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Distance dependence of two-atom dipole interactions with one atom in an excited state

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We present a Heisenberg-picture approach to the electric dipole interaction of two generally nonidentical atoms, one of which is initially excited, and address the question of whether the dependence of the interaction energy on the interatomic separation r is purely monotonic or is sinusoidally modulated as it falls off with r. We derive energies of both types and associate them with different model assumptions and physical effects. The sinusoidally modulated form is the interaction energy involved in reversible exchange of excitation ("pendulation"). The monotonic form characterizes an energy shift associated with effectively irreversible (Förster) excitation transfer.

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I. INTRODUCTION

The interaction of two atoms, one initially in its first excited state and the other in its ground state, has been considered in many papers [1]. Stephen [2] and McLachlan [3], among others, showed for identical atoms a sinusoidal modulation of the radiation rate and the interaction energy as a function of the interatomic separation r, just as would be expected from the interaction of two identical, classical dipole oscillators. A similar dependence on r was later obtained for nonidentical atoms [4–6]. Later work gave interaction energies of nonidentical atoms that decrease monotonically with r [7–12], but more recent work [13–16] again predicts a sinusoidally modulated interaction.

The purpose of this paper is to revisit the problem in a way that in our opinion helps to clarify the difference between the two forms of the interaction and shows that they are obtained under different assumptions and describe different physical effects. The sinusoidally modulated interaction describes the change in the transition frequency (and radiation rate) due to excitation exchange; it can be understood in terms of the coherent scattering by the unexcited atom of the field from the excited atom [16]. The monotonic form, in contrast, describes the energy shift of the initially unexcited "acceptor" as excitation is transferred from the initially excited "donor"; it is the shift in the ground-state energy of the acceptor associated with an effectively irreversible Förster excitation transfer [17,18]. A similar sort of distinction has been made between temporally modulated and monotonic excitation transfer rates corresponding, respectively, to "pendulation" (back-and-forth exchange of excitation) and "golden-rule" (irreversible excitation transfer) processes [19–21]. Here we focus mainly on energies.

Our approach is based on Heisenberg-picture operators. As in much of the cited work, we base the treatment on the model in which each atom (or molecule) is a two-state system at zero temperature. We do not explicitly address questions relating to poles in expressions for interaction energies, which have been a focus of recent work [13–16] that has been critical of the Power-Thirunamachandran papers [7,8], nor do we take issue with specific aspects of the calculations in any of the more recent papers. Our main point is simply that the two forms of interaction apply under different assumptions about the two-particle system.

In the following section we present the Heisenberg equations of motion used in our calculations. In Sec. III we consider the effect of the initially excited atom A on the initially unexcited atom B. We first illustrate the Heisenberg-picture approach by rederiving old results [1] for the excitation probability of atom B and then consider the shift in the energy levels and transition frequency of atom B associated with absorption of energy from atom A. These shifts have the same purely monotonic dependence on r obtained by Power and Thirunamachandran [7,8], and we relate the ground-state shift to the interaction energy accompanying Förster transfer that was derived by Cohen and Mukamel [17,18]. In Sec. IV we consider the level shift of atom A due to the scattering of its field by atom B [16] and derive the sinusoidally modulated dependence on r obtained by different methods in recent analyses. In Sec. V we summarize our results and conclusions.

II. HEISENBERG OPERATOR EQUATIONS

The atom-field Hamiltonian for our purposes is

$$\begin{aligned} H &= \hbar\omega_A\sigma_A^\dagger\sigma_A + \hbar\omega_B\sigma_B^\dagger\sigma_B + \sum_{\mathbf{k}\lambda}\hbar\omega_k a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}\lambda} \\ &\quad - i\sum_{\mathbf{k}\lambda}\sum_{j=A,B}\left(\frac{2\pi\hbar\omega_k}{V}\right)^{1/2}[a_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}_j} - a_{\mathbf{k}\lambda}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}_j}] \\ &\quad \times [\sigma_j + \sigma_j^\dagger]\mathbf{d}_j\cdot\mathbf{e}_{\mathbf{k}\lambda}. \end{aligned} \tag{1}$$

Here σ_j and $\sigma_j^\dagger$ are the two-state lowering and raising operators, respectively, and $a_{\mathbf{k}\lambda}$ ($a_{\mathbf{k}\lambda}^\dagger$) is the photon annihilation (creation) operator for the free-space field mode with wave vector $\mathbf{k}$ ($k = |\mathbf{k}| = \omega_k/c$) and polarization label λ ($\mathbf{k}\cdot\mathbf{e}_{\mathbf{k}1} = \mathbf{k}\cdot\mathbf{e}_{\mathbf{k}2} = \mathbf{e}_{\mathbf{k}1}\cdot\mathbf{e}_{\mathbf{k}2} = 0$). V is a quantization volume. We take the transition electric dipole moments $\mathbf{d}_j$ and the polarization unit vectors $\mathbf{e}_{\mathbf{k}\lambda}$ to be real. ω_j and $\mathbf{r}_j$ are, respectively, the transition angular frequency and the fixed position of atom j (j = A, B).

From the Pauli commutation relations satisfied by the two-state operators we obtain the Heisenberg equations of motion for the operators σ_A and $\sigma_{zA} = \sigma_A^\dagger \sigma_A - \sigma_A \sigma_A^\dagger$:

$$\dot{\sigma}_A(t) = -i\omega_A \sigma_A(t) - i[\sigma_{zA}(t)\mathcal{E}_{TA}^{(+)}(t) + \mathcal{E}_{TA}^{(-)}(t)\sigma_{zA}(t)], \quad (2)$$

$$\begin{aligned}\dot{\sigma}_{zA}(t) = {} & -2i[\sigma_A(t)\mathcal{E}_{TA}^{(+)}(t) + \mathcal{E}_{TA}^{(-)}(t)\sigma_A(t)] \\ & + 2i[\sigma_A^\dagger(t)\mathcal{E}_{TA}^{(+)}(t) + \mathcal{E}_{TA}^{(-)}(t)\sigma_A^\dagger(t)], \end{aligned} \quad (3)$$

$$\mathcal{E}_{TA}^{(\pm)}(t) = (\mathbf{d}_A/\hbar)\cdot \mathbf{E}_{TA}^{(\pm)}(t). \quad (4)$$

$\mathbf{E}_{TA}^{(+)}(t)$ and $\mathbf{E}_{TA}^{(-)}(t)$ are the parts of the total electric field operator at the position of atom A that derive from operators $a_{\mathbf{k}\lambda}$ and $a_{\mathbf{k}\lambda}^\dagger$, respectively. We have chosen to put the commuting (equal-time) atom and field operators in normal order. Equations (2) and (3), and the corresponding equations with A ↔ B, are the standard Heisenberg equations of motion for two-state atoms in an electric field. The field acting on atom A consists of a radiative reaction part, a source-free ("vacuum") part, and a part associated with any sources in addition to atom A. In the Markovian approximation the effect of the radiative reaction field is to replace $-i\omega_A\sigma_A(t)$ in Eq. (2) by $-i(\omega_A - i\beta_A)\sigma_A(t)$ and to add $-2\beta_A[\sigma_{zA}(t) + 1]$ to the right-hand side of Eq. (3), where $2\beta_A$ is the rate in free space of radiative decay of the excited state of atom A [22]. We denote the source-free field acting on atom A by $\mathbf{E}_{A0}(t)$ and define

$$\mathcal{E}_{A0}^{(\pm)} = (\mathbf{d}_A/\hbar)\cdot \mathbf{E}_{A0}^{(\pm)}(t). \quad (5)$$

We denote the field from atom B acting on atom A by $\mathbf{E}_{AB}(t)$ and define

$$\mathcal{E}_{AB}^{(\pm)}(t) = (\mathbf{d}_A/\hbar)\cdot \mathbf{E}_{AB}^{(\pm)}(t). \quad (6)$$

In the problem of interest there are no other "external" fields acting on atom A. The corresponding operators for the field experienced by atom B are defined in like manner.

In addition to the Markovian approximation we will make a rotating-wave approximation (RWA) in which we ignore "counterrotating" terms on the right-hand side of (2) and rapidly oscillating terms on the right-hand side of (3). Thus we replace (2) and (3) by

$$\dot{\sigma}_A(t) \cong -i(\omega_A - i\beta_A)\sigma_A(t) - i\sigma_{zA}(t)\mathcal{E}_A^{(+)}(t) \quad (7)$$

and

$$\begin{aligned}\dot{\sigma}_{zA}(t) \cong {} & -2\beta_A[\sigma_{zA}(t) + 1] \\ & + 2i\sigma_A^\dagger(t)\mathcal{E}_A^{(+)}(t) - 2i\mathcal{E}_A^{(-)}(t)\sigma_A(t), \end{aligned} \quad (8)$$

where

$$\mathcal{E}_A^{(\pm)}(t) = \mathcal{E}_{A0}^{(\pm)}(t) + \mathcal{E}_{AB}^{(\pm)}(t). \quad (9)$$

From the Hamiltonian and the commutation relations for the operators $a_{\mathbf{k}\lambda}$ and $a_{\mathbf{k}\lambda}^\dagger$ we obtain, in the free-space, mode continuum limit ($V \to \infty$),

$$\begin{aligned}\mathcal{E}_{AB}^{(+)}(t) \cong \frac{d_A d_B}{\hbar}\bigg\{ & -\frac{\mathcal{A}}{c^2 r}\ddot{\sigma}_B(t - r/c) \\ & + \mathcal{B}\left[\frac{1}{cr^2}\dot{\sigma}_B(t - r/c) + \frac{1}{r^3}\sigma_B(t-r/c)\right]\bigg\}\theta(t-r/c), \end{aligned} \quad (10)$$

where $\theta(t)$ is the unit step function and

$$\mathcal{A} = [\hat{\mathbf{d}}_A \cdot \hat{\mathbf{d}}_B - (\hat{\mathbf{d}}_A \cdot \hat{\mathbf{r}})(\hat{\mathbf{d}}_B \cdot \hat{\mathbf{r}})], \quad (11)$$

$$\mathcal{B} = 3(\hat{\mathbf{d}}_A \cdot \hat{\mathbf{r}})(\hat{\mathbf{d}}_B \cdot \hat{\mathbf{r}}) - \hat{\mathbf{d}}_A \cdot \hat{\mathbf{d}}_B. \quad (12)$$

Here $\hat{\mathbf{d}}_A$ and $\hat{\mathbf{d}}_B$ are unit vectors in the directions of $\mathbf{d}_A$ and $\mathbf{d}_B$, respectively. In writing (10) we have made the approximation of dropping counterrotating terms involving $\sigma_B^\dagger(t - r/c)$ [23].

Similarly,

$$\dot{\sigma}_B(t) \cong -i(\omega_B - i\beta_B)\sigma_B(t) - i\sigma_{zB}(t)\mathcal{E}_B^{(+)}(t) \quad (13)$$

and

$$\begin{aligned}\dot{\sigma}_{zB}(t) \cong {} & -2\beta_B[\sigma_{zB}(t) + 1] \\ & + 2i\sigma_B^\dagger(t)\mathcal{E}_B^{(+)}(t) - 2i\mathcal{E}_B^{(-)}(t)\sigma_B(t), \end{aligned} \quad (14)$$

$$\mathcal{E}_B^{(\pm)}(t) = \mathcal{E}_{B0}^{(\pm)}(t) + \mathcal{E}_{BA}^{(\pm)}(t), \quad (15)$$

$$\begin{aligned}\mathcal{E}_{BA}^{(+)}(t) \cong \frac{d_A d_B}{\hbar}\bigg\{ & -\frac{\mathcal{A}}{c^2 r}\ddot{\sigma}_A(t - r/c) \\ & + \mathcal{B}\left[\frac{1}{cr^2}\dot{\sigma}_A(t - r/c) + \frac{1}{r^3}\sigma_A(t-r/c)\right]\bigg\}\theta(t-r/c). \end{aligned} \quad (16)$$

III. EFFECT OF ATOM A ON ATOM B

A. Excitation probability of atom B

We consider first the effect of the initially excited atom A on the initially unexcited atom B. With $|\psi(t)\rangle$, the state of the atom-field system at time t, and $U(t)$, the time evolution operator, the probability that B is excited at time t is the expectation value over the initial state $|\psi(0)\rangle$ of the Heisenberg-picture operator $\sigma_B^\dagger(t)\sigma_B(t)$:

$$\begin{aligned} P_B(t) &= \langle\psi(t)|\sigma_B^\dagger(0)\sigma_B(0)|\psi(t)\rangle \\ &= \langle\psi(0)|U^\dagger(t)\sigma_B^\dagger(0)\sigma_B(0)U(t)|\psi(0)\rangle \\ &= \langle\psi(0)|\sigma_B^\dagger(t)\sigma_B(t)|\psi(0)\rangle = \langle\sigma_B^\dagger(t)\sigma_B(t)\rangle. \end{aligned} \quad (17)$$

From (13),

$$\dot{\sigma}_B(t) \cong -i(\omega_B - i\beta_B)\sigma_B(t) - i\sigma_{zB}((0)\mathcal{E}_B^{(+)}(t) \quad (18)$$

to lowest order in the atom-field coupling. Then, since atom B is initially unexcited and the field is initially in its vacuum state, $\langle\sigma_B^\dagger(0)\sigma_B(0)\rangle = 0$, $\langle\sigma_B^\dagger(0)\sigma_{zB}(0)\rangle = -\langle\sigma_B^\dagger(0)\rangle = 0$, $\mathcal{E}_{B0}^{(+)}(t)|\psi(0)\rangle = 0$, and

$$P_B(t) \cong \int_0^t dt' \int_0^t dt'' \langle\mathcal{E}_{BA}^{(-)}(t'')\mathcal{E}_{BA}^{(+)}(t')\rangle e^{i\omega_B(t'-t'')} e^{\beta_B(t'+t''-2t)}. \quad (19)$$

We have used the identity $\sigma_{zB}^2(0) = 1$.

Now from (7) and (16) with

$$\sigma_A(t - r/c) \cong \sigma_A(0)e^{-i(\omega_A - i\beta_A)(t-r/c)}, \quad (20)$$

$$\mathcal{E}_{BA}^{(+)}(t) \cong F\theta(t - r/c)\sigma_A(0)e^{-i(\omega_A - i\beta_A)(t-r/c)}, \quad (21)$$

where we have defined

$$F = \frac{d_A d_B}{\hbar} k_A^3 \left[\frac{\mathcal{A}}{k_A r} - \frac{i\mathcal{B}}{k_A^2 r^2} + \frac{\mathcal{B}}{k_A^3 r^3} \right]. \tag{22}$$

($k_A = \omega_A/c$.) From the assumption that atom A is initially excited [$\langle \sigma_A^\dagger(0)\sigma_A(0)\rangle = 1$] it follows that, to lowest order in $|F|$,

$$P_B(t) \cong \frac{|F|^2}{\Delta^2 + \gamma^2} \theta(t - r/c)[e^{-2\beta_A(t-r/c)} + e^{-2\beta_B(t-r/c)} - 2e^{-(\beta_A+\beta_B)(t-r/c)} \cos \Delta(t - r/c)], \tag{23}$$

$$\Delta = \omega_A - \omega_B, \quad \gamma = \beta_A - \beta_B. \tag{24}$$

For $\Delta^2 \gg \gamma^2$ and times $\gg r/c$ but much shorter than the radiative lifetimes,

$$P_B(t) \cong \frac{4|F|^2}{\Delta^2} \sin^2 \frac{1}{2}\Delta t. \tag{25}$$

The result (23) with $k_A r \gg 1$ was obtained many years ago by Breit [1]. For $\beta_A \gg \beta_B$, $\beta_A(t - r/c) \gg 1$, and $\beta_B(t - r/c) \ll 1$, for example,

$$P_B(t) \cong \frac{|F|^2}{\Delta^2 + \beta_A^2} \theta(t - r/c), \tag{26}$$

which is essentially the result obtained by Fermi [1]. In the case of identical atoms ($k_A = k_B = k_0$, $d_A = d_B = d$, and $\beta_A = \beta_B = \beta$), (23) reduces to

$$P_B(t) \cong |F e^{-\beta(t-r/c)}(t - r/c)|^2 \theta(t - r/c), \tag{27}$$

which is the first in a series of terms involving $t - nr/c$, with n being odd, obtained in Ref. [24] for the initially unexcited atom; for the initially excited atom there is likewise a series of such terms with n being even. All terms in the excitation-exchange series must be retained. Successive excitation-exchange probabilities for *nonidentical* atoms, however, fall off with increasingly higher powers of F/Δ.

We note for later reference that

$$|F|^2 \to \frac{2d_A^2 d_B^2}{9\hbar^2} k_A^6 \left[\frac{1}{k_A^2 r^2} + \frac{1}{k_A^4 r^4} + \frac{3}{k_A^6 r^6} \right] \tag{28}$$

when we average over random, independent orientations of $\hat{\mathbf{d}}_A$ and $\hat{\mathbf{d}}_B$, thus replacing $\mathcal{A}^2$ by 2/9, $\mathcal{B}^2$ by 2/3, and $2\mathcal{A}\mathcal{B}$ by −2/9.

B. Energy shift of atom B

We now turn our attention to the shift in energy of atom B in the field of atom A. For this purpose we return to the approximate equation (13) and take expectation values on both sides after inserting the formal solution of Eq. (14):

$$\langle \dot{\sigma}_B(t)\rangle \cong -i(\omega_B - i\beta_B)\langle \sigma_B(t)\rangle + (\cdots) - 2\int_0^t dt' \langle \mathcal{E}_{BA}^{(-)}(t')\sigma_B(t')\mathcal{E}_{BA}^{(+)}(t)\rangle e^{2\beta_B(t'-t)}. \tag{29}$$

Here $(\cdots)$ denotes terms that do not directly involve σ_B. To lowest (fourth) order in the atom-field coupling we obtain, using $\sigma_A^\dagger(0)\sigma_A(0)|\psi(0)\rangle = 1$, the approximation (21), and

$$\sigma_B(t') \cong \sigma_B(t) e^{-i(\omega_B - i\beta_B)(t'-t)}, \tag{30}$$

$$\begin{aligned}
\langle \dot{\sigma}_B(t)\rangle &\cong -i(\omega_B - i\beta_B)\langle \sigma_B(t)\rangle + (\cdots) \\
&\quad - 2|F|^2 \theta(t - r/c) e^{-2\beta_A(t-r/c)} \langle \sigma_B(t)\rangle \\
&\quad \times \int_{r/c}^t dt' e^{i(\Delta + i\gamma)(t'-t)} \\
&= -i(\omega_B - i\beta_B)\langle \sigma_B(t)\rangle + (\cdots) \\
&\quad + \frac{2i|F|^2}{\Delta + i\gamma} \theta(t - r/c)\langle \sigma_B(t)\rangle \\
&\quad \times \{e^{-2\beta_A(t-r/c)} - e^{-i\Delta(t-r/c)} e^{-(\beta_A+\beta_B)(t-r/c)}\}.
\end{aligned} \tag{31}$$

The factor proportional to $|F|^2$ and multiplying $\langle \sigma_B(t)\rangle$ can be related to a modification of the resonance frequency and homogeneous linewidth of atom B. The modification of the resonance frequency can be related to an interaction energy, but of course we can define an interaction energy only in a quasistationary regime in which radiative decay is negligible [2]. To most easily relate such an interaction energy to the energy calculated by Power and Thirunamachandran [7,8], we assume $\beta_A \ll \beta_B$, $\beta_A(t - r/c) \ll 1$, and $\beta_B(t - r/c) \gg 1$, so that deexcitation of atom A is negligible but atom B is rapidly deexcited; then, averaging over the temporal oscillations at frequency Δ, we obtain, for $t > r/c$,

$$\langle \dot{\sigma}_B(t)\rangle \cong -i(\omega_B + \Delta\omega_B - i[\beta_B + \Delta\beta_B])\langle \sigma_B(t)\rangle + (\cdots), \tag{32}$$

where

$$\Delta\omega_B = -\frac{2\Delta|F|^2}{\Delta^2 + \beta_B^2}, \tag{33}$$

$$\Delta\beta_B = \frac{2\beta_B|F|^2}{\Delta^2 + \beta_B^2}. \tag{34}$$

$\Delta\omega_B$ is the shift in the transition frequency of atom B: the difference between the upper- and lower-state energy shifts. It vanishes in the case of *identical* atoms ($\Delta = 0$). Since the real parts of the upper- and lower-state polarizabilities of a two-state atom have opposite signs [25] and the level shifts are proportional to the real parts of the polarizabilities, the level shift of the upper state is $-\Delta E_B$, where ΔE_B is the level shift of the lower state of atom B. In other words,

$$\Delta E_B = -\frac{1}{2}\hbar\Delta\omega_B = \frac{\hbar\Delta}{\Delta^2 + \beta_B^2}|F|^2 \cong \frac{\hbar}{\Delta}|F|^2. \tag{35}$$

We are assuming $|\Delta| \gg \beta_B$ as part of the condition that the two atoms are nonidentical. Now recall that we have made a rotating-wave approximation. Without this approximation we pick up additional terms involving $1/(\omega_A + \omega_B)$ in addition to $1/\Delta = 1/(\omega_A - \omega_B)$, with the result that $1/\Delta$ is replaced by

$$\frac{1}{\Delta} + \frac{1}{\omega_A + \omega_B} = \frac{2\omega_A}{\omega_A^2 - \omega_B^2} \tag{36}$$

and (35) is replaced by

$$\Delta E_B \cong \frac{4}{9}\frac{d_A^2 d_B^2}{\hbar c}\frac{k_B k_A^6}{k_A^2 - k_B^2}\left[\frac{1}{k_A^2 r^2} + \frac{1}{k_A^4 r^4} + \frac{3}{k_A^6 r^6}\right] \tag{37}$$

when we average over dipole orientations as in (28). This is exactly the result of Power and Thirunamachandran [7,8] for the energy shift of the initial state with atom A excited, atom B unexcited, and the field in the vacuum state in the model in which the two atoms are modeled as two-state systems. It involves the real part of the polarizability of atom B,

$$\alpha_B(\omega_A) = \frac{2\omega_B d_B^2/\hbar}{\omega_B^2 - \omega_A^2}, \tag{38}$$

and has the form of a quadratic Stark shift of the lower state of atom B caused by the electric field from atom A. This was the physical basis of the calculations of Power and Thirunamachandran in Ref. [7].

A crucial assumption made in our derivation of (37) is that atom A is not affected by the presence of atom B. Atom A simply produces an electric field that causes a quadratic Stark shift ΔE_B in atom B. This model is clearly the one adopted by Power and Thirunamachandran [7] in their calculation of "intermolecular energy shifts from energy densities." They subsequently [8] calculated these shifts in time-independent perturbation theory, evidently choosing the prescription for dealing with energy denominators that results in the same (monotonic) interaction energy they derived earlier. This is discussed further in Sec. V.

C. Relation to Förster resonance excitation transfer

As we now show, the rate $R = \Delta\beta_B/2\pi$ can be related to the Förster excitation transfer rate from a donor molecule to an acceptor, while the energy ΔE_B is the energy shift in the acceptor that accompanies this transfer.

Consider first

$$R = \Delta\beta_B = 2\pi S_B(\omega_A)|F|^2, \tag{39}$$

where $S_B(\omega)$ is the (normalized) absorption line-shape function of atom B that effectively defines a "density of final states"; in the particular model considered here, this is just a homogeneously broadened Lorentzian. The absorption cross section of atom B is

$$\sigma_b(\omega) = \frac{\lambda^2\gamma_B}{8\pi n^2(\omega)} 2\pi S_B(\omega), \tag{40}$$

where $\lambda = 2\pi c/\omega$ and $\gamma_B = n(\omega)A_B$ is the radiative decay rate of the excited state of atom B in a host medium of (real) refractive index $n(\omega)$ and $A_B = 4d_B^2\omega_B^3/3\hbar c^3$ is the radiative decay rate in vacuum. (We ignore possible local field corrections.) Then, with the expression $A_a = 4\omega_A^3 d_A^2 n(\omega_A)/3\hbar c^3$ for the radiative decay rate of the excited state of atom A in the medium and the approximation $\omega_A \approx \omega_B$,

$$R = \frac{3n(\omega_A)\hbar c}{2\pi\omega_A d_B^2}\sigma_b(\omega_A)|F|^2 = \frac{9\mathcal{B}^2 c^4 A_a}{8\pi r^6}\frac{\sigma_b(\omega_A)}{n^4(\omega_A)\omega_A^4}. \tag{41}$$

We have used (22) with $k_A r \ll 1$ and introduced a factor $1/n^4(\omega)$ to account for the dependence of the electric field on the refractive index of the medium ($E^2 \propto 1/n^4$). Finally, we allow for all emission frequencies of atom A by integrating over its (normalized) emission line shape $S_A(\omega)$ and replacing (41) by

$$R = \frac{9\mathcal{B}^2 c^4 A_a}{8\pi r^6}\int_0^\infty d\omega \frac{\sigma_b(\omega)S_A(\omega)}{n^4(\omega)\omega^4}, \tag{42}$$

which is a well-known expression for the Förster excitation transfer rate [26].

ΔE_B can be similarly generalized. For $k_A r \ll 1$ and without dipole orientational averaging,

$$\Delta E_B = -\alpha_B(\omega_A)\frac{d_A^2\mathcal{B}^2}{r^6 n^4(\omega_A)}, \tag{43}$$

where we have once again introduced the factor $1/n^4(\omega_A)$. Relating d_A^2 to A_a and integrating over the normalized emission spectrum $S_A(\omega)$ of the donor A,

$$\Delta E_B = -\frac{3\mathcal{B}^2\hbar c^3 A_a}{4r^6}\int_0^\infty d\omega \frac{\alpha_B(\omega)S_A(\omega)}{\omega^3 n^5(\omega)}. \tag{44}$$

This is exactly the interaction energy accompanying the Förster transfer that was obtained by Cohen and Mukamel [17,18,27]. The interaction energy obtained by Power and Thirunamachandran has exactly the same physical origin. As Cohen and Mukamel note, this energy and the transfer rate involve the real and imaginary parts, respectively, of the acceptor polarizability.

IV. EFFECT OF ATOM B ON ATOM A

The dipole moment induced in atom B by the field from atom A results in a field of frequency ω_A scattered by B and acting back on A. This effect of B on A obviously occurs only after a time $2r/c$.

The field from atom B on atom A is given in the RWA by Eq. (10). $\sigma_B(t)$ in that expression satisfies (13), or

$$\sigma_B(t) \cong -i\int_0^t dt'\sigma_{zB}(t')\mathcal{E}_{BA}^{(+)}(t')e^{i\omega_B(t'-t)} + (\cdots) \tag{45}$$

for times t short compared to the radiative lifetime of B. Here $(\cdots)$ denotes terms independent of A. From (16) we have, for times short compared to the radiative lifetime of A,

$$\mathcal{E}_{BA}^{(+)}(t') \cong F\theta(t' - r/c)\sigma_A(t' - r/c) + (\cdots), \tag{46}$$

where we have made the approximation $\dot{\sigma}_A(t) \cong -i\omega_A\sigma_A(t)$. Then

$$\begin{aligned}\sigma_B(t) &\cong -iF\theta(t - r/c)\sigma_{zB}(0)\sigma_A(t - r/c)\\ &\quad\times\int_{r/c}^t dt' e^{-i\Delta(t'-t)} + (\cdots)\\ &\cong \frac{F}{\Delta}\sigma_{zB}(0)\sigma_A(t - r/c) + (\cdots)\end{aligned} \tag{47}$$

to lowest order in $|F/\Delta|$. We have again averaged over the oscillations of $e^{i\Delta t}$. From (10), therefore,

$$\mathcal{E}_{AB}^{(+)}(t) \cong \frac{F^2}{\Delta}\theta(t - 2r/c)\sigma_{zB}(0)\sigma_A(t - 2r/c) + (\cdots), \tag{48}$$

and, from (7),

$$\begin{aligned}\langle\dot{\sigma}_A(t)\rangle &\cong -i(\omega_A - i\beta_A)\langle\sigma_A(t)\rangle + i\frac{F^2}{\Delta}\theta(t-2r/c)\\ &\quad\times\langle\sigma_{zA}(0)\sigma_{zB}(0)\sigma_A(t-2r/c)\rangle\\ &= -i(\omega_A - i\beta_A)\langle\sigma_A(t)\rangle - i\frac{F^2}{\Delta}\theta(t-2r/c)\\ &\quad\times\langle\sigma_A(t-2r/c)\rangle\\ &\cong -i(\omega_A - i\beta_A)\langle\sigma_A(t)\rangle - i\frac{F^2}{\Delta}\theta(t-2r/c)\langle\sigma_A(t)\rangle e^{2ik_Ar}\\ &= [-i(\omega_A+\Delta\omega_A) - \beta_A']\langle\sigma_A(t)\rangle \end{aligned} \tag{49}$$

for $t > 2r/c$. We have used $\langle(\cdots)\rangle = 0$ and $\langle\sigma_{zA}(0)\sigma_{zB}(0)\sigma_A(t-2r/c)\rangle = -\langle\sigma_A(t-2r/c)\rangle$ for the initial condition in which A is excited and B is unexcited and have defined

$$\Delta\omega_A = \mathcal{R}\left[\frac{F^2}{\Delta}e^{2ik_Ar}\right] \tag{50}$$

and

$$\beta_A' = \beta_A - \mathcal{R}\left[\frac{iF^2}{\Delta}e^{2ik_Ar}\right]. \tag{51}$$

For $k_Ar \gg 1$,

$$\Delta\omega_A \cong \frac{d_A^2 d_B^2 \mathcal{A}^2 k_A^6}{\hbar^2\Delta(k_Ar)^2}\cos(2k_Ar) \tag{52}$$

and

$$\beta_A' \cong \beta_A + \frac{d_A^2 d_B^2 \mathcal{A}^2 k_A^6}{\hbar^2\Delta(k_Ar)^2}\sin(2k_Ar). \tag{53}$$

Since in lowest order A only experiences a field scattered from B when A is excited, only the excited state of A is affected by B [28]. $\hbar\Delta\omega_A$ is therefore the energy shift of the initial (excited) state of A. This energy exhibits sinusoidal modulation [29] with the separation r as in Refs. [13–16]. Here $2\beta_A'$ is the radiative lifetime of atom A in the presence of atom B and has just the (spatially modulated) form previously obtained by Craig and Thirunamachandran [30] and Berman and Milonni [31] in connection with spontaneous emission in a dielectric medium.

V. SUMMARY AND CONCLUSIONS

We conclude from these calculations that the spatially monotonic [7–12] and the sinusoidally modulated [4–6,13–16] interaction energies derived previously are both valid but that they describe distinctly different physical settings.

The sinusoidally modulated energy is associated with reversible, back-and-forth excitation exchange between A and B. In the case $|\Delta| \gg |F|$ we have considered, the reexcitation of B is negligible, and the interaction energy can be interpreted as the level shift of A due to the field scattered back to A by B when B has a dipole moment induced by the field from A [16]. In the near-field case of most interest, the probability amplitude for the initial state in which A is excited and B is unexcited is, for times short compared to any relaxation times,

$$c_A(t) = e^{-i(E_A+E_B)t/\hbar}\left[\cos\frac{1}{2}\Omega t - \frac{i\Delta}{\Omega}\sin\frac{1}{2}\Omega t\right], \tag{54}$$

where $\Omega = (\Delta^2 + 4F^2)^{1/2}$, E_A, E_B are the excited-state energies of A, B, and F is real. For $|\Delta| \gg |F|$,

$$c_A(t) \cong e^{-i(E_A+F^2/\Delta)t/\hbar}, \tag{55}$$

implying the interaction energy $\hbar F^2/\Delta$, consistent with Eq. (50) for $k_Ar \ll 1$.

The spatially monotonic energy is associated with an irreversible rate of excitation transfer from the initially excited atom A to the initially unexcited atom B. This excitation rate is the absorption rate of B in the field of A and can be obtained simply from Fermi's golden rule [see Eq. (34)], treating atom A as an "external" source of a single-photon field of frequency ω_A. The spatially monotonic energy obtained by Power and Thirunamachandran [7,8], who considered the energy shift of atom B but not excitation transfer, is just the quadratic Stark shift accompanying this absorption process. Atom B was assumed to be bathed in the field of atom A and to have no effect on A [7]. In their subsequent calculation [8] based on time-independent perturbation theory, Power and Thirunamachandran introduced $i\epsilon$ terms ($\epsilon \to 0^+$) to avoid vanishing energy denominators and evidently chose the signs of these terms such that the spatially monotonic energy obtained in their first calculation was reproduced.

From the perspective of the calculations we have presented, the validity of the monotonic form of the energy requires an assumption not explicitly made by Power and Thirunamachandran: excitation acquired by B must relax so quickly to other states or degrees of freedom that the excitation cannot be transferred back to A. To model Förster excitation transfer with our simple model, we must allow for a dense distribution $\rho(\Delta)$ of final states and replace (25), for example, by

$$P_B(t) \cong 4|F|^2\int d\Delta\frac{\sin^2\frac{1}{2}\Delta t}{\Delta^2}\rho(\Delta) \tag{56}$$

to obtain an irreversible golden-rule rate of excitation of B. In other words, we would describe the effect on B of the field from A in the rate-equation approximation, as in the calculations of Sec. III.

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[29] If we do not take an average over oscillations at frequency Δ in expression (47), for example, we obtain instead of (50) a time-dependent $\Delta\omega_A \cong (d_A^2 d_B^2 k_A^4 \mathcal{A}^2/\hbar^2 r^2 \Delta)[\cos(2k_A r) - \cos[(k_A + k_B)r + t\Delta]]$ for $k_A r \gg 1$; this is similar in form to expression (6) of Ref. [15].

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