphi}(\mathbf{r}) | \{1_l(\mathbf{s}, \omega)\} \rangle [\nabla \cdot \hat{\mathbf{j}}_{mm'(m'm)}^{\parallel}(\mathbf{r})] \\ &= - \int d^3\mathbf{r} \langle \{0\} | \hat{\varphi}(\mathbf{r}) | \{1_l(\mathbf{s}, \omega)\} \rangle \dot{\rho}_{mm'(m'm)}(\mathbf{r}), \end{aligned} \quad (\text{B1})$$

where

$$\hat{\mathbf{j}}_{mm'(m'm)}^{\parallel}(\mathbf{r}) \equiv \langle m(m') | \hat{\mathbf{j}}_M(\mathbf{r}) | m'(m) \rangle, \quad (\text{B2a})$$

$$\rho_{mm'(m'm)}(\mathbf{r}) \equiv \langle m(m') | \hat{\rho}_M(\mathbf{r}) | m'(m) \rangle \quad (\text{B2b})$$

are the elements of the transition charge density and transition current density for the entity M . To obtain Eq. (B1), we first use the symmetry of orthogonal projections to get the longitudinal electric field and then take the integration by parts to get the divergence of the transition current density. Furthermore, by utilizing the continuity equation $\nabla \cdot \hat{\mathbf{j}}_{mm'(m'm)}^{\parallel}(\mathbf{r}) = -\dot{\rho}_{mm'(m'm)}(\mathbf{r})$, we replace the divergence of the transition current density by the time derivative of transition charge density. It is worth noting that the continuity equation is valid as we suppose that charge transfer processes do not happen between entities, i.e., the number of charges for each entity is conserved. In addition, the time derivative transition charge density $\dot{\rho}_{mm'(m'm)}(\mathbf{r})$ can be replaced according to the relation

$$\begin{aligned} \dot{\rho}_{mm'(m'm)}(\mathbf{r}) &= \langle m(m') | \frac{1}{i\hbar} [\hat{\rho}_M(\mathbf{r}), \hat{H}_M] | m'(m) \rangle \\ &= \mp i\omega_{m'm} \rho_{mm'(m'm)}(\mathbf{r}), \end{aligned} \quad (\text{B3})$$

where $\omega_{m'm} = \omega_{m'} - \omega_m$ and $\hbar\omega_{m'm}$ is the energy of the state $|m'(m)\rangle$. Substituting Eq. (B3) into Eq. (B1), we obtain the relation

$$\begin{aligned} & \int d^3\mathbf{r} \langle \{0\} | \hat{\varphi}(\mathbf{r}) | \{1_l(\mathbf{s}, \omega)\} \rangle \rho_{mm'(m'm)}(\mathbf{r}) \\ &= \int d^3\mathbf{r} \langle \{0\} | \hat{\mathbf{E}}(\mathbf{r}) | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \frac{\hat{\mathbf{j}}_{mm'(m'm)}^{\parallel}(\mathbf{r})}{\pm i\omega_{m'm}}. \end{aligned} \quad (\text{B4})$$

Moreover, it is convenient to express the couplings in the frequency domain because the polariton states are portrayed in the frequency domain. By definition, the electric-field operator is the integral of the auxiliary electric-field operator [defined in Eq. (6)] and its Hermitian conjugate

$$\hat{\mathbf{E}}(\mathbf{r}) = \int_0^{\infty} d\omega [\hat{\mathbf{E}}(\mathbf{r}, \omega) + \text{H.c.}]. \quad (\text{B5})$$

By inserting Eq. (B5) into Eq. (B4) and defining the longitudinal auxiliary transition current density as

$$\hat{\mathbf{j}}_{mm'}^{\parallel}(\mathbf{r}; -\omega) \equiv \frac{-\omega}{\omega_{m'm}} \hat{\mathbf{j}}_{mm'}^{\parallel}(\mathbf{r}), \quad (\text{B6a})$$

$$\hat{\mathbf{j}}_{m'm}^{\parallel}(\mathbf{r}; +\omega) \equiv \frac{+\omega}{\omega_{m'm}} \hat{\mathbf{j}}_{m'm}^{\parallel}(\mathbf{r}), \quad (\text{B6b})$$

we obtain that

$$\int d^3\mathbf{r} \langle \{0\} | \hat{\varphi}(\mathbf{r}) | \{1_l(\mathbf{s}, \omega)\} \rangle \rho_{mm'}(\mathbf{r}) = - \int d^3\mathbf{r} \int d\omega' (i\omega')^{-1} \langle \{0\} | \hat{\mathbf{E}}(\mathbf{r}, \omega') | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \mathcal{J}_{mm'}^{\parallel}(\mathbf{r}; -\omega'), \quad (\text{B7a})$$

$$\int d^3\mathbf{r} \langle \{0\} | \hat{\varphi}(\mathbf{r}) | \{1_l(\mathbf{s}, \omega)\} \rangle \rho_{m'm}(\mathbf{r}) = - \int d^3\mathbf{r} \int d\omega' (i\omega')^{-1} \langle \{0\} | \hat{\mathbf{E}}(\mathbf{r}, \omega') | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \mathcal{J}_{m'm}^{\parallel}(\mathbf{r}; \omega'). \quad (\text{B7b})$$

Note that the denominator $\omega_{m'm}$ in Eq. (B6) is always defined as the positive transition frequency whatever the initial and final eigenkets are. Note that the electric-field operator in the frequency domain contains $\hat{\mathbf{E}}(\mathbf{r}, \omega)$ and its Hermitian conjugate $\hat{\mathbf{E}}^\dagger(\mathbf{r}, \omega)$. Here, only the operator $\hat{\mathbf{E}}(\mathbf{r}, \omega)$ is preserved because the element of $\hat{\mathbf{E}}^\dagger(\mathbf{r}, \omega)$ gives a zero, i.e.,

$$\langle \{0\} | \hat{\mathbf{E}}^\dagger(\mathbf{r}, \omega') | \{1_l(\mathbf{s}, \omega)\} \rangle \propto \langle \{0\} | \hat{\mathbf{f}}^\dagger(\mathbf{r}, \omega') | \{1_l(\mathbf{s}, \omega)\} \rangle = 0. \quad (\text{B8})$$

Similarly, by using the definition of the vector potential operator in Eq. (4b), we rewrite the vector coupling $[\hat{\mathbf{A}}(\mathbf{r}) \cdot \hat{\mathbf{j}}_M(\mathbf{r})]$ in the frequency domain

$$\int d^3\mathbf{r} \langle \{0\} | \hat{\mathbf{A}}(\mathbf{r}) | \{1_l(\mathbf{s}, \omega)\} \rangle \mathbf{j}_{mm'}(\mathbf{r}) = \int d^3\mathbf{r} \int_0^\infty d\omega' (i\omega')^{-1} \langle \{0\} | \hat{\mathbf{E}}(\mathbf{r}, \omega') | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \mathcal{J}_{mm'}^\perp(\mathbf{r}; -\omega'), \quad (\text{B9a})$$

$$\int d^3\mathbf{r} \langle \{0\} | \hat{\mathbf{A}}(\mathbf{r}) | \{1_l(\mathbf{s}, \omega)\} \rangle \mathbf{j}_{m'm}(\mathbf{r}) = \int d^3\mathbf{r} \int_0^\infty d\omega' (i\omega')^{-1} \langle \{0\} | \hat{\mathbf{E}}(\mathbf{r}, \omega') | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \mathcal{J}_{m'm}^\perp(\mathbf{r}; \omega'), \quad (\text{B9b})$$

where we use

$$\mathbf{j}_{mm'}^\perp(\mathbf{r}) = \mathcal{J}_{mm'}^\perp(\mathbf{r}; \omega) \quad (\text{B10})$$

to denote the transverse auxiliary transition current density because the transverse part of the auxiliary transition current density is independent of ω . From Eqs. (B6) and (B10), the total auxiliary transition current density finally becomes

$$\mathcal{J}_{mm'}(\mathbf{r}; \omega) = \mathcal{J}_{mm'}^\parallel(\mathbf{r}; \omega) + \mathcal{J}_{mm'}^\perp(\mathbf{r}; \omega). \quad (\text{B11})$$

According to Eqs. (B7), (B9), (B11), and (13), the above elements of $\hat{V}_{\text{pol},M}$ become

$$\langle a; \{0\} | \hat{V}_{\text{pol},A} | a'; \{1_l(\mathbf{s}, \omega)\} \rangle = - \int d^3\mathbf{r} \int_0^\infty d\omega' (i\omega')^{-1} \langle \{0\} | \hat{\mathbf{E}}(\mathbf{r}, \omega') | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \mathcal{J}_{aa'}(\mathbf{r}; -\omega'), \quad (\text{B12a})$$

$$\langle b'; \{0\} | \hat{V}_{\text{pol},B} | b; \{1_l(\mathbf{s}, \omega)\} \rangle = - \int d^3\mathbf{r} \int_0^\infty d\omega' (i\omega')^{-1} \langle \{0\} | \hat{\mathbf{E}}(\mathbf{r}, \omega') | \{1_l(\mathbf{s}, \omega)\} \rangle \cdot \mathcal{J}_{b'b}(\mathbf{r}; \omega'). \quad (\text{B12b})$$

Similarly, by taking the same procedure addressed above, we can obtain the rest of the elements listed in Eq. (26),

$$\langle b'; \{1_l(\mathbf{s}, \omega)\} | \hat{V}_{\text{pol},B} | b; \{0\} \rangle = \int d^3\mathbf{r} \int_0^\infty d\omega' (i\omega')^{-1} \langle \{1_l(\mathbf{s}, \omega)\} | \hat{\mathbf{E}}^\dagger(\mathbf{r}, \omega') | \{0\} \rangle \cdot \mathcal{J}_{b'b}(\mathbf{r}; -\omega'), \quad (\text{B13a})$$

$$\langle a; \{1_l(\mathbf{s}, \omega)\} | \hat{V}_{\text{pol},A} | a'; \{0\} \rangle = \int d^3\mathbf{r} \int_0^\infty d\omega' (i\omega')^{-1} \langle \{1_l(\mathbf{s}, \omega)\} | \hat{\mathbf{E}}^\dagger(\mathbf{r}, \omega') | \{0\} \rangle \cdot \mathcal{J}_{aa'}(\mathbf{r}; \omega'). \quad (\text{B13b})$$

Incidentally, it is easy to check the correctness of Eq. (B13) by taking the complex conjugate of Eq. (B12).

APPENDIX C: INTEGRAL ω ALONG PATH C_2

In this Appendix we present the details of evaluating the line integral of $I(\mathbf{r}, \mathbf{r}', \omega)$ along the semicircular path C_2 in the upper half plane. By definition, the integral is equal to

$$\int_{C_2} I(\mathbf{r}, \mathbf{r}', \Omega) d\Omega = \lim_{|\Omega| \rightarrow \infty} \int_0^\pi I(\mathbf{r}, \mathbf{r}', \Omega) i\Omega d\theta. \quad (\text{C1})$$

Recall that $\Omega = \omega e^{i\theta}$. Here we define $I(\mathbf{r}, \mathbf{r}', \Omega) = I_1(\mathbf{r}, \mathbf{r}', \Omega) + I_2(\mathbf{r}, \mathbf{r}', \Omega)$, where the two functions are

$$I_1(\mathbf{r}, \mathbf{r}', \Omega) = \frac{1}{2ic^2} \frac{\mathcal{J}_{b'b}(\mathbf{r}; \Omega) \cdot \overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \Omega) \cdot \mathcal{J}_{aa'}(\mathbf{r}'; \Omega)}{\hbar(\omega_T - \Omega) + i\eta \operatorname{sgn}(\Omega)},$$

$$I_2(\mathbf{r}, \mathbf{r}', \Omega) = \frac{-1}{2ic^2} \frac{\mathcal{J}_{b'b}(\mathbf{r}; \Omega) \cdot \overline{\mathbf{G}}^*(\mathbf{r}, \mathbf{r}', \Omega) \cdot \mathcal{J}_{aa'}(\mathbf{r}'; \Omega)}{\hbar(\omega_T - \Omega) + i\eta \operatorname{sgn}(\Omega)},$$

respectively. Using the identity of the dyadic Green's function

$$\lim_{|\Omega| \rightarrow \infty} \frac{\Omega^2}{c^2} \overline{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \Omega) = -\overline{\mathbf{I}}\delta(\mathbf{r} - \mathbf{r}'), \quad (\text{C2})$$

we evaluate the limit of $i\Omega I_1(\mathbf{r}, \mathbf{r}', \Omega)$ and obtain that

$$\lim_{|\Omega| \rightarrow \infty} i\Omega I_1(\mathbf{r}, \mathbf{r}', \Omega) = \frac{1}{2\omega_T^2} \mathbf{j}_{b'b}^{\parallel}(\mathbf{r}) \cdot \mathbf{j}_{aa'}^{\parallel}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'). \quad (\text{C3})$$

Note that the asymptotic behavior of the auxiliary current density is

$$\mathcal{J}_{m'm}(mm')(\mathbf{r}; \Omega) \sim \frac{\Omega}{\omega_{m'm}} \mathbf{j}_{m'm}(mm')(\mathbf{r}), \quad |\Omega| \rightarrow \infty,$$

and recall that $\omega_{a'a} = \omega_{b'b} = \omega_T$. A similar procedure is done on $I_2(\mathbf{r}, \mathbf{r}', \omega)$, but we should utilize the Schwarz reflection principle of the dyadic Green's function [57] and transform the integral variable to $\Omega \rightarrow -\Omega^*$ first. Finally, we obtain the

same result

$$\lim_{|\Omega| \rightarrow \infty} i\Omega I_2(\mathbf{r}, \mathbf{r}', \Omega) = \frac{1}{2\omega_T^2} \mathbf{j}_{b'b}^{\parallel}(\mathbf{r}) \cdot \mathbf{j}_{aa'}^{\parallel}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'). \quad (\text{C4})$$

It is obvious that the integrand in Eq. (C1) is no longer dependent of θ after taking the limit, as shown in Eqs. (C3) and (C4). Thus, the integral associated with $I_1(\mathbf{r}, \mathbf{r}', \omega)$ is π . Moreover, because we take the transformation $\Omega \rightarrow -\Omega^*$, the integral becomes

$$\int_0^{\pi} d\theta \rightarrow -\int_0^{-\pi} d\theta = \pi. \quad (\text{C5})$$

According to Eqs. (C3)–(C5), Eq. (C1) eventually becomes

$$\int_{C_2} I(\mathbf{r}, \mathbf{r}', \Omega) d\Omega = \frac{\pi}{\hbar\omega_T^2} \mathbf{j}_{b'b}^{\parallel}(\mathbf{r}) \cdot \mathbf{j}_{aa'}^{\parallel}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'). \quad (\text{C6})$$

APPENDIX D: INTERACTION OF LONGITUDINAL TRANSITION CURRENT DENSITIES

We prove that the interaction between two longitudinal transition current densities is exactly the Coulomb interaction, namely,

$$\frac{1}{\epsilon_0\omega_T^2} \int d^3\mathbf{r} \mathbf{j}_{b'b}^{\parallel}(\mathbf{r}) \cdot \mathbf{j}_{aa'}^{\parallel}(\mathbf{r}) = \langle a; b' | \hat{V}_{AB} | a'; b \rangle. \quad (\text{D1})$$

According to the definition of longitudinal fields [83], the longitudinal transition current density can be described as

$$\begin{aligned} \mathbf{j}_{m'm(mm')}^{\parallel}(\mathbf{r}) &\equiv \frac{-1}{4\pi} \nabla \int d^3\mathbf{r}' \frac{\nabla' \cdot \mathbf{j}_{m'm(mm')}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{\pm 1}{4\pi} \nabla \int d^3\mathbf{r}' \frac{i\omega_T \rho_{m'm(mm')}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (\text{D2})$$

Note that $\nabla \cdot \mathbf{j}_{m'm}(\mathbf{r}) = -i\omega_T \rho_{m'm}(\mathbf{r})$ and $\nabla \cdot \mathbf{j}_{mm'}(\mathbf{r}) = i\omega_T \rho_{mm'}(\mathbf{r})$ [recall Eq. (B3)]. By using the definition of charge density operator [Eq. (11)], the longitudinal transition current density of the molecule M becomes

$$\mathbf{j}_{m'm(mm')}^{\parallel}(\mathbf{r}) = \pm \frac{i\omega_T}{4\pi} \nabla \langle m'(m) | \sum_{\xi \in M} \frac{q_{\xi}}{|\mathbf{r} - \hat{\mathbf{r}}_{\xi}|} | m(m') \rangle. \quad (\text{D3})$$

Thus, the left-hand side of Eq. (D1) becomes

$$\begin{aligned} &\frac{1}{\epsilon_0\omega_T^2} \int d^3\mathbf{r} \mathbf{j}_{b'b}^{\parallel}(\mathbf{r}) \cdot \mathbf{j}_{aa'}^{\parallel}(\mathbf{r}) \\ &= \frac{1}{16\pi^2\epsilon_0} \int d^3\mathbf{r} \langle a; b' | \sum_{\xi \in A} \sum_{\zeta \in B} q_{\xi} q_{\zeta} K(\mathbf{r}, \hat{\mathbf{r}}_{\xi}, \hat{\mathbf{r}}_{\zeta}) | a'; b \rangle, \end{aligned} \quad (\text{D4})$$

where

$$K(\mathbf{r}, \hat{\mathbf{r}}_{\xi}, \hat{\mathbf{r}}_{\zeta}) = \nabla g(\mathbf{r}, \hat{\mathbf{r}}_{\xi}) \cdot \nabla g(\mathbf{r}, \hat{\mathbf{r}}_{\zeta}), \quad (\text{D5})$$

with $g(\mathbf{r}, \hat{\mathbf{r}}_{\xi}) = 1/|\mathbf{r} - \hat{\mathbf{r}}_{\xi}|$ the Green's function of Poisson's equation

$$\nabla^2 g(\mathbf{r}, \hat{\mathbf{r}}_{\xi}) = -4\pi \delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}). \quad (\text{D6})$$

By using the Green's identity, $K(\mathbf{r}, \hat{\mathbf{r}}_{\alpha}, \hat{\mathbf{r}}_{\beta})$ becomes

$$K(\mathbf{r}, \hat{\mathbf{r}}_{\xi}, \hat{\mathbf{r}}_{\zeta}) = \nabla \cdot [g(\mathbf{r}, \hat{\mathbf{r}}_{\xi}) \cdot \nabla g(\mathbf{r}, \hat{\mathbf{r}}_{\zeta})] - g(\mathbf{r}, \hat{\mathbf{r}}_{\xi}) \nabla^2 g(\mathbf{r}, \hat{\mathbf{r}}_{\zeta}). \quad (\text{D7})$$

Plugging the result of $K(\mathbf{r}, \hat{\mathbf{r}}_{\xi}, \hat{\mathbf{r}}_{\zeta})$ into Eq. (D4) and using the definition of the Green's function in Eq. (D6), we obtain that

$$\begin{aligned} &\frac{1}{\epsilon_0\omega_T^2} \int d^3\mathbf{r} \mathbf{j}_{b'b}^{\parallel}(\mathbf{r}) \cdot \mathbf{j}_{aa'}^{\parallel}(\mathbf{r}) \\ &= \frac{1}{4\pi\epsilon_0} \langle a; b' | \sum_{\xi \in A} \sum_{\zeta \in B} q_{\xi} q_{\zeta} g(\hat{\mathbf{r}}_{\xi}, \hat{\mathbf{r}}_{\zeta}) | a'; b \rangle \\ &= \langle a; b' | \hat{V}_{AB} | a'; b \rangle, \end{aligned} \quad (\text{D8})$$

which is exactly the Coulomb interaction between molecules A and B . Note that the first term in Eq. (D7) is associated with a surface integral at $\mathbf{r} \rightarrow \infty$; thus it converges to zero after the integration.

APPENDIX E: TRANSITION CURRENT DENSITY AND SINGLE-ELECTRON REDUCED WAVEFUNCTION

In the Appendix we show that the transition current density can be expressed by single-electron reduced wavefunctions. Beginning from the consequence of the Condon-like approximation in Eq. (38), we separate the nuclear degrees of freedom and define the electronic transition current density as

$$\begin{aligned} \mathbf{j}_{\gamma\gamma'}^M(\mathbf{r}) &\equiv \langle \phi_{M,\gamma} | \hat{\mathbf{j}}_M(\mathbf{r}) | \phi_{M,\gamma'} \rangle_{\{\mathbf{R}\}} \\ &= \langle \phi_{M,\gamma} | \sum_{\xi \in M_{\text{el}}} \frac{q_{\xi}}{2m_{\xi}} [\delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}) \hat{\mathbf{p}}_{\xi} + \text{H.c.}] | \phi_{M,\gamma'} \rangle_{\{\mathbf{R}\}}, \end{aligned} \quad (\text{E1})$$

where M_{el} is the set of electrons in the entity M . To project the states to the position-spin coordinates, we use the fermionic completeness relation [84]

$$\frac{1}{N!} \int \mathcal{D}\{\mathbf{x}_{\mu}\} |\{\mathbf{x}_{\mu}\}\rangle \langle\{\mathbf{x}_{\mu}\}| = \hat{\mathbf{I}}, \quad (\text{E2})$$

where N is the total number of position-spin coordinates, $\hat{\mathbf{I}}$ is the identity operator, and the integration symbol is defined as

$$\int \mathcal{D}\{\mathbf{x}_{\mu}\} \equiv \int d\mathbf{x}_1 \cdots \int d\mathbf{x}_N. \quad (\text{E3})$$

Here the μ th position-spin coordinate is denoted by $\mathbf{x}_{\mu} \equiv (\mathbf{r}_{\mu}, \omega_{\mu})$, where ω_{μ} is the spin coordinate. Moreover, the antisymmetrized state $|\{\mathbf{x}_{\mu}\}\rangle \equiv |\mathbf{x}_1, \dots, \mathbf{x}_N\rangle$ is the collection of position-spin coordinates. After inserting the identity into Eq. (E1), the electronic transition current density becomes

$$\begin{aligned} \mathbf{j}_{\gamma\gamma'}^M(\mathbf{r}) &= \frac{1}{(N_{\text{el}}!)^3} \int \mathcal{D}\{\mathbf{x}_{\mu}\} \int \mathcal{D}\{\mathbf{x}'_{\mu}\} \int \mathcal{D}\{\mathbf{x}''_{\mu}\} \\ &\quad \times \sum_{\xi \in M_{\text{el}}} \frac{q_{\xi}}{2m_{\xi}} \langle \phi_{M,\gamma} | \{\mathbf{x}_{\mu}\} \rangle_{\{\mathbf{R}\}} [|\{\mathbf{x}_{\mu}\}\rangle \delta(\mathbf{r} - \hat{\mathbf{r}}_{\xi}) |\{\mathbf{x}'_{\mu}\}\rangle \langle\{\mathbf{x}'_{\mu}\}| \hat{\mathbf{p}}_{\xi} |\{\mathbf{x}''_{\mu}\}\rangle + \text{c.c.}] \langle\{\mathbf{x}''_{\mu}\}| \phi_{M,\gamma'} \rangle_{\{\mathbf{R}\}}. \end{aligned} \quad (\text{E4})$$

Recall that N_{el} is the total number of electrons in the entity M and the subscript $\{\mathbf{R}\}$ represents that the electronic state is based on specific nuclear coordinates. In Eq. (E4) the projection of states to position-spin coordinates is related to the multielectron wavefunction. According to the previous study [84], the multielectron wavefunction can be expressed as

$$\phi_{M,\gamma(\gamma')}(\{\mathbf{x}_\mu\}; \{\mathbf{R}\}) = \frac{1}{\sqrt{N!}} \langle \{\mathbf{x}_\mu\} | \phi_{M,\gamma(\gamma')} \rangle_{\{\mathbf{R}\}}. \quad (\text{E5})$$

Note that $\phi_{M,\gamma(\gamma')}(\{\mathbf{x}_\mu\})$ is normalized. Furthermore, according to the two identities [84]

$$\langle \{\mathbf{x}_\mu\} | \delta(\mathbf{r} - \hat{\mathbf{r}}_\xi) | \{\mathbf{x}'_\mu\} \rangle = \delta(\mathbf{r} - \mathbf{r}_\xi) \sum_P (-1)^P \prod_{\mu \in M_{\text{el}}} \delta(\mathbf{x}_\mu - \mathbf{x}'_{P(\mu)}) \quad (\text{E6})$$

and

$$\langle \{\mathbf{x}'_\mu\} | \hat{\mathbf{p}}'_\xi | \{\mathbf{x}''_\mu\} \rangle = -i\hbar \nabla'_\xi \sum_P (-1)^P \prod_{\mu \in M_{\text{el}}} \delta(\mathbf{x}'_\mu - \mathbf{x}''_{P(\mu)}), \quad (\text{E7})$$

we can simplify the electronic transition current density to

$$\mathbf{j}_{\gamma\gamma'}^M(\mathbf{r}) = -\frac{i\hbar e N_{\text{el}}}{2m_{\text{el}}} \int \mathcal{D}\{\mathbf{x}'_\mu\} \delta(\mathbf{r} - \mathbf{r}_1) [\phi_{M,\gamma}^*(\{\mathbf{x}'_\mu\}; \{\mathbf{R}\}) \nabla'_1 \phi_{M,\gamma'}(\{\mathbf{x}'_\mu\}; \{\mathbf{R}\}) - \phi_{M,\gamma'}(\{\mathbf{x}'_\mu\}; \{\mathbf{R}\}) \nabla'_1 \phi_{M,\gamma}^*(\{\mathbf{x}'_\mu\}; \{\mathbf{R}\})], \quad (\text{E8})$$

where e is the elementary charge of an electron and m_{el} is electron mass. Note that the summations of P in Eqs. (E6) and (E7) denote the summations of all different permutations. To obtain Eq. (E8), we simplify the summation of $\xi \in M_{\text{el}}$ by multiplying N_{el} because electrons are indistinguishable, i.e., the total electronic transition current density is N_{el} times of the single-electron transition current density. Therefore, we express the single-electron transition current density by choosing $\xi = 1$ ($\mathbf{r}_\xi = \mathbf{r}_1$ and $\nabla'_\xi = \nabla'_1$). The other electronic degrees of freedoms for $\mu \neq \xi$ in multielectron wavefunctions ($\phi_{M,\gamma'}$ and $\phi_{M,\gamma}^*$) have been taken account in the overlap integral in Eq. (40),

$$\tilde{\phi}_{M,\gamma}^*(\mathbf{x}_1; \{\mathbf{R}\}) \tilde{\phi}_{M,\gamma'}(\mathbf{x}_1; \{\mathbf{R}\}) \equiv \int \mathcal{D}\{\mathbf{x}_{\mu \neq 1}\} \phi_{M,\gamma}^*(\{\mathbf{x}_\mu\}; \{\mathbf{R}\}) \phi_{M,\gamma'}(\{\mathbf{x}_\mu\}; \{\mathbf{R}\}),$$

and finally we derive the electronic transition current density as

$$\mathbf{j}_{\gamma\gamma'}^M(\mathbf{r}) = \frac{-i\hbar e N_{\text{el}}}{2m_{\text{el}}} [\tilde{\phi}_{M,\gamma}^*(\mathbf{r}; \{\mathbf{R}\}) \nabla \tilde{\phi}_{M,\gamma'}(\mathbf{r}; \{\mathbf{R}\}) - \tilde{\phi}_{M,\gamma'}(\mathbf{r}; \{\mathbf{R}\}) \nabla \tilde{\phi}_{M,\gamma}^*(\mathbf{r}; \{\mathbf{R}\})]. \quad (\text{E9})$$

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