Resonant excitation transfer: A quantum electrodynamical study

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A new quantum electrodynamical (QED) method is presented, based in the Schrödinger representation, for the calculation of the rate of energy transfer between identical molecules. In contrast to existing methods in this representation, the new treatment gives explicitly causal and energy-conserving results. By returning to perturbation theory the correct, complex form for the electric dipole–electric dipole interaction tensor is obtained, without recourse to the physical, "outgoing wave" arguments of quantum scattering theory necessary if the Fermi rule is used. This method also allows a new interpretation for the role of the time-ordered diagrams involved, which may be useful in the rigorous treatment of higher order cooperative processes. The QED treatment uses virtual photon coupling, and incorporates both the Coulombic, R^{-6} dependence, and the R^{-2} dependence characteristic of two-step radiative transfer.

I. INTRODUCTION

In a very wide range of phenomena in chemical physics, the observed behavior of a system is determined by intermolecular interactions. Such interactions are strongest over short distances where wave function overlap and electron exchange occur, but they nonetheless remain significant over longer distances where individual molecules can be regarded as chemically distinct. The mechanism for these longer-range interactions is electromagnetic, and is illustrated by the well-known R^{-6} London potential associated with an induced-dipole–induced-dipole interaction.

In the Power–Zienau–Woolley formalism of molecular quantum electrodynamics (QED)[1,2] there are no Coulombic (longitudinal) intermolecular fields and all intermolecular interactions are mediated by the propagation of (transverse) virtual photons.[3] The term "virtual" arises because these photons cannot be observed, their role being similar to that of the virtual molecular states which are involved in the description of scattering and other multiphoton processes. In the diagrammatic construction of perturbational QED,[4] the "real" photons may be distinguished from the virtual photons since the latter exist merely as part of the intermediate states and thus have two space–time termini corresponding to creation and annihilation, whereas the former are parts of the final or initial states and thus have only one terminus. Another way of describing these interactions is to consider separate electrodynamical molecular processes to be linked via coupling to a radiation mode.

Quantum electrodynamical calculations based on virtual photon coupling provide fully retarded results, allowing time for the signal to travel between the molecules, and thus providing a causal description. This has important consequences, for example, in modifying the R^{-6} dependence of the London potential at large distances to the correct long-range R^{-7} dependence given by the Casimir–Polder results.[5] However, many other phenomena can be described as virtual photon processes, such as cooperative absorption[6–8] and optical rotation resulting from the dissymmetric juxtaposition of chromophores in polyatomic molecules.[9]

Regrettably, there has been some confusion in the literature as to the correct details of the electric-dipole–electric-dipole coupling tensor. In some places this has been represented as a real function,[10,11] while elsewhere it contains both a real and an imaginary part.[12] In a recent series of papers,[13–15] expressions for Maxwell fields were developed in which the coupling tensor correctly appeared in its complex form, but a transformation to the Heisenberg representation seemed necessary for its derivation. In the Heisenberg representation, the time dependence of operators is explicit, while in the Schrödinger representation the time dependence is only explicit once observables are calculated. There is a conventional preference for the former representation when the fields are the primary operators, and for the latter representation when the molecules are primary, though of course both must lead to the same results.

In this paper by considering the very simplest process which can involve virtual photons, namely the resonant transfer of excitation between two molecules, the limitations of the standard Schrödinger representation approach are demonstrated, while by careful use of time-dependent perturbation theory it is shown that a correct result is obtainable in this representation. Inclusion of the imaginary part of the coupling tensor is shown to be important in ensuring the correct long-range behavior, when the overall optical process becomes separable into distinct interactions at the two centers. The conditional nature of the integrals and of the final results are emphasized as they arise, since this is shown to allow a physical interpretation of the roles of the time-ordered diagrams.

II. THE STANDARD APPROACH[16]

The resonant transfer of energy can be described as a process in which the initial system state consists of molecule (a) in state $|\alpha\rangle$ and molecule (b) in state $|0\rangle$, while the final system state is that in which the molecule (a) is in state $|0\rangle$ and molecule (b) is in state $|\beta\rangle$. Although the two molecules are regarded as chemically identical so that, in principle, symmetric and antisymmetric combination states may be formed, such radiation-free stationary states are not appropriate for a treatment of radiation transfer in which time dependence and causality are to be examined. Here, states which are formed from the bare product of wave functions

for each center are a suitable basis. There is assumed to be no observable change in the radiation field, though intermediate states in which the radiation field is excited relative to the initial and final states are included as mediators of the energy transfer process.

The conventional starting point for the development of the theory is the Fermi rule rate equation

$$\Gamma = (2\pi/\hbar)|M_{fi}|^2\rho_f , \tag{1}$$

where ρ_f represents a density of final states, and M_{fi} is the matrix element connecting the initial and final states of the system, which has the perturbation expansion

$$M_{fi} = \langle f|H_{int}|i\rangle + \sum_r \frac{\langle f|H_{int}|r\rangle\langle r|H_{int}|i\rangle}{(E_i - E_r)} , \tag{2}$$

where H_{int} is the perturbation operator on the basis eigenstates of the unperturbed radiation and molecular Hamiltonians. For present purposes it is sufficient to consider the electric dipole approximation

$$H_{int} = -\epsilon_0^{-1}\boldsymbol{\mu}\cdot\mathbf{d}^\perp. \tag{3}$$

Here $\boldsymbol{\mu}$ is the electric dipole operator, and $\mathbf{d}^\perp$ is the transverse electric displacement operator. The appropriate time-ordered diagrams are shown in Figs. 1(a) and 1(b), and arise from the second-order term in the matrix element (2),
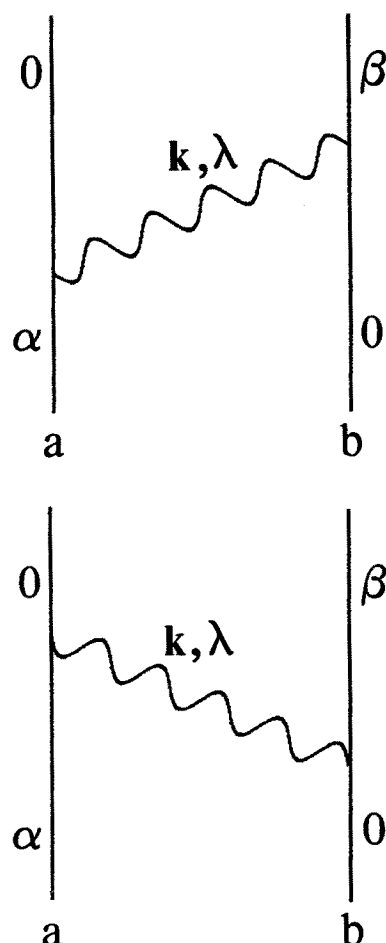

FIG. 1. (a) and (b) The time-ordered diagrams for resonant energy transfer.

where the corresponding intermediate states are given by

$$\text{(a)} \quad |r\rangle \equiv |0(a); 0(b); e(\mathbf{k},\lambda)\rangle, \tag{4}$$

$$\text{(b)} \quad |r\rangle \equiv |\alpha(a); \beta(b); e(\mathbf{k},\lambda)\rangle. \tag{5}$$

Here $e(\mathbf{k},\lambda)$ represents the state of a virtual photon with wave vector $\mathbf{k}$ and polarization vector $\mathbf{e}^{(\lambda)}$. Summing the above contributions to the M_{fi} gives an expression

$$M_{fi} = \sum_{\mathbf{k},\lambda} \frac{\hbar ck}{2\epsilon_0 V}\mu_i^{\alpha 0}(a)\mu_j^{\beta 0}(b)\left[e_i\bar{e}_j \frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{E_{\alpha 0} - \hbar ck}\right.$$
$$\left. - e_j\bar{e}_i \frac{e^{-i\mathbf{k}\cdot\mathbf{R}}}{E_{\beta 0} + \hbar ck}\right], \tag{6}$$

where summation over repeated tensor indices is implied. This leads to a physical model where the two centers are coupled to each other via the intermediate photon states, in the same way that the initial and final molecular states in the tensor representing a nonlinear optical process are linked via intermediate molecular states.

The λ summation gives

$$M_{fi} = \sum_{\mathbf{k}} (2\epsilon_0 V)^{-1}\mu_i^{\alpha 0}\mu_j^{\beta 0}(\delta_{ij} - \hat{k}_i\hat{k}_j)k$$
$$\times \left[\frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{K_{\alpha 0} - k} - \frac{e^{-i\mathbf{k}\cdot\mathbf{R}}}{K_{\beta 0} + k}\right], \tag{7}$$

where $K_{\alpha 0} = E_{\alpha 0}/\hbar c$, $K_{\beta 0} = E_{\beta 0}/\hbar c$, and the denominators serve to extract the value of k which corresponds to that required through the energy conservation condition.

The procedure is then to replace the summation by an integral facilitated in the limit of a large quantization volume through the corresponding increase in the density of allowed $\mathbf{k}$ values. The appropriate conversion is

$$\sum_{\mathbf{k}} \Rightarrow \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{k^2 V}{(2\pi)^3}\sin\theta\,dk\,d\theta\,d\phi, \tag{8}$$

giving for Eq. (7):

$$M_{fi} = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{1}{2(2\pi)^3\epsilon_0}\mu_i^{\alpha 0}\mu_j^{\beta 0}$$
$$\times(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)dk\,d\theta\,d\phi$$
$$\times k\sin\theta\left[\frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{K_{\alpha 0} - k} - \frac{e^{-i\mathbf{k}\cdot\mathbf{R}}}{K_{\beta 0} + k}\right]. \tag{9}$$

Usually the principle of energy conservation is introduced at this early stage, requiring that $K_{\alpha 0} = K_{\beta 0} = K$, so that on performing the angular integrations the integral over k may be extended to negative values. The result may then be expressed as

$$M_{fi} = \mu_i^{\alpha 0}\mu_j^{\beta 0}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\frac{1}{4\pi^2\epsilon_0}G(K,R), \tag{10}$$

where $G(K,R)$ is the Green's function

$$G(K,R) = \int_{-\infty}^{\infty} (2R)^{-1}\sin(kR)\left[\frac{1}{K-k} - \frac{1}{K+k}\right]dk. \tag{11}$$

This Green's function must lead to a real result since the integrand is real, and when the Cauchy principal value is

taken, it gives

$$G(K,R) = -\pi \frac{\cos KR}{R}, \tag{12}$$

giving for the matrix element

$$M_{fi} = \mu_i^{\alpha 0}\mu_j^{\beta 0}\sigma_{ij}(K,R), \tag{13}$$

with the coupling tensor $\sigma_{ij}(K,R)$ given by

$$\sigma_{ij}(K,R) = \frac{K^3}{4\pi\epsilon_0}\left\{(\delta_{ij} - 3\hat{R}_i\hat{R}_j)\left(\frac{\cos KR}{K^3R^3} + \frac{\sin KR}{K^2R^2}\right)\right.$$
$$\left. - (\delta_{ij} - \hat{R}_i\hat{R}_j)\frac{\cos KR}{KR}\right\}. \tag{14}$$

The limiting behavior of the coupling tensor is neatly separated into two regions; the *near zone*, where $KR \ll 1$, and the *wave zone*, where $KR \gg 1$. The tensor in these regions is then approximated as

near zone: $\sigma_{ij}(K,R) = \sigma_{ij}(0,R)$

$$= \{(4\pi\epsilon_0)^{-1}(\delta_{ij} - 3\hat{R}_i\hat{R}_j)R^{-3}\}, \tag{15}$$

wave zone: $\sigma_{ij}(K,R) = -(\delta_{ij} - \hat{R}_i\hat{R}_j)\dfrac{K^2\cos KR}{4\pi\epsilon_0 R}$, $\tag{16}$

the former giving the $K \to 0$ limit corresponding to the longitudinal coupling between permanent moments, and the latter the transverse R^{-1} dependence expected for the radiative field on an oscillating dipole. Note that although the coupling is longitudinal with respect to R in the near zone, it is mediated by a photon polarized transverse with respect to k.

A case which illustrates the error of using this form for the coupling tensor concerns calculation of the rate of resonant energy transfer between two identical molecules in the wave zone limit. If Eq. (13) is then substituted into the Fermi rule expression (1) and the result is averaged isotropically for application to a fluid phase, the rate is given by

$$\Gamma \simeq \frac{|\mu^{\alpha 0}|^4K^4}{36\pi\epsilon_0^2\hbar R^2}\cos^2 KR\rho_f, \quad KR \gg 1. \tag{17}$$

This result is inconsistent with that obtained classically, owing to the presence of the oscillatory $\cos^2 KR$ term; in Sec. VI the correct nonoscillatory result is shown to arise when the full, complex form for the interaction tensor is used.

III. THE GREEN'S FUNCTION

An exactly similar Green's function to that appearing in Eq. (11) arises in the treatment of quantum scattering problems.[17] Here a complex result is obtained from the Green's function, either by forcing the poles to be displaced through the introduction of an infinitesimal imaginary part to the denominators of Eq. (11)[18]:

$$G(K,R) = \lim \psi \to 0 \int_0^\infty R^{-1}$$

$$\times \sin kR \left[\frac{1}{K-k+i\psi} - \frac{1}{K+k-i\psi}\right]dk, \tag{18}$$

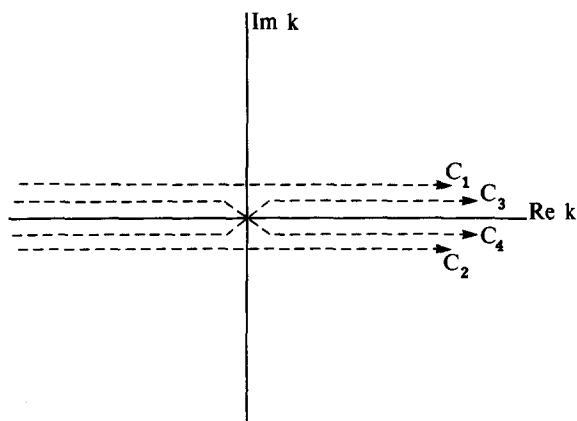or by changing the contour of integration.[19] The sine func-

FIG. 2. Four choices of contours to avoid poles on the axis. They are closed by continuation with a semicircle in either the upper or lower plane.

tion in Eq. (11) may be expanded to give two integrals:

$$G(K,R) = \frac{1}{4iR}\int_\infty^{-\infty}\frac{e^{ikR}}{K-k} - \frac{e^{ikR}}{K+k}dk$$

$$- \frac{1}{4iR}\int_\infty^{-\infty}\frac{e^{-ikR}}{K-k} - \frac{e^{-ikR}}{K+k}dk, \tag{19}$$

which give for each of the contours C_1 to C_4 in Fig. 2:

$G(K,R)$ for $C_1 = 0 - (\pi/R)\cos KR$, $\tag{20}$

$G(K,R)$ for $C_2 = -(\pi/R)\cos KR + 0$, $\tag{21}$

$G(K,R)$ for $C_3 = -(\pi/2R)\exp(-iKR)$
$$- (\pi/2R)\exp(-iKR), \tag{22}$$

$G(K,R)$ for $C_4 = -(\pi/2R)\exp(iKR)$
$$- (\pi/2R)\exp(iKR), \tag{23}$$

where continuation of the contour by a vanishing integral has been accomplished by the appropriate semicircle. To ensure an outgoing wave solution the contour C_4 is chosen, though of course this has no *a priori* mathematical basis.

Neither of these approaches is particularly thorough, the latter method having no simple physical justification in itself. The overwhelming physical argument used in both cases is that the solution must behave as a pure outgoing wave in the limit of large R. This gives the correct form for $G(K,R)$ as required classically:

$$G(K,R) = -\pi\frac{e^{ikR}}{R}. \tag{24}$$

Rigorously, this approach should be avoided since knowledge of the long-range form of the interaction is necessary for calculation of the general behavior, which is only physically justified as a boundary condition for scattering problems. In the type of problem under consideration in this paper only the molecular system can have boundary conditions, since the virtual photon is unobservable. In the following section it is shown that by returning to time-dependent perturbation theory and carefully proceeding to the rate equation the correct form can be obtained without recourse to this fundamentally recursive argument.

IV. TIME-DEPENDENT PERTURBATION THEORY REVISITED

The full second-order expression for the time-dependent probability amplitude $C_{fi}(t)$ is

$$C_{fi}(t) = \sum_r \langle f|H_{int}|r\rangle\langle r|H_{int}|i\rangle$$
$$\times \left[\frac{e^{i\omega_{fi}t}-1}{E_{fi}E_{ri}} - \frac{e^{i\omega_{fr}t}-1}{E_{fr}E_{ri}}\right], \tag{25}$$

where again it should be emphasised that both states and energies refer to the entire system, and, for example, E_{fi} is the zeroth order energy difference between the initial and final states. In the conventional approach to a rate expression the second oscillatory term is neglected as being only significant when intermediate state resonances are important.[20] For molecular response tensors this approximation is generally valid, since the experimental conditions at which resonance occurs can be avoided by a suitable choice of irradiation frequency. In the case of the time-ordered diagram in Fig. 1 (a), however, the virtual photon comprises the intermediate state, and its frequency is integrated over an infinite range. In this case, therefore, the resonance condition (when the intermediate state energy is equivalent to the initial or final state energy) is logically significant.

If the appropriate intermediate states are inserted in Eq. (25), the probability amplitude becomes

$$C_{fi}(t) = -\mu_i^{\alpha0}(a)\mu_j^{\beta0}(b)\hbar c(4\pi^2\epsilon_0)^{-1}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)$$
$$\times \int_0^\infty dk\,\frac{\sin kR}{R}\left[\frac{e^{i(K_{\beta0}-K_{\alpha0})ct}-1}{(E_{\alpha0}-E_{\beta0})(E_{\alpha0}-\hbar ck)}\right.$$
$$+ \frac{e^{i(K_{\beta0}-k)ct}-1}{(E_{\alpha0}-\hbar ck)(E_{\beta0}-\hbar ck)}$$
$$- \frac{e^{i(K_{\beta0}-K_{\alpha0})ct}-1}{(E_{\beta0}+\hbar ck)(E_{\alpha0}-E_{\beta0})}$$
$$\left.- \frac{e^{-i(K_{\alpha0}+k)ct}-1}{(E_{\beta0}+\hbar ck)(E_{\alpha0}+\hbar ck)}\right]. \tag{26}$$

This integral is causal, vanishing for times where $R > ct$, while the denominators impose restrictions on the signs of the various energy terms. The detailed form of the contributions to the new Green's function are

Case (a1): $R < ct$ and $E_{\alpha0} > 0$:

$$G(R,t) = \frac{e^{i(K_{\beta0}-K_{\alpha0})ct}}{(E_{\beta0}-E_{\alpha0})}\times\frac{\pi e^{iK_{\alpha0}R}}{\hbar cR}. \tag{27}$$

Case (a2): $R < ct$ and $E_{\beta0} > 0$:

$$G(R,t) = -\frac{\pi e^{iK_{\beta0}R}}{(E_{\beta0}-E_{\alpha0})\hbar cR}. \tag{28}$$

Case (b1): $R < ct$ and $E_{\beta0} < 0$:

$$G(R,t) = \frac{e^{i(K_{\beta0}-K_{\alpha0})ct}}{(E_{\beta0}-E_{\alpha0})}\times\frac{\pi e^{-iK_{\beta0}R}}{\hbar cR}. \tag{29}$$

Case (b2): $R < ct$ and $E_{\alpha0} < 0$:

$$G(R,t) = -\frac{\pi e^{-iK_{\alpha0}R}}{(E_{\beta0}-E_{\alpha0})\hbar cR}. \tag{30}$$

The case identifier, (a) or (b), refers the terms to their appropriate time-ordered diagram in Fig. 1, whereas the numeric identifier has no similar significance. It is interesting to note that the contribution which arises from the first of the oscillatory terms in Eq. (25), that which is used in the conventional derivation of the Fermi rule, is exactly cancelled by a contribution from the other oscillatory term.

Examination of the energy requirements of cases (a) and (b) allows the time-ordered diagrams of Fig. 1 to be interpreted as follows: (a) corresponds to the transfer of energy from molecule (a) to molecule (b), with the necessary requirement that $E_{\alpha0}$ and $E_{\beta0}$ are positive; (b) corresponds to the transfer of energy from molecule (b) to molecule (a), with the requirement that $E_{\alpha0}$ and $E_{\beta0}$ are negative. Hence the time-ordered diagrams describe the two directions of energy transfer, and thus only one can contribute for any particular problem.

In the next section, by choosing one of the possible cases, (a), the rate equation is derived, allowing the energy conservation condition to arise naturally. The rate equation for the other case is obvious from the derivation, so that finally the results for both cases are obtained.

V. CALCULATION OF THE RATE EQUATION

In order to evaluate the rate of energy transfer from molecule (a) to molecule (b), first the time-dependent probability $P_{fi}(t)$, given by the square modulus of the probability amplitudes (26)–(30), must be calculated:

$$P_{fi}(t) = |\mu_i^{\alpha0}(a)\mu_j^{\beta0}(b)(4\pi\epsilon_0)^{-1}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)$$
$$\times\{(E_{\beta0}-E_{\alpha0})R\}^{-1}\{e^{i(K_{\beta0}-K_{\alpha0})ct}e^{iK_{\alpha0}R}$$
$$- e^{iK_{\beta0}R}\}|^2. \tag{31}$$

This may be expanded as

$$P_{fi}(t) = \{\mu_i^{\alpha0}(a)\mu_j^{\beta0}(b)(4\pi\epsilon_0)^{-1}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)R^{-1}\}$$

$$\times\{\mu_k^{\alpha0}(a)\mu_l^{\beta0}(b)(4\pi\epsilon_0)^{-1}(-\nabla'^2\delta_{kl} + \nabla_k'\nabla_l')R'^{-1}\}\times\frac{1}{(E_{\beta0}-E_{\alpha0})^2}$$

$$\times[2 - e^{i(K_{\beta0}-K_{\alpha0})ct}e^{iK_{\alpha0}R}e^{-iK_{\beta0}R'} - e^{-i(K_{\beta0}-K_{\alpha0})ct}e^{iK_{\beta0}R}e^{-iK_{\alpha0}R'}], \tag{32}$$

where the label R' has been introduced to ensure that each distance variable is only operated on by the appropriate differential operators ∇, ∇'.

Since it is the rate which is sought, expression (32) must be differentiated with respect to time. Hence the molecular components and other parameters not included in the square brackets, which are not explicitly dependent on time, need not be considered. Differentiating the terms within the square bracket then gives

$$\left[e^{iK_{\beta 0}(R-ct)}e^{-iK_{\alpha 0}(R'-ct)} - e^{-iK_{\beta 0}(R'-ct)}e^{iK_{\alpha 0}(R-ct)} \right]$$
$$\times ic(K_{\beta 0} - K_{\alpha 0}), \tag{33}$$

where it should be emphasized that $R < ct$, from Eq. (26).

As in the standard approach to the Fermi rule, a density of energy states ρ_f, is introduced, and the final states are then summed. In this case the final state energy is $E_{\beta 0}$, and by manipulating the summation to an integral over $K_{\beta 0}$, the rate becomes

$$\Gamma = |N_{fi}|^2 \int_{-\infty}^{+\infty} \frac{i\{e^{iK_{\beta 0}(R-ct) - iK_{\alpha 0}(R'-ct)} - e^{-iK_{\beta 0}(R'-ct) + iK_{\alpha 0}(R-ct)}\}}{\hbar(K_{\beta 0} - K_{\alpha 0})} \rho_f dK_{\beta 0}, \tag{34}$$

where N_{fi} is the operator

$$N_{fi} = \{\mu_k^{\alpha 0}(a)\mu_l^{\beta 0}(b)(4\pi\epsilon_0)^{-1}(-\nabla^2\delta_{kl} + \nabla_k\nabla_l)R^{-1}\}. \tag{35}$$

In the integral (34), the pole ensures the energy conservation condition $K_{\beta 0} = K_{\alpha 0} = K$, while the detailed form leads to

$$\Gamma = |N_{fi}|^2 (2\pi\rho_f/\hbar)\{e^{iKR} \times e^{-iKR'}\}, \tag{36}$$

from which the matrix element M_{fi} can be inferred by comparison with the standard Fermi rule expression (1), and by ensuring that the operator N_{fi} only operates on the appropriate phase factor

$$M_{fi} = N_{fi}e^{iKR}$$
$$= \mu_i^{\alpha 0}(a)\mu_j^{\beta 0}(b)(4\pi\epsilon_0)^{-1}(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\frac{e^{iKR}}{R}, \tag{37}$$

which has the correct R dependence, as required by the correspondence principle.

Before proceeding to examine the form of the interaction tensor, it is pertinent to state the result that would have been obtained if the conditions necessary for case (b) had been used. For case (b) the interaction tensor is expressed as

$$\theta_{ij} = -(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\frac{e^{-iKR}}{4\pi\epsilon_0 R}, \tag{38}$$

which allows a simple generalization, applicable to both cases:

$$\theta_{ij} = -(-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\frac{e^{i|K|R}}{4\pi\epsilon_0 R}. \tag{39}$$

Thus, in this section a rigorous method for the derivation of the correct R and K dependence has been obtained, which incidentally ensures the appropriate conditions of $K_{\beta 0}$ and $K_{\alpha 0}$ without recourse to physical arguments.

VI. SOME PROPERTIES OF THE TRUE INTERACTION TENSOR

In an analogous fashion to Eq. (14) for σ_{ij}, the interaction tensor θ_{ij} may be written

$$\theta_{ij}(K,R) = \frac{e^{i|K|R}K^3}{4\pi\epsilon_0} \left\{ (\delta_{ij} - 3\hat{R}_i\hat{R}_j)\left(\frac{1}{K^3R^3} + \frac{i}{K^2R^2}\right) - (\delta_{ij} - \hat{R}_i\hat{R}_j)\frac{1}{KR} \right\}, \tag{40}$$

or alternatively the real and imaginary parts may be separated to give

$$\theta_{ij} = \sigma_{ij} + i\tau_{ij}, \tag{41}$$

where σ_{ij} is given by Eq. (14) and τ_{ij} is defined as

$$\tau_{ij}(K,R) = \frac{K^3}{4\pi\epsilon_0} \left\{ (\delta_{ij} - 3\hat{R}_i\hat{R}_j)\left(\frac{\cos KR}{K^2R^2} - \frac{\sin KR}{K^3R^3}\right) + (\delta_{ij} - \hat{R}_i\hat{R}_j)\frac{\sin KR}{KR} \right\}. \tag{42}$$

In passing, it should be noted that the definitions of σ_{ij} and τ_{ij} used here differ from those adopted by Power and Thirunamachandran[15] by a factor of $4\pi\epsilon_0$.

If the rate expression (36) is now used to calculate the rate of transfer of energy from molecule (a) to molecule (b), then after rotational averaging the counterpart to the result of Eq. (17) is

$$\Gamma = \frac{|\mu^{\alpha 0}|^4 K^4}{36\pi\epsilon_0^2\hbar R^2} \{3(KR)^{-4} + (KR)^{-2} + 1\}\rho_f, \tag{43}$$

which is correct for all $R < ct$. As opposed to the earlier calculation, this rate is nonoscillatory, smoothly changing from a long-range R^{-2} behavior to a short-range, K-independent, R^{-6} behavior. To further elucidate the nature of the rate expression, a simple comparison can be made with the rate expected for the radiative transfer of energy between the two centers.

In this calculation, molecule (a) is now regarded as the radiator which decays spontaneously, and molecule (b) behaves as a resonant detector in the field of this radiator. The rate of spontaneous emission can, after rotational averaging, be expressed[21]

$$\Gamma = \frac{K^3}{3\epsilon_0\pi\hbar} |\mu^{\alpha 0}|^2, \tag{44}$$

or in terms of power per unit area, the resultant irradiance at

a distance R is given by

$$I(R) = \frac{\Gamma \hbar c K}{4\pi R^2} \equiv \frac{cK^4}{12\pi^2 \epsilon_0 R_2} |\mu^{\alpha 0}|^2. \tag{45}$$

If this irradiance is then substituted into the standard absorption rate equation, the overall rate expression becomes

$$\Gamma = \frac{K^4 |\mu^{\alpha 0}|^4}{36\pi \epsilon_0^2 \hbar R^2} \rho_f. \tag{46}$$

When Eqs. (46) and (43) are compared, it seems that the long-range behavior of the virtual photon adequately describes the system coupled via a real photon. Hence, it appears that using the virtual photon formalism, QED is able to describe electromagnetic interactions at all ranges, including the wave zone where conventionally the theory is cast in terms of a real photon.

VII. DISCUSSION

In Sec. V a new method of extracting the virtual-photon coupling tensor has been introduced in the Schrödinger representation. While it can be shown that in the Heisenberg representation the same *result* can be extracted,[14] the method used here is unique in making explicit the source of the conditional nature of the result. The advantages of the Schrödinger representation for understanding the dynamics of the molecular system are obvious, though of course with regard to causality the two representations can be regarded as complementary.

The unsatisfactory nature of the conventional method, when treated in a rigorous fashion, has been shown to lead to the wrong result (Sec. II). In Sec. III it was shown that by using physical arguments the correct result could be obtained, but this method has no sound mathematical basis. It has nonetheless been demonstrated that a rigorous method does exist which leads to the correct physical results, and reveals the conditional, causal, and resonant nature of the process in a particularly clear manner. The treatment has also allowed further elucidation of the nature of the two time-ordered diagrams, showing that Fig. 1(a) represents the transfer of energy *to* molecule (b), and that Fig. 1 (b) represents the transfer of energy *from* molecule (b).

In coupled oscillator models for optical rotation and multiphoton cooperative absorption, the virtual photon formalism is required for a full quantum electrodynamical treatment.[9] Previous work in the Schrödinger representation, based on the Fermi rule, has demonstrated that the same electric dipole interaction tensor results for all such higher order processes mediated by a single virtual photon. While the results presented here offer a new and detailed insight into the nature of two-center resonance coupling, the method requires that the usual Fermi rule route to the rate is abandoned. Hence, an exact treatment of such higher order processes would strictly require for each a similar analysis, and thus from this calculation alone the interaction tensor cannot necessarily be assumed to take the same form for all virtual photon processes.

From preliminary work on cooperative single-photon absorption, the six time-ordered diagrams for which are shown in Fig. 3, it appears possible to use the results of Sec. V to justify the perturbing of the Green's function (Sec. III) to
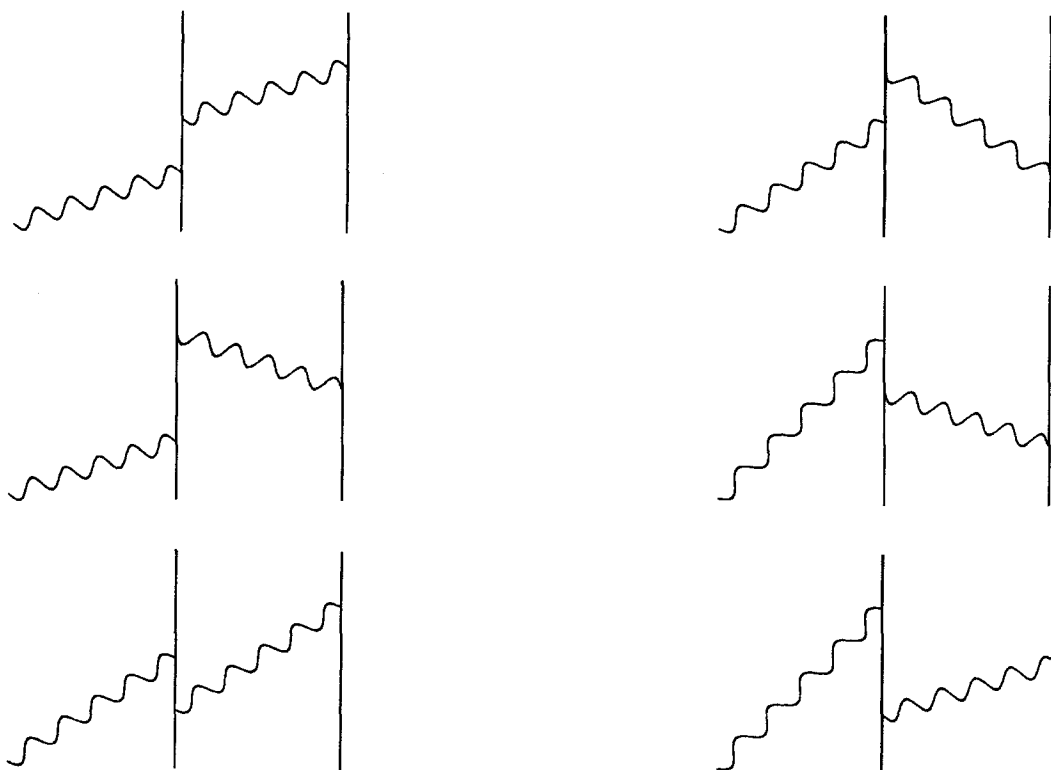

FIG. 3. The six time-ordered diagrams for cooperative single-photon absorption by a pair of molecules.

give the correct result of Eq. (39). Unfortunately, even for this relatively simple process, the rigorous calculation requires the calculation of nearly 2000 integrals. Again no generalization of the coupling tensor can be made, and already conditions are apparent where the use of the methods in Secs. II and III are inadequate, such as when molecular resonances are important. A full treatment of this cooperative process will be the subject of a future paper.

Finally, the results for the long-range rate show that virtual photon coupling gives the same results as associated with real photon transfer. This ties in neatly with *absorber theory*,[22] in which rather than having boundary conditions introduced as a condition of closure within a certain volume, the allowed photon states are made countable by confining the system within an infinite array of perfect absorbers. Thus, the real photons used in conventional calculations of, say, the spontaneous emission rate, become effectively virtual since they are absorbed by one of the array of absorbers. This condition, that a photon once emitted must be absorbed, also amounts to an energy conservation condition on the system being studied. It is pertinent to note that the real photon of absorption calculations is only real because the effective of the absorbing center on the source has been neglected.

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