Quantum electrodynamics with nonrelativistic sources. II. Maxwell fields in the vicinity of a molecule

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The electromagnetic field operators and the electron field operators for the coupled system governed by the multipolar Hamiltonian are obtained within the Heisenberg picture. Their causal behavior and their relationship to the minimal-coupling forms are discussed. The basic fields of the multipolar theory, namely, the displacement vector and the magnetic field, are calculated up to terms quadratic in the multipole moment sources. The terms linear in the transition moments are the quantum counterparts of the classical fields and do not change the photon occupation number. The quadratic terms have no classical analogs: they act in both the photon and electron occupation-number spaces. It is shown that it is necessary to include these second-order terms in the calculation of the Poynting vector for an emitting dipole, thus demonstrating their role in the transport of radiative energy.

I. INTRODUCTION

In this paper, the multipolar formalism discussed in paper I (Ref. 1) is applied to the calculation of the electromagnetic fields in the neighborhood of a molecule. For many purposes it is sufficient to use the electric dipole approximated form of the complete multipolar Hamiltonian developed previously. The extension to higher multipolar moments is straightforward. We choose $t=0$ as the time at which the Heisenberg operators are equal to the Schrödinger operators, the Maxwell operators acting in the photon occupation-number space only and the electron field operators in the fermion occupation-number space. However, for $t>0$, the Heisenberg operators act in the composite space. Thus the electromagnetic field operators are complicated functions of the annihilation and creation operators for both electrons and photons. To express the fields in terms of the annihilation and creation operators at $t=0$, it is convenient to expand the fields in power series involving the transition moments. The explicit forms of the first few terms of the electric displacement vector and the magnetic fields are given in Sec. II. The moment-independent terms are clearly the free field operators. The terms linear in the transition moments are shown to be the analogs of the classical fields: They operate solely in the molecule space leading to changes in the molecular state. Some novel features occur in the quadratic term: They have no direct classical counterparts. As for the free field they are linear in the photon creation and annihilation operators; however, they also effect changes of molecular states.

In Sec. III, the Maxwell fields obtained are used to calculate the energy flux from a molecule in an excited state. The use of the linear, pseudoclassical terms alone does not give the complete result. It is shown that the quadratic terms are essential to derive the total emission rate.

II. ELECTROMAGNETIC FIELDS NEAR A DIPOLE

A. Displacement vector field

The Hamiltonian (3.14) of paper I (Ref. 1) for an electric dipole source, ignoring self-energies, is

$$H_{\text{mult}}=\int \bar{\phi}(\vec{q}\,)\left[-\frac{\hbar^2}{2m}(\nabla^{(q)})^2+V(\vec{q}\,)\right]\phi(\vec{q}\,)d^3q +\frac{1}{8\pi}\int [d^{\perp 2}(\vec{r}\,)+b^2(\vec{r}\,)]d^3r -\int \bar{\phi}(\vec{q}\,)\vec{\mu}\cdot\vec{d}^{\perp}(\vec{R}\,)\phi(\vec{q}\,)d^3q \;, \tag{2.1}$$

where $d^{\perp}(\vec{r}\,)$ is related to the canonical momentum by $d^{\perp}(\vec{r}\,)=-4\pi c\,\vec{\pi}(\vec{r}\,)$, and $\vec{R}$ is the position vector of the molecular dipole. It is advantageous to effect a mode decomposition of the fields and hence find the equations of motion for the creation and annihilation operators for the modes. The standard decomposition for the vector potential and its canonical momentum are, in familiar notation,

$$\vec{a}(\vec{r},t)=\sum_{\vec{k},\lambda}\left[\frac{2\pi\hbar c}{Vk}\right]^{1/2}[\vec{e}^{\,(\lambda)}(\vec{k}\,)a(t)e^{i\vec{k}\cdot\vec{r}} +\bar{\vec{e}}^{\,(\lambda)}(\vec{k}\,)a^{\dagger}(t)e^{-i\vec{k}\cdot\vec{r}}]\;, \tag{2.2}$$

$$-4\pi c\,\vec{\pi}(\vec{r},t)=i\sum_{\vec{k},\lambda}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\times[\vec{e}^{(\lambda)}(\vec{k})a(t)e^{i\vec{k}\cdot\vec{r}}-\bar{\vec{e}}^{(\lambda)}(\vec{k})a^{\dagger}(t)e^{-i\vec{k}\cdot\vec{r}}]\ . \quad (2.3)$$

In (2.2) and (2.3) the $\vec{k}$ and λ dependence of the creation and annihilation operators $a(t)$ and $a^{\dagger}(t)$ are implicit. For the electron wave field, we write

$$\phi(\vec{q})=\sum_n b_n(t)\phi_n(\vec{q})\ , \quad (2.4)$$

where $\phi_n(\vec{q})$ are the orthonormal electron field modes. With these expansions, the multipolar Hamiltonian (2.1) becomes

$$H_{\mathrm{mult}}=\sum_n b_n^{\dagger}b_nE_n+\sum_{\vec{k},\lambda}a^{\dagger}a\hbar\omega-i\sum_{\substack{\vec{k},\lambda\\ m,n}}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}b_m^{\dagger}b_n\vec{\mu}^{mn}\cdot(\vec{e}ae^{i\vec{k}\cdot\vec{R}}-\bar{\vec{e}}a^{\dagger}e^{-i\vec{k}\cdot\vec{R}}) \quad (2.5)$$

where $\vec{\mu}^{mn}$ is the transition moment of the electric dipole and is given by

$$\int\bar{\phi}^m(\vec{q})\vec{\mu}\phi^n(\vec{q})d^3q\ .$$

The equations of motion for the operators a and b follow from (2.5) and the quantum-mechanical relations $[a,a^{\dagger}]_-=1$ and $[b,b^{\dagger}]_+=1$;

$$i\hbar\dot{a}=[a,H_{\mathrm{mult}}]_-=\hbar\omega a+i\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\sum_{m,n}b_m^{\dagger}b_n\vec{\mu}^{mn}\cdot\bar{\vec{e}}\ , \quad (2.6)$$

$$i\hbar\dot{b}_n=[b_n,H_{\mathrm{mult}}]_-=\hbar\omega_nb_n-i\sum_{\substack{\vec{k},\lambda,\\ m}}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}b_m\vec{\mu}^{nm}\cdot(\vec{e}a-\bar{\vec{e}}a^{\dagger})\ . \quad (2.7)$$

In (2.6) and (2.7) the molecular dipole is assumed to be at the origin ($\vec{R}=0$), and $E_n=\hbar\omega_n$. After putting $a(t)=\alpha(t)e^{-i\omega t}$ and $b_n(t)=\beta_n(t)e^{-i\omega_nt}$, we find

$$\dot{\alpha}(t)=\frac{1}{\hbar}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\sum_{m,n}e^{i(\omega_{mn}+\omega)t}\times\vec{\mu}^{mn}\cdot\bar{\vec{e}}\beta_m^{\dagger}(t)\beta_n(t) \quad (2.8)$$

and

$$\dot{\beta}_n(t)=-\frac{1}{\hbar}\sum_{\substack{\vec{k},\lambda\\ m}}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\beta_m(t)\vec{\mu}^{nm}\cdot[\vec{e}\alpha(t)e^{-i(\omega_{mn}+\omega)t}-\bar{\vec{e}}\alpha^{\dagger}(t)e^{-i(\omega_{mn}-\omega)t}]\ , \quad (2.9)$$

whence

$$\alpha(t)=\alpha(0)+\frac{1}{\hbar}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\sum_{m,n}\vec{\mu}^{mn}\cdot\bar{\vec{e}}\int_0^t e^{i(\omega_{mn}+\omega)t'}\beta_m^{\dagger}(t')\beta_n(t')dt' \quad (2.10)$$

and

$$\beta_n(t)=\beta_n(0)-\frac{1}{\hbar}\sum_{\substack{\vec{k},\lambda,\\ m}}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\vec{\mu}^{nm}\cdot\int_0^t[\vec{e}e^{-i(\omega_{mn}+\omega)t'}\beta_m(t')\alpha(t')-\bar{\vec{e}}e^{-i(\omega_{mn}-\omega)t'}\beta_m(t')\alpha^{\dagger}(t')]dt'\ . \quad (2.11)$$

From (2.3) the transverse displacement vector $d_i^{\perp}$ in the Heisenberg picture at time t is

$$d_i^{\perp}(t)=\sum_{\vec{k},\lambda}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}i[e_i\alpha(t)e^{i\vec{k}\cdot\vec{r}-i\omega t}-\bar{e}_i\alpha^{\dagger}(t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}] \quad (2.12)$$

which we evaluate as a series in powers of the dipole transition moments as in (2.13)

$$d_i^{\perp}(t)=d_i^{(0)}(t)+d_i^{(1)}(t)+d_i^{(2)}(t)+\cdots\ . \quad (2.13)$$

This is accomplished by expanding the operators $\alpha(t)$ and $\beta(t)$ in powers of the dipole moments. The leading term arises from $\alpha(t)$ and $\beta(t)$ evaluated at $t=0$, so that

$$d_i^{(0)}(t)=\sum_{\vec{k},\lambda}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}i[e_i\alpha(0)e^{i\vec{k}\cdot\vec{r}-i\omega t}-\bar{e}_i\alpha^{\dagger}(0)e^{-i\vec{k}\cdot\vec{r}+i\omega t}] \quad (2.14)$$

which is the free field operator at time t. The term linear in the transition moment is of the form

$$d_i^{(1)}(t)=\sum_{\vec{k},\lambda}\left[\frac{2\pi\hbar c k}{V}\right]^{1/2} i[e_i\alpha^{(1)}(t)e^{i\vec{k}\cdot\vec{r}-i\omega t} -\bar{e}_i\alpha^{(1)\dagger}(t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}]\,, \tag{2.15}$$

where, from (2.10)

$$\alpha^{(1)}(t)=\frac{1}{\hbar}\left[\frac{2\pi\hbar c k}{V}\right]^{1/2}\sum_{m,n}\mu_j^{mn}\bar{e}_j\beta_m^{\dagger}(0)\beta_n(0) \times\frac{e^{i(\omega_{mn}+\omega)t}-1}{i(\omega_{mn}+\omega)}\,. \tag{2.16}$$

Hence

$$d_i^{(1)}(t)=\frac{i}{\hbar}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left[\frac{2\pi\hbar c k}{V}\right]\left[\mu_j^{mn}\beta_m^{\dagger}(0)\beta_n(0)e_i\bar{e}_j \times e^{i\vec{k}\cdot\vec{r}-i\omega t}\frac{e^{i(\omega_{mn}+\omega)t}-1}{\omega_{mn}+\omega} + \text{H.c.}\right]. \tag{2.17}$$

After the polarization sum and the angular integration over the photon wave-vector direction, we obtain

$$d_i^{(1)}(t)=\frac{1}{\pi}\sum_{m,n}\mu_j^{mn}\beta_m^{\dagger}(0)\beta_n(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j) \times\frac{1}{r}\int_0^{\infty}\frac{e^{ikr}-e^{-ikr}}{2i}\,\frac{e^{ik_{mn}ct}-e^{-ikct}}{k_{mn}+k}dk +\text{H.c.} \tag{2.18}$$

Noting that the replacement of k by $-k$ in the Hermitian-conjugate term gives essentially the same contribution as the first term, we may write

$$d_i^{(1)}(\vec{r},t)=\frac{1}{2\pi i}\sum_{m,n}\mu_j^{mn}\beta_m^{\dagger}(0)\beta_n(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j) \times\frac{1}{r}\int_{-\infty}^{+\infty}\frac{e^{ikr}e^{-ik_{mn}ct}-e^{ik(r-ct)}-e^{-ikr}e^{-ik_{nm}ct}+e^{-ik(r+ct)}}{k-k_{nm}}dk\,. \tag{2.19}$$

The k integral in (2.19) is easily evaluated subject to a prescription that ensures causality. Thus the retarded solution is found to be

$$d_i^{(1)}(\vec{r},t)=\begin{cases}0, & t<r/c\\ \sum_{m,n}\mu_j^{mn}\beta_m^{\dagger}(0)\beta_n(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j) \times\dfrac{e^{ik_{nm}(r-ct)}}{r}, & t>r/c\,.\end{cases} \tag{2.20, 2.21}$$

The transverse displacement vector field in this order has a simple operator behavior with no effect on the photon field. For the transition from state ϕ_n to state ϕ_m its value is

$$\langle m\,|\,d_i^{(1)}(\vec{r},t)\,|\,n\rangle=e^{-i\omega_{nm}t}\mu_j^{nm}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j) \times\frac{e^{ik_{nm}r}}{r} \tag{2.22}$$

which is the familiar classical result[2] for the complex electric dipole field with an oscillator of circular frequency ω_{nm}. It is useful to define the tensor field

$$F_{ij}(k_{nm};\vec{r})=(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{e^{ik_{nm}r}}{r} \tag{2.23}$$

so that

$$d_i^{(1)mn}(\vec{r},t)=\mu_j^{mn}e^{-i\omega_{nm}t}F_{ij}(k_{nm};\vec{r})\,. \tag{2.24}$$

It must be emphasized that this field is the transverse displacement vector and not the transverse electric field. However, outside the source, the *total* electric field is equal to the transverse displacement field. This is because $\vec{d}^{\parallel}=0$ for a neutral system and hence $\vec{d}^{\perp}=\vec{d}^{\text{tot}}=\vec{e}^{\text{tot}}+4\pi\vec{p}$; for a point dipole at the origin, this is $\vec{e}^{\text{tot}}+4\pi\vec{\mu}\delta(\vec{r})$. In Sec. II C we consider this relationship using the minimal-coupling formalism where the transverse electric field is the canonical momentum.

As we noted earlier, the transverse displacement vector $\vec{d}^{\perp}(\vec{r},t)$ has higher-order contributions; these have not been considered hitherto, and we now evaluate the second-order contribution that depends quadratically on the transition moments. The contribution is of the form

$$d_i^{(2)}(\vec{r},t)=\sum_{\vec{k},\lambda}\left[\frac{2\pi\hbar c k}{V}\right]^{1/2} \times i[e_i\alpha^{(2)}(t)e^{i\vec{k}\cdot\vec{r}-i\omega t} -\bar{e}_i\alpha^{(2)\dagger}(t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}] \tag{2.25}$$

To evaluate $\alpha^{(2)}(t)$ it is necessary to use the equation of motion (2.11) for $\beta_n(t)$ in addition to (2.10). From (2.10) we find

$$\alpha^{(2)}(t)=\frac{1}{\hbar}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\sum_{m,n}\mu_j^{mn}\bar{e}_j\int_0^t e^{i(\omega_{mn}+\omega)t'}[\beta_m^{(0)\dagger}(t')\beta_n^{(1)}(t')+\beta_m^{(1)\dagger}(t')\beta_n^{(0)}(t')]dt' \tag{2.26}$$

and from (2.11) we have

$$\beta_n^{(1)}(t)=-\frac{1}{\hbar}\sum_{\substack{\vec{k}',\lambda'\\p}}\left[\frac{2\pi\hbar ck'}{V}\right]^{1/2}\mu_k^{np}\beta_p(0)\left[e_k'\alpha'(0)\frac{e^{-i(\omega_{pn}+\omega')t}-1}{-i(\omega_{pn}+\omega')}-\bar{e}_k'\alpha'^{\dagger}(0)\frac{e^{-i(\omega_{pn}-\omega')t}-1}{-i(\omega_{pn}-\omega')}\right] \tag{2.27}$$

so that the second-order contribution to $\alpha(t)$ is

$$\begin{aligned}\alpha^{(2)}(t)=&-\frac{1}{\hbar^2}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\\&\times\sum_{\substack{m,n\\p}}\mu_j^{mn}\bar{e}_j\int_0^t e^{i(\omega_{mn}+\omega)t'}\left[\beta_m^{\dagger}(0)\beta_p(0)\sum_{\vec{k},\lambda'}\left[\frac{2\pi\hbar ck'}{V}\right]^{1/2}\mu_k^{np}\left[\bar{e}_k'\alpha'(0)\frac{e^{-i(\omega_{pn}+\omega')t'}-1}{-i(\omega_{pn}+\omega')}\right.\right.\\&\qquad\left.-\bar{e}_k'\alpha'^{\dagger}(0)\frac{e^{-i(\omega_{pn}-\omega')t'}-1}{-i(\omega_{pn}-\omega')}\right]\\&\qquad+\beta_p^{\dagger}(0)\beta_n(0)\sum_{\vec{k}',\lambda'}\left[\frac{2\pi\hbar ck'}{V}\right]^{1/2}\mu_k^{pm}\left[\bar{e}_k'\alpha'^{\dagger}(0)\frac{e^{i(\omega_{pm}+\omega')t'}-1}{i(\omega_{pm}+\omega')}\right.\\&\qquad\left.\left.-e_k'\alpha'(0)\frac{e^{i(\omega_{pm}-\omega')t'}-1}{i(\omega_{pm}-\omega')}\right]\right]dt'\ .\end{aligned} \tag{2.28}$$

The integrated form of (2.28) and its Hermitian conjugate when used in the expansion (2.25) for $\vec{d}^{(2)}$ give

$$\begin{aligned}d_i^{(2)}(\vec{r},t)=i\sum_{\substack{\vec{k},\lambda,\\m,p}}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}&\left\{e_k\alpha(0)\beta_m^{\dagger}(0)\beta_p(0)\right.\\&\times(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\left[\sum_n\left[\frac{\mu_j^{mn}\mu_k^{np}}{E_{np}-\hbar\omega}+\frac{\mu_k^{mn}\mu_j^{np}}{E_{nm}+\hbar\omega}\right]\frac{e^{i(k_{pm}+k)(r-ct)}}{r}\right.\\&\qquad-\sum_n\frac{\mu_j^{mn}\mu_k^{np}}{E_{np}-\hbar\omega}\frac{e^{ik_{nm}(r-ct)}}{r}\\&\qquad\left.\left.-\sum_n\frac{\mu_k^{mn}\mu_j^{np}}{E_{nm}+\hbar\omega}\frac{e^{-ik_{np}(r-ct)}}{r}\right]\right\}+\text{H.c.}\end{aligned} \tag{2.29}$$

This operator, in contrast to $\vec{d}^{(0)}$ and $\vec{d}^{(1)}$, operates in both the photon and the electron field spaces. $\vec{d}^{(0)}$ annihilates and creates photons but does not change the electron states, $\vec{d}^{(1)}$ changes the electron states leaving the photon states unchanged. As we see from (2.29), $\vec{d}^{(2)}$ changes the photon number by one and, in general, changes the electron state. It should be noted that the first term within the square brackets has the interaction picture time dependence of the annihilation and creation operators. The remaining terms do not show a similar interaction picture type of time dependence. Matrix elements of such terms show sinusoidal time variation and in our applications they need to be considered only at near resonance when they are almost stationary. For the case where the electron state remains unchanged, the first term of $\vec{d}^{(2)}(\vec{r},t)$ can be expressed in terms of dynamic polarizability $\alpha_{jk}(\omega)$ for that state so that

$$d_i^{(2)}(\vec{r},t)=i\sum_{\vec{k},\lambda}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\alpha_{jk}(\omega)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\left[e_k\alpha(0)\frac{e^{ik(r-ct)}}{r}-\bar{e}_k\alpha^{\dagger}(0)\frac{e^{-ik(r-ct)}}{r}\right]+\cdots \tag{2.30}$$

where the ellipsis stands for resonant-type terms. We use this result in a later section to evaluate the Poynting vector, leading to the Einstein A coefficient.

Higher-order terms in the expansion (2.13) for $\vec{d}(\vec{r},t)$ with more powers of the dipole moments may be obtained in a similar way. The resultant operators will, in general, act in both the photon and electron spaces and need to be considered in the study of multiphoton processes.

B. Magnetic field of an oscillating electric dipole

The magnetic field $b_i(\vec{r},t)$ of an electric dipole can be found in the Heisenberg picture by using the expressions for $\alpha(t)$ and $\beta(t)$ given in the preceding section. The mode expansion for the magnetic field is

$$b_i(\vec{r},t)=\sum_{\vec{k},\lambda}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2} i[(\hat{k}\times\vec{e})_i\alpha(t)e^{i\vec{k}\cdot\vec{r}-i\omega t}-(\hat{k}\times\bar{\vec{e}})_i\alpha^\dagger(t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}] . \tag{2.31}$$

As for $\vec{d}(\vec{r},t)$, $\vec{b}(\vec{r},t)$ may be expressed as a series in powers of the electric transition moments. The first term, $b_i^{(0)}(\vec{r},t)$ is obtained from (2.31) with the approximation $\alpha(t)=\alpha(0)$. The second term, linear in the dipole moment, is easily found to be

$$b_i^{(1)}(\vec{r},t)=\begin{cases}\sum_{m,n}\mu_j^{mn}\beta_m^\dagger(0)\beta_n(0)(ik_{nm}\epsilon_{ijk}\nabla_k)\\ \quad\times\dfrac{e^{ik_{nm}(r-ct)}}{r}, & t>r/c\\ 0, & t<r/c\ .\end{cases} \tag{2.32}$$

It is convenient to introduce a tensor field $G_{ij}(k_{nm};\vec{r})$ analogous to $F_{ij}(k_{nm};\vec{r})$ of Eq. (2.23),

$$G_{ij}(k_{nm};\vec{r})=ik_{nm}\epsilon_{ijk}\nabla_k\left[\frac{e^{ik_{nm}r}}{r}\right] . \tag{2.33}$$

Then, for $t>r/c$,

$$b_i^{(1)}(\vec{r},t)=\sum_{m,n}\mu_j^{mn}\beta_m^\dagger(0)\beta_n(0)e^{-i\omega_{nm}t}G_{ij}(k_{nm};\vec{r}) . \tag{2.34}$$

This operator, as for $\vec{d}^{(1)}$, acts only on the electron states. The mnth matrix element of $\vec{b}^{(1)}$ is, for $t>r/c$,

$$b_i^{(1)mn}(\vec{r},t)=-\epsilon_{ijk}\mu_j^{mn}\hat{r}_k k_{nm}^2 \times\frac{e^{ik_{nm}(r-ct)}}{r}\left[1-\frac{1}{ik_{nm}r}\right] \tag{2.35}$$

which is the well-known classical result[2] for the magnetic field of an electric dipole.

The calculation of $\vec{b}^{(2)}(\vec{r},t)$ follows the same lines as $\vec{d}^{(2)}(\vec{r},t)$ and the result has a structure similar to (2.29), namely,

$$b_i^{(2)}(\vec{r},t)=i\sum_{\substack{\vec{k},\lambda\\ m,p}}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\left\{e_k\alpha(0)\beta_m^\dagger(0)\beta_p(0)\right.\times(i\epsilon_{ijl}\nabla_l)\left[\sum_n\left[\frac{\mu_j^{mn}\mu_k^{np}}{E_{np}-\hbar\omega}+\frac{\mu_k^{mn}\mu_j^{np}}{E_{nm}+\hbar\omega}\right](k_{pm}+k)\frac{e^{i(k_{pm}+k)(r-ct)}}{r}\right.$$
$$\left.\left.-\sum_n\frac{\mu_j^{mn}\mu_k^{np}}{E_{np}-\hbar\omega}k_{nm}\frac{e^{ik_{nm}(r-ct)}}{r}-\sum_n\frac{\mu_k^{mn}\mu_j^{np}}{E_{nm}+\hbar\omega}k_{pn}\frac{e^{-ik_{np}(r-ct)}}{r}\right]\right\}+\text{H.c.} \tag{2.36}$$

C. Comparison with the minimal-coupling approach

Before proceeding to use the above results in the calculation of the Poynting vector, it is instructive to examine how these fields may be obtained from the minimal-coupling Hamiltonian. In this formalism, the canonical field momentum $\vec{\Pi}(\vec{r},t)$ is $-4\pi c\vec{e}^{\perp}(\vec{r},t)$. Therefore, the mode expansion (2.3) now applies to the transverse electric field $\vec{e}^{\perp}(\vec{r},t)$,

$$\vec{e}^{\perp}(\vec{r},t)=i\sum_{\vec{k},\lambda}\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}[\vec{e}a(t)e^{i\vec{k}\cdot\vec{r}}-\bar{\vec{e}}a^\dagger(t)e^{-i\vec{k}\cdot\vec{r}}] . \tag{2.37}$$

Although the structure of the expansion is similar in the two cases, it must be emphasized that the equations of motion for the operators are different. The equations follow from the respective Hamiltonians.

In the minimal-coupling formalism, the Hamiltonian is

$$H_{\min}=\sum_n b_n^\dagger b_n E_n+\sum_{\vec{k},\lambda}a^\dagger a\hbar\omega+\frac{e}{mc}\sum_{\substack{\vec{k},\lambda,\\ m,n}}\left[\frac{2\pi\hbar c}{Vk}\right]^{1/2}b_m^\dagger b_n\vec{p}^{mn}\cdot(\vec{e}a+\bar{\vec{e}}a^\dagger) , \tag{2.38}$$

where we have omitted the e^2 terms since we confine our calculations in this section to the first-order fields. In (2.38) the matrix element of the electron momentum is related to the transition moment by

$$\vec{p}^{mn} = -\frac{im}{e\hbar} E_{mn} \vec{\mu}^{mn} . \tag{2.39}$$

The equation of motion for $\alpha(t)$, analogous to (2.8), that follows from $i\hbar\dot{a} = [a, H_{\min}]$ is

$$\dot{\alpha}(t) = \frac{-ie}{\hbar mc} \left[\frac{2\pi\hbar c}{Vk} \right]^{1/2} \sum_{m,n} \vec{p}^{mn} \cdot \bar{\vec{e}} \beta_m^\dagger(t) \beta_n(t) e^{i(\omega_{mn}+\omega)t} . \tag{2.40}$$

From (2.40) we obtain

$$\alpha^{(1)}(t) = \frac{-ie}{\hbar mc} \left[\frac{2\pi\hbar c}{Vk} \right]^{1/2} \sum_{m,n} \vec{p}^{mn} \cdot \bar{\vec{e}} \beta_m^\dagger(0) \beta_n(0) \frac{e^{i(\omega_{mn}+\omega)t} - 1}{i(\omega_{mn}+\omega)} . \tag{2.41}$$

If (2.41) is substituted into Eq. (2.37), we get, for $t > r/c > 0$,

$$e_i^{(1)}(\vec{r},t) = \frac{e}{mc} \sum_{m,n} \beta_m^\dagger(0)\beta_n(0) p_j^{mn} (-\nabla^2\delta_{ij} + \nabla_i\nabla_j) \frac{1}{r} \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{e^{ikr} - e^{-ikr}}{k} \frac{e^{ik_{mn}ct} - e^{-ikct}}{i(k - k_{nm})} dk$$

$$= \sum_{m,n} \beta_m^\dagger(0)\beta_n(0) \mu_j^{mn} e^{-ik_{nm}ck} (-\nabla^2\delta_{ij} + \nabla_i\nabla_j) \frac{e^{ik_{nm}r} - 1}{r} \tag{2.42}$$

$$= d_i^{(1)\perp}(\vec{r},t) + \sum_{m,n} \beta_m^\dagger(0)\beta_n(0) \mu_j^{mn} e^{-ik_{nm}ct} \frac{\delta_{ij} - 3\hat{r}_i\hat{r}_j}{r^3} , \tag{2.43}$$

where we have used (2.22) for $d_i^{(1)}(\vec{r},t)$. Using the fact that for $r > 0$, $\delta_{ij}^\perp(\vec{r}) = -(\delta_{ij} - 3\hat{r}_i\hat{r}_j)/4\pi r^3$, the second term of (2.43) is seen to be the transverse dipole polarization field operator $-4\pi p_i^{\perp(1)}(\vec{r},t)$. The longitudinal electric field to this order is

$$-\sum_{m,n} \beta_m^\dagger(0)\beta_n(0) \mu_j^{mn} e^{-ik_{nm}ct} \frac{\delta_{ij} - 3\hat{r}_i\hat{r}_j}{r^3} \tag{2.44}$$

and hence

$$e_i^{\text{tot}(1)}(\vec{r},t) = \sum_{m,n} \beta_m^\dagger(0)\beta_n(0) \mu_j^{mn} (-\nabla^2\delta_{ij} + \nabla_i\nabla_j) \times \frac{e^{ik_{nm}(r-ct)}}{r}, \quad r > 0 . \tag{2.45}$$

Thus we see that the often-quoted classical result represents the total electric field rather than the transverse electric field.

III. POYNTING VECTOR AND ENERGY FLUX

In this section we use the Heisenberg representation for the electromagnetic fields to calculate the energy flux from a molecule in an excited state. This application shows the importance of the second-order field terms in quantum electrodynamics. In fact, it will be seen that the first-order pseudopotential terms do not give the full contribution to the flux. Although the conventional classical calculation uses the first-order fields only, it may be used to obtain the total rate of energy emission by a quantal system with the aid of a correspondence principle relating the classical dipole moment with its quantum counterpart.[3,4] A measure of the energy flux density is given by the Poynting vector,

$$\vec{S}(\vec{r},t) = (c/8\pi)[\vec{e}^{\,\text{tot}}(\vec{r},t) \times \vec{b}(\vec{r},t) - \vec{b}(\vec{r},t) \times \vec{e}^{\,\text{tot}}(\vec{r},t)] . \tag{3.1}$$

As noted in Sec. II, the total electric field is equal to the transverse displacement vector field outside the source; thus

$$S_i(\vec{r},t) = (c/8\pi)\epsilon_{ijk}[d_j^\perp(\vec{r},t) b_k(\vec{r},t) + b_k(\vec{r},t) d_j^\perp(\vec{r},t)] . \tag{3.2}$$

The expectation value of this vector field for the state $|p;0\rangle$, where the molecule is in the excited state $|p\rangle$ and the electromagnetic field is the vacuum state, is

$$\langle S_i(\vec{r},t)\rangle = (c/8\pi)\epsilon_{ijk}\langle 0;p \,|\, (d_j^{(0)} + d_j^{(1)} + d_j^{(2)} + \cdots)(b_k^{(0)} + b_k^{(1)} + b_k^{(2)} + \cdots) \,|\, p;0\rangle + \text{c.c.}$$

$$= (c/8\pi)\epsilon_{ijk}\langle 0;p \,|\, (d_j^{(1)} b_k^{(1)} + d_j^{(0)} b_k^{(2)} + d_j^{(2)} b_k^{(0)} + \cdots) \,|\, p;0\rangle + \text{c.c.} \tag{3.3}$$

We confine our calculations to the terms of $S_i(\vec{r},t)$ that are quadratic in the transition moments. The contribution from the first-order fields is

$$\frac{c}{8\pi}\epsilon_{ijk}\langle 0;p\,|\,d_j^{(1)}b_k^{(1)}\,|\,p;0\rangle+\text{c.c.} \tag{3.4}$$

$$=\frac{c}{8\pi}\epsilon_{ijk}\langle 0;p\,|\sum_{m,n}\mu_{j'}^{mn}e^{-ik_{nm}ct}\beta_m^\dagger(0)\beta_n(0)F_{jj'}(k_{nm};\vec{r})\sum_{m',n'}\mu_{k'}^{m'n'}e^{-ik_{n'm'}ct}\beta_{m'}^\dagger(0)\beta_{n'}(0)G_{kk'}(k_{n'm'};\vec{r})\,|\,p;0\rangle+\text{c.c.} \tag{3.5}$$

$$=\frac{c}{8\pi}\epsilon_{ijk}\sum_n\mu_{j'}^{pn}\mu_{k'}^{np}\left[(-\nabla^2\delta_{jj'}+\nabla_j\nabla_{j'})\frac{e^{ik_{np}r}}{r}\right]\left[i\epsilon_{kk'l}k_{pn}\nabla_l\frac{e^{ik_{pn}r}}{r}\right]+\text{c.c.} \tag{3.6}$$

To evaluate the energy flux it is sufficient to use a large spherical surface whose center is the molecular origin. For $r\gg\lambda\!\!\!^{-}_{np}$, the far-zone form of (3.6) is

$$-\frac{c}{4\pi r^2}\epsilon_{ijk}\epsilon_{kk'l}\sum_n k_{pn}^4\mu_{j'}^{pn}\mu_{k'}^{np}(\delta_{jj'}-\hat{r}_j\hat{r}_{j'})\hat{r}_l\ . \tag{3.7}$$

The contribution of this term to the energy radiated per second is

$$\frac{c}{4\pi}\sum_n k_{pn}^4\mu_{j'}^{pn}\mu_{k'}^{np}\int(\delta_{j'k'}-\hat{r}_{j'}\hat{r}_{k'})dr=\tfrac{2}{3}c\sum_n k_{pn}^4\,|\,\mu^{pn}\,|^2\ . \tag{3.8}$$

It is important to note that both downward *and* upward transitions contribute to (3.8) since (3.8) is independent of the sign of k_{pn}. This paradox is resolved when we take into account the contributions from the second-order fields.

The contributions to the energy flux density, quadratic in the transition moments, from the second-order fields are

$$\frac{c}{8\pi}\epsilon_{ijk}\langle 0;p\,|\,d_j^{(0)}b_k^{(2)}+d_j^{(2)}b_k^{(0)}\,|\,p;0\rangle+\text{c.c.} \tag{3.9}$$

Since both $\vec{d}^{\,(0)}$ and $\vec{d}^{\,(2)}$ (and $\vec{b}^{\,(0)},\vec{b}^{\,(2)}$) are linear in the photon annihilation and creation operators, we can write (3.9) as

$$\frac{c}{8\pi}\epsilon_{ijk}\sum_{\vec{k},\lambda}(\langle 0;p\,|\,d_j^{(0)}\,|\,p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p\,|\,b_k^{(2)}\,|\,p;0\rangle+\langle 0;p\,|\,d_j^{(2)}\,|\,p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p\,|\,b_k^{(0)}\,|\,p;0\rangle)+\text{c.c.} \tag{3.10}$$

To evaluate the matrix elements of $\vec{d}^{(2)}$ and $\vec{b}^{(2)}$, we used the expansions (2.30) and (2.36). As shown in the Appendix, the resonant-type terms do not contribute to the Poynting vector, so that using the polarizability-dependent terms we obtain

$$\frac{c}{8\pi}\epsilon_{ijk}\sum_{\vec{k},\lambda}[e_j\bar{e}_{k'}e^{i\vec{k}\cdot\vec{r}}\alpha_{k'j'}(k)\bar{G}_{kj'}(k;\vec{r})+e_{k'}(\hat{\vec{k}}\times\bar{\vec{e}})_k e^{-i\vec{k}\cdot\vec{r}}\alpha_{j'k'}(k)F_{jj'}(k;\vec{r})]+\text{c.c.} \tag{3.11}$$

After the polarization sum and the angular integration over the direction of the wave vector, (3.11) becomes

$$\frac{c}{8\pi}\epsilon_{ijk}\int_0^\infty\hbar c\alpha_{j'k'}(k)\frac{k\,dk}{2\pi i}\left[\left[(-\nabla^2\delta_{jk'}+\nabla_j\nabla_{k'})\frac{e^{ikr}-e^{-ikr}}{r}\right]\times\left[-i\epsilon_{kj'l}\nabla_l\frac{e^{-ikr}}{r}\right]+\left[(-\nabla^2\delta_{jj'}+\nabla_j\nabla_{j'})\frac{e^{ikr}}{r}\right]\left[i\epsilon_{k'kl}\nabla_l\frac{e^{ikr}-e^{-ikr}}{r}\right]\right]+\text{c.c.} \tag{3.12}$$

Using the j',k' symmetry of the polarizability tensor, and doing the k integral, we get

$$-\frac{c}{8\pi}\epsilon_{ijk}\sum_n\mu_{j'}^{pn}\mu_{k'}^{np}k_{np}\left[(-\nabla^2\delta_{jj'}+\nabla_j\nabla_{j'})\frac{e^{-ik_{np}r}}{r}\right]\left[-i\epsilon_{kk'l}\nabla_l\frac{e^{-ik_{np}r}}{r}\right]+\text{c.c.},\quad k_{np}>0 \tag{3.13a}$$

and

$$-\frac{c}{8\pi}\epsilon_{ijk}\sum_n\mu_{j'}^{pn}\mu_{k'}^{np}k_{np}\left[(-\nabla^d\delta_{jj'}+\nabla_j\nabla_{j'})\frac{e^{ik_{np}r}}{r}\right]\left[-i\epsilon_{kk'l}\nabla_l\frac{e^{ik_{np}r}}{r}\right]+\text{c.c.},\quad k_{np}<0\ . \tag{3.13b}$$

In the far zone, these reduce to

$$c\sum_n(\pm)\frac{k_{np}^4}{4\pi r^2}\mu_{j'}^{pn}\mu_{k'}^{np}\epsilon_{ijk}\epsilon_{kk'l}(\delta_{jj'}-\hat{r}_j\hat{r}_{j'})\hat{r}_l\ , \tag{3.14}$$

the plus sign holding for $k_{np}>0$ and the minus sign for $k_{np}<0$. The contribution of (3.14) to the energy radiated per second can be calculated in a manner similar to that leading to (3.8). We get

$$\tfrac{2}{3}c\sum_n(\text{sgn}k_{pn})k_{pn}^4\,|\,\vec{\mu}^{\,pn}\,|^2\ . \tag{3.15}$$

The total rate of energy loss P is found by adding (3.15) to (3.8):

$$P=\frac{4}{3}c \sum_{n\,(k_{pn}>0)} k_{pn}^4 \,|\vec{\mu}^{pn}|^2 . \tag{3.16}$$

Thus as expected, we find that only the spontaneously allowed transitions contribute to this total power. It is clear that (3.16) leads directly to the Einstein A coefficient, $(4/3\hbar)k_{pn}^3 \,|\vec{\mu}^{pn}|^2$, for the spontaneous transition rate. This method of obtaining the power may be contrasted with the conventional approach[5] employing the Fermi rate. Despite the somewhat lengthy manipulation, our method has direct physical appeal and shows the role of the Maxwell fields in the transport of energy emitted by a molecule.

APPENDIX

We show that the resonant-type terms, independent of the polarizability of the molecule, in $\vec{d}^{(2)}$ and $\vec{b}^{(2)}$ do not contribute to the time-averaged Poynting vector. Using these terms from (2.29) and (2.36) in

$$\frac{c}{8\pi}\epsilon_{ijk}\langle 0;p\,|\,d_j^{(0)}b_k^{(2)}+d_j^{(2)}b_k^{(0)}\,|\,p;0\rangle \tag{A1}$$

we have

$$\frac{c}{8\pi}\epsilon_{ijk}\sum_{\vec{k},\lambda,n}\left[\frac{2\pi\hbar c k}{V}\right]\left[e_j\bar{e}_l e^{i\vec{k}\cdot\vec{r}}e^{-ikct}\left[\frac{\mu_l^{pn}\mu_m^{np}}{E_{pn}+\hbar\omega}\bar{G}_{km}(k_{np};\vec{r})e^{ik_{np}ct}+\frac{\mu_m^{pn}\mu_l^{np}}{E_{pn}-\hbar\omega}\bar{G}_{km}(k_{pn};\vec{r})e^{ik_{pn}ct}\right]\right.$$
$$\left.+e_m[\hat{k}\times\bar{\vec{e}}]_k e^{-i\vec{k}\cdot\vec{r}}e^{ikct}\left[\frac{\mu_l^{pn}\mu_m^{np}}{E_{pn}+\hbar\omega}F_{jl}(k_{np};\vec{r})e^{-ik_{np}ct}+\frac{\mu_m^{pn}\mu_l^{np}}{E_{pn}-\hbar\omega}F_{jl}(k_{pn};\vec{r})e^{-ik_{pn}ct}\right]\right] . \tag{A2}$$

In (A2) only one pair of terms will contribute to the time average depending on the sign of k_{pn}. For example, with $k_{pn}>0$, the relevant pair of terms in (A2), after polarization sum and angular integration, is

$$\frac{c}{8\pi}\epsilon_{ijk}\sum_n\int\left[\left[(-\nabla^2\delta_{jl}+\nabla_j\nabla_l)\frac{\sin(kr)}{\pi r}\right]e^{-ikct}\frac{\mu_l^{pn}\mu_m^{np}}{k_{pn}-k}\bar{G}_{km}(k_{pn};\vec{r})e^{ik_{pn}ct}\right.$$
$$\left.-\left[ik\epsilon_{kmn}\nabla_n\frac{\sin(kr)}{\pi r}\right]e^{ikct}\frac{\mu_m^{pn}\mu_l^{np}}{k_{pn}-k}F_{jl}(k_{pn};\vec{r})e^{-ik_{pn}ct}\right]dk . \tag{A3}$$

The time dependence of the integrand of (A3) shows that the important contribution to the k integration comes from the pole at $k=k_{pn}$ and hence the integration limits can be extended to cover the full range $-\infty$ to ∞. The pole contribution is evaluated subject to the causality condition, namely that for $r>ct$ the integral must vanish. Thus for $r<ct$, (A3) gives

$$\frac{c}{8\pi}\epsilon_{ijk}\sum_n\mu_l^{pn}\mu_m^{np}\left[\left[-(\nabla^2\delta_{jl}+\nabla_j\nabla_l)\frac{e^{ik_{pn}(r-ct)}}{r}\right]\bar{G}_{km}(k_{pn};\vec{r})e^{ik_{pn}ct}-\left[ik_{pn}\epsilon_{kmn}\nabla_n\frac{e^{ik_{pn}(r-ct)}}{r}\right]F_{jl}(k_{pn};\vec{r})e^{-ik_{pn}ct}\right]$$
$$=-\frac{c}{8\pi}\epsilon_{ijk}\sum_n\mu_l^{pn}\mu_m^{np}[F_{jl}(k_{pn};\vec{r})\bar{G}_{km}(kn;\vec{r})+G_{km}(k_{np};\vec{r})F_{jl}(k_{pn};\vec{r})]=0 , \tag{A4}$$

where we have used $\bar{G}_{km}(k_{pn};\vec{r})=-G_{km}(k_{np};\vec{r})$.

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