Maxwell field operators, the energy density, and the Poynting vector calculated using the minimal-coupling framework of molecular quantum electrodynamics in the Heisenberg picture

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The time-dependent total electric- and magnetic-field operators in the neighborhood of a molecule are calculated in the minimal-coupling formalism of Coulomb gauge quantum electrodynamics. The spatial variations of the vector potential are taken into account, enabling the fields correct to second order in the electronic charge to include magnetic-dipole- and electric-quadrupole-dependent terms in addition to contributions arising from the electric-dipole interaction term. The minimal-coupling Maxwell fields are compared and contrasted with their analogs previously derived in the multipolar framework. The electric- and magnetic-radiation-field operators derived in the minimal-coupling formalism are then used to calculate the expectation values of the Thomson energy density and the Poynting vector, and the results obtained are shown to be identical to those of the multipolar theory. [S1050-2947(97)08310-8]

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I. INTRODUCTION

Two forms of the Hamiltonian function commonly used in the quantum-mechanical description of the interaction of electromagnetic radiation with atoms and molecules are the minimal-coupling and multipolar Hamiltonians [1–16]. Various studies have been concerned with the equivalence of the two Hamiltonians in radiation-molecule interactions [7,8,11–16]. Although the application of the multipolar version of the theory to problems occurring in the areas of chemical physics and quantum optics is widespread, the minimal-coupling Hamiltonian still retains its importance fundamentally, originating from the classical Lagrangian function for the interaction of a charged particle with a radiation field. Despite the minimal- and multipolar-coupling Hamiltonians being different, identical matrix elements are obtained for processes where conservation of energy holds. This is a direct consequence of the equivalent nature of the two Hamiltonians; in the quantum theory one route by which the multipolar Hamiltonian may be generated is by the application of a canonical transformation to the minimal-coupling Hamiltonian. Equal matrix elements are therefore obtained ''on the energy shell,'' and this has been demonstrated explicitly for processes such as one- and two-photon absorption [13,17] and Rayleigh and Raman scattering of light [18].

For the treatment of radiation-molecule and intermolecular interactions in the time-dependent multipolar formalism [11], the Heisenberg equation of motion for a time-dependent dynamical variable is calculated followed by the Maxwell field operators in the neighborhood of a molecule [19–21]. For a neutral system the first Maxwell equation states that the divergence of the electric displacement field $\vec{d}(\vec{r})$ vanishes; hence $\vec{d}(\vec{r})$ is entirely transverse. The transverse electric displacement and magnetic fields are expanded in series of powers of the molecular source multipole moments and the expectation value of a physical quantity expressed in terms of time-dependent operators is then evaluated.

In this paper the Maxwell fields in the vicinity of a molecule are derived starting from the minimal-coupling Hamiltonian. In this formalism the momentum conjugate to the vector potential is proportional to the transverse component of the electric field $\vec{e}(\vec{r})$, in contrast to the multipolar case where the conjugate momentum is proportional to the transverse component of the displacement field, with $\vec{d}(\vec{r}) = \varepsilon_0 \vec{e}(\vec{r}) + \vec{p}(\vec{r})$, where $\vec{p}(\vec{r})$ is the electric polarization field. Instead of evaluating the displacement field in the proximity of a source as in the multipolar framework, in the minimal-coupling approach the transverse electric-field operator is calculated. For neutral atoms and molecules the total electric field is equal to the transverse displacement field outside the source since the longitudinal component of the displacement field is zero. Also, since the transverse electric polarization field is nonlocal, $\varepsilon_0 \vec{e}^{\perp}(\vec{r}) \neq \vec{d}^{\perp}(\vec{r})$ outside the source. This has the important consequence that $\vec{e}^{\perp}(\vec{r})$ is unretarded, in contrast to the source-dependent total electric field $\vec{e}^{\,\mathrm{tot}}(\vec{r})$, which is fully retarded. A retarded result for $\vec{e}^{\,\mathrm{tot}}(\vec{r})$ is obtained after cancellation of the nonretarded contributions arising from the transverse polarization field with those from the transverse electric field. Although $\vec{d}(\vec{r})$ is the same as $\vec{e}^{\,\mathrm{tot}}(\vec{r})$, the time evolution of the displacement field as calculated using the multipolar Hamiltonian gives $\vec{d}(\vec{r},t)$ which is different from $\vec{e}^{\,\mathrm{tot}}(\vec{r},t)$ obtained with the minimal-coupling Hamiltonian. Noting also that the dynamical equations of motion for the system do not affect the magnetic field $\vec{b}(\vec{r})$, the magnetic-field operators in both approaches are different since the Heisenberg operator equations of motion are different in both formalisms. Hence $\vec{b}(\vec{r})$ is also determined in

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minimal-coupling.

This treatment extends previous work [19], in which the equivalence of the first-order total electric field with the corresponding electric displacement field was demonstrated in the electric-dipole approximation by evaluating the first- and second-order higher multipole total electric and magnetic fields. The derivation given takes into account the leading correction term arising from the inclusion of the first derivative of the vector potential. This is equivalent to the inclusion of the electric-quadrupole and magnetic-dipole coupling terms in the multipolar framework. Sum rules and identities that enable minimal-coupling matrix elements to be written explicitly in terms of molecular multipole moments will be used and will facilitate comparison with Maxwell fields previously calculated in the multipolar framework. The first-order radiation field operators are found to be identical in both formalisms, in contrast to the second-order minimal-coupling Maxwell fields, which differ from their multipolar analogs. The electric-dipole-dependent minimal-coupling Maxwell field operators will then be used to evaluate the Thomson energy density and the Poynting vector of the radiation field correct to second order in the moments. The expectation value of these quadratic operators will be shown to be identical to those previously obtained using the multipolar Maxwell fields [22].

The Heisenberg equations of motion for the electron and photon field operators are developed in the next section, followed by the calculation of the total-electric- and magnetic-field operators in Secs. III and IV, respectively. The electric and magnetic energy density is calculated in Sec. V and the Poynting vector in Sec. VI. The work is summarized in Sec. VII.

II. OPERATOR EQUATIONS OF MOTION

The starting point in the derivation of the Maxwell fields in the vicinity of a molecule is the minimal-coupling Hamiltonian

$$H_{\min}=\frac{\vec{p}^{\,2}}{2m}+V+\frac{1}{2}\,\varepsilon_0\int\{\vec{e}^{\perp 2}(\vec{r})+c^2\vec{b}^{\,2}(\vec{r})\}d^3\vec{r}+\frac{e}{m}\,\vec{p}\cdot\vec{a}(\vec{q})+\frac{e^2}{2m}\,\vec{a}^2(\vec{q}),\tag{2.1}$$

a sum of familiar molecular, radiation field, and interaction terms, with the electron sum implicit. The first term represents the total energy of a particle of charge e, mass m, position vector $\vec{q}$, momentum $\vec{p}$, and intramolecular potential energy V; $\vec{e}^{\perp}(\vec{r})$ and $\vec{b}(\vec{r})$ are, respectively, the transverse component of the electric field and the magnetic field for electromagnetic radiation of vector potential $\vec{a}(\vec{q})$.

In a previous study [19] the variation of the vector potential over the extent of the molecules was ignored; $\vec{a}(\vec{q})$ was replaced by $\vec{a}(\vec{R})$, $\vec{R}$ being the molecular center and usually taken to be the origin. This is equivalent to the electric-dipole approximation in the multipolar formalism. For the inclusion of magnetic-dipole and electric-quadrupole moments in the evaluation of the electromagnetic radiation fields it is essential that the spatial variations of the vector potential to first order are accounted for by including the first derivative of $\vec{a}(\vec{q})$. The second quantized minimal-coupling Hamiltonian can then be written as

$$\begin{aligned}H_{\min}=&\sum_n b_n^\dagger b_n E_n+\sum_{\vec{k},\lambda} a^\dagger a\hbar\omega+\frac{e}{m}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\\ &\times b_m^\dagger b_n\{e_j a[p_j^{mn}+ik_k(p_jq_k)^{mn}]\\ &+\overline{e_j}a^\dagger[p_j^{mn}-ik_k(p_jq_k)^{mn}]\}\\ &+\frac{e^2}{2m}\sum_{\substack{m,n,\vec{k}',\lambda'\\ k'',\lambda''}}\left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2}\left(\frac{\hbar}{2\varepsilon_0 ck''V}\right)^{1/2}\\ &\times b_m^\dagger b_n[e_j'e_j''a'a''(1+ik_k'q_k^{mn}+ik_k''q_k^{mn})\\ &+e_j'\overline{e_j''}a'a''^\dagger(1+ik_k'q_k^{mn}-ik_k''q_k^{mn})\\ &+\overline{e_j'}e_j''a'^\dagger a''(1-ik_k'q_k^{mn}+ik_k''q_k^{mn})+\overline{e_j'e_j''}a'^\dagger a''^\dagger\\ &\times(1-ik_k'q_k^{mn}-ik_k''q_k^{mn})],\end{aligned}\tag{2.2}$$

where Einstein's summation convention for repeated Cartesian tensor indices is adopted and use has been made of the mode expansion of the vector potential

$$\vec{a}(\vec{r},t)=\sum_{\vec{k},\lambda}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\{\vec{e}^{(\lambda)}(\vec{k})a^{(\lambda)}(\vec{k},t)e^{i\vec{k}\cdot\vec{r}}+\overline{\vec{e}^{(\lambda)}}(\vec{k})a^{\dagger(\lambda)}(\vec{k},t)e^{-i\vec{k}\cdot\vec{r}}\}.\tag{2.3}$$

In expressions (2.2) and (2.3), a and $a^\dagger$ respectively represent time-dependent annihilation and creation operators of the second quantized formalism for a photon of wave vector $\vec{k}$ and index of polarization λ; $\vec{e}^{(\lambda)}(\vec{k})$ is the electric polarization vector for radiation of mode $(\vec{k},\lambda)$ and frequency $\omega=c|k|$. $b_n^\dagger$ and b_n are the analogous time-dependent fermion creation and destruction operators for the molecular state $|n\rangle$ of energy E_n. The time dependence of the boson and fermion operators in Eq. (2.2) is implicit, as is the mode dependence of the photon creation and annihilation operators and electric polarization vectors.

The time development of the operators a and b_n are found from the Heisenberg equations of motion

$$\begin{aligned}i\hbar\dot{a}=&[a,H_{\min}]_-\\ =&\hbar\omega a+\frac{e}{m}\sum_{m,n}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}b_m^\dagger b_n\overline{e_j}[p_j^{mn}\\ &-ik_k(p_jq_k)^{mn}]\\ &+\frac{e^2}{m}\sum_{\vec{k}',\lambda',m,n}\left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2}\\ &\times\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}b_m^\dagger b_n\overline{e_j}q[e_j'a'(1+ik_k'q_k^{mn}-ik_kq_k^{mn})\\ &+\overline{e_j'}a'^\dagger(1-ik_k'q_k^{mn}-ik_kq_k^{mn})]\end{aligned}\tag{2.4}$$

and

$$i\hbar\dot{b}_n=[b_n,H_{\min}]_-=\hbar\omega_n b_n+\frac{e}{m}\sum_{\substack{\vec{k},\lambda\\ m}}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}b_m\{e_j a[p_j^{nm}+ik_k(p_jq_k)^{nm}]+\overline{e_j}a^\dagger[p_j^{nm}-ik_k(p_jq_k)^{nm}]\}. \quad (2.5)$$

In expression (2.5) the term of order e^2 has been ignored since this will not be required in the derivation of the fields for terms quadratic in the moments. The coupled equations of motion are solved by successive iteration, generating solutions in series of powers of the electronic charge. By employing the interaction representation through the substitutions $a(t)=\alpha(t)\exp(-i\omega t)$ and $b_n(t)=\beta_n(t)\exp(-i\omega_n t)$ and integrating Eq. (2.4), it is found that

$$\begin{aligned}\alpha(t)=\alpha(0)&+\frac{e}{i\hbar m}\sum_{m,n}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\overline{e_j}[p_j^{mn}-ik_k(p_jq_k)^{mn}]\int_0^t dt' e^{i(\omega_{mn}+\omega)t'}\beta_m^\dagger(t')\beta_n(t')\\
&+\frac{e^2}{i\hbar m}\sum_{\vec{k}',\lambda',m,n}\left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\overline{e_j}\int_0^t dt'\beta_m^\dagger(t')\beta_n(t')[e_j'\alpha'(t')e^{i(\omega_{mn}+\omega-\omega')t'}\\
&\times(1+ik_k'q_k^{mn}-ik_kq_k^{mn})+\overline{e_j'}\alpha'^\dagger(t')e^{i(\omega_{mn}+\omega+\omega')t'}\\
&\times(1-ik_k'q_k^{mn}-ik_kq_k^{mn}],\end{aligned} \quad (2.6)$$

while the electron-field operator linear in the electric charge from Eq. (2.5) is

$$\begin{aligned}\beta_n^{(1)}(t)=\frac{e}{\hbar m}\sum_{\substack{\vec{k},\lambda\\ m}}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\beta_m(0)\Bigg\{&e_j a(0)[p_j^{nm}+ik_k(p_jq_k)^{nm}]\left(\frac{e^{-i(\omega_{mn}+\omega)t}-1}{\omega_{mn}+\omega}\right)+\overline{e_j}\alpha^\dagger(0)[p_j^{nm}-ik_k(p_jq_k)^{nm}]\\
&\times\left(\frac{e^{-i(\omega_{mn}-\omega)t}-1}{\omega_{mn}-\omega}\right)\Bigg\}.\end{aligned} \quad (2.7)$$

To evaluate the first-order Maxwell fields, it is sufficient to find $\alpha(t)$ to first order. From Eq. (2.6)

$$\alpha^{(1)}(t)=\frac{e}{i\hbar m}\sum_{m,n}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\beta_m^\dagger(0)\beta_n(0)\overline{e_j}[p_j^{mn}-ik_k(p_jq_k)^{mn}]\left(\frac{e^{i(\omega_{mn}+\omega)t}-1}{i(\omega_{mn}+\omega)}\right). \quad (2.8)$$

To determine the second-order Maxwell field operators, $\alpha^{(2)}(t)$ is required to order e^2 and is obtained by iterating the term linear in the electric charge in Eq. (2.6) to first order and the contribution quadratic in e to zeroth order, which after using Eq. (2.7) and its Hermitian conjugate and performing the time integral becomes

$$\begin{aligned}\alpha^{(2)}(t)=\left(\frac{e}{i\hbar m}\right)^2&\sum_{\substack{\vec{k}',\lambda'\\ m,n,p}}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2}\beta_m^\dagger(0)\beta_p(0)\\
&\times\overline{e_j}\Bigg(e_l'\alpha'(0)\Bigg\{[p_l^{mn}p_j^{np}+ik_m'(p_lq_m)^{mn}p_j^{np}-ik_kp_l^{mn}(p_jq_k)^{np}]\\
&\times\left[\left(\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{mp}+\omega-\omega')(\omega_{mn}-\omega')}\right)-\left(\frac{e^{i(\omega_{np}+\omega)t}-1}{(\omega_{np}+\omega)(\omega_{mn}-\omega')}\right)\right]+[p_j^{mn}p_l^{np}-ik_k(p_jq_k)^{mn}p_l^{np}+ik_m'p_j^{mn}(p_lq_m)^{np}]\\
&\times\left[\left(\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{mp}+\omega-\omega')(\omega_{pn}+\omega')}\right)-\left(\frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{mn}+\omega)(\omega_{pn}+\omega')}\right)\right]\Bigg\}\\
&+\overline{e_l'}\alpha'^\dagger(0)\Bigg\{[p_l^{mn}p_j^{np}-ik_m'(p_lq_m)^{mn}p_j^{np}-ik_kp_l^{mn}(p_jq_k)^{np}]\\
&\times\left[\left(\frac{e^{i(\omega_{mp}+\omega+\omega')t}-1}{(\omega_{mp}+\omega+\omega')(\omega_{mn}+\omega')}\right)-\left(\frac{e^{i(\omega_{np}+\omega)t}-1}{(\omega_{np}+\omega)(\omega_{mn}+\omega')}\right)\right]+[p_j^{mn}p_l^{np}-ik_k(p_jq_k)^{mn}p_l^{np}-ik_m'p_j^{mn}(p_lq_m)^{np}]\\
&\times\left[\left(\frac{e^{i(\omega_{mp}+\omega+\omega')t}-1}{(\omega_{mp}+\omega+\omega')(\omega_{pn}-\omega')}\right)-\left(\frac{e^{i(\omega_{mn}+\omega)t}-1}{(\omega_{mn}+\omega)(\omega_{pn}-\omega')}\right)\right]\Bigg\}+\hbar m\delta_{jl}\Bigg[e_l'\alpha'(0)(1-ik_kq_k^{mp}+ik_k'q_k^{mp})\\
&\times\left(\frac{e^{i(\omega_{mp}+\omega-\omega')t}-1}{(\omega_{mp}+\omega-\omega')}\right)+\overline{e_l'}\alpha'^\dagger(0)(1-ik_kq_k^{mp}-ik_k'q_k^{mp})\left(\frac{e^{i(\omega_{mp}+\omega+\omega')t}-1}{(\omega_{mp}+\omega+\omega')}\right)\Bigg]\Bigg),\end{aligned} \quad (2.9)$$

with $\alpha^{(2)\dagger}(t)$ given by the Hermitian conjugate of expression (2.9).

III. TOTAL ELECTRIC-FIELD OPERATOR

Before going on to derive the magnetic field, the total electric field in the neighborhood of a molecule is obtained. Its transverse component is proportional to the canonical field momentum in the minimal-coupling approach and is given by the mode expansion

$$e_i^{\perp}(\vec{r},t)=i\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}[e_i\alpha(t)e^{i\vec{k}\cdot\vec{r}-i\omega t} -\overline{e_i}\alpha^{\dagger}(t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}], \tag{3.1}$$

which is evaluated as a power series in the electric charge as

$$e_i^{\perp}(\vec{r},t)=e_i^{\perp(0)}(\vec{r},t)+e_i^{\perp(1)}(\vec{r},t)+e_i^{\perp(2)}(\vec{r},t)+\cdots \tag{3.2}$$

by using the operator equations (2.8) and (2.9). The zeroth-order transverse electric field independent of all sources is simply the free field operator.

A. First-order contribution

The first-order electric field is obtained by substituting the first-order operator equation (2.8) $\alpha^{(1)}(t)$ into the mode expansion (3.1). The molecular multipole moment matrix elements to this order of approximation may be extracted with the use of the identity [23]

$$-\frac{e}{m}e_i[p_i\mp ik_j(p_iq_j)]^{mn}=\frac{i}{\hbar}e_iE_{mn}\mu_i^{mn}\mp ikb_im_i^{mn} \pm\frac{1}{\hbar}e_ik_jE_{mn}Q_{ij}^{mn}, \tag{3.3}$$

where $E_{mn}=E_m-E_n$ and $\vec{\mu}$, $\vec{m}$, and $\vec{\vec{Q}}$ are the electric-dipole, magnetic-dipole, and electric-quadrupole moments, respectively. Inserting relation (3.3) into Eq. (2.8) then yields

$$\alpha^{(1)}(t)=\frac{1}{\hbar}\sum_{m,n}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\beta_m^{\dagger}(0)\beta_n(0)\left[\frac{i}{\hbar}\overline{e_i}E_{mn}\mu_i^{mn} -ik\overline{b_i}m_i^{mn}+\frac{1}{\hbar}\overline{e_ik}_jE_{mn}Q_{ij}^{mn}\right]\left(\frac{e^{i(\omega_{mn}+\omega)t}-1}{\omega_{mn}+\omega}\right). \tag{3.4}$$

Substituting Eq. (3.4) into Eq. (3.1), the first-order transverse electric field is

$$e_i^{\perp(1)}(\vec{r},t)=\frac{i}{2\varepsilon_0 V}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left\{\beta_m^{\dagger}(0)\beta_n(0)e_ie^{i\vec{k}\cdot\vec{r}} \times\left[\frac{i}{\hbar}\overline{e_j}E_{mn}\mu_j^{mn}-ik\overline{b_j}m_j^{mn}+\frac{1}{\hbar}\overline{e_jk}_kE_{mn}Q_{jk}^{mn}\right] \times\left(\frac{e^{i\omega_{mn}t}-e^{-i\omega t}}{\omega_{mn}+\omega}\right)+\text{H.c.}\right\}, \tag{3.5}$$

where H.c. denotes the Hermitian conjugate. Performing the polarization sums, converting the wave-vector sum to an integral, carrying out the angular averages [13], and finally evaluating the k integral for $r<ct$ results in

$$e_i^{\perp(1)}(\vec{r},t)=\frac{1}{4\pi\varepsilon_0}\sum_{m,n}\beta_m^{\dagger}(0)\beta_n(0)\left\{\mu_j^{mn}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j) \times\frac{e^{-ik_{nm}ct}}{r}(e^{ik_{nm}r}-1)-\frac{1}{c}m_j^{mn}(ik_{nm}\varepsilon_{ijk}\nabla_k) \times\frac{e^{ik_{nm}(r-ct)}}{r}-Q_{jk}^{mn}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_k \times\frac{e^{-ik_{nm}ct}}{r}(e^{ik_{nm}r}-1)\right\}, \tag{3.6}$$

while for $r>ct$ the field is zero. It should be noted that the electric-dipole- and electric-quadrupole-dependent contributions to the first-order transverse electric field contain nonretarded terms, arising from the pole occurring at $k=0$ when evaluating the k integral. In contrast, the magnetic-dipole-dependent term is fully retarded since physically a magnetic dipole has no static electric field.

To determine the total electric field to this order, the longitudinal electric field is required. The latter is given by

$$\varepsilon_0 e_i^{\parallel}(\vec{r},t)=-p_i^{\parallel}(\vec{r},t) =p_i^{\perp}(\vec{r},t) =\sum_{m,n}(\mu_j^{mn}-Q_{jk}^{mn}\nabla_k)\beta_m^{\dagger}(t)\beta_n(t)\delta_{ij}^{\perp}(\vec{r})e^{-i\omega_{nm}t}. \tag{3.7}$$

Noting that for $r\neq 0$ the transverse delta dyadic

$$\delta_{ij}^{\perp}(\vec{r})=-\frac{1}{4\pi r^3}(\delta_{ij}-3\hat{r}_i\hat{r}_j), \tag{3.8}$$

it follows that the first-order longitudinal electric field is

$$-\frac{1}{4\pi r^3}\sum_{m,n}\beta_m^{\dagger}(0)\beta_n(0)e^{-i\omega_{nm}t}(\mu_j^{mn}-Q_{jk}^{mn}\nabla_k) \times(\delta_{ij}-3\hat{r}_i\hat{r}_j). \tag{3.9}$$

To obtain the *total* electric field correct to this order of approximation, Eq. (3.9) is added to Eq. (3.6), resulting in

$$e_i^{\text{tot}(1)}(\vec{r},t)=\frac{1}{4\pi\varepsilon_0}\sum_{m,n}\beta_m^{\dagger}(0)\beta_n(0)\left[\mu_j^{mn}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j) -\frac{1}{c}m_j^{mn}(ik_{nm}\varepsilon_{ijk}\nabla_k) -Q_{jk}^{mn}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_k\right]\frac{e^{ik_{nm}(r-ct)}}{r} =\varepsilon_0^{-1}d_i^{\perp(1)}(\vec{r},t). \tag{3.10}$$

It is seen that the longitudinal electric field exactly cancels the instantaneous type terms in $\vec{e}^{\perp(1)}(\vec{r},t)$, Eq. (3.6) with the

retarded total electric field equal to ε_0^{-1} times the transverse displacement field operator of the multipolar formalism [20,21]. This completes the derivation of the first-order total electric field in the proximity of a molecule in the minimal-coupling framework. The transverse component of $\vec{e}(\vec{r})$ was obtained directly from the mode expansion for the momentum canonically conjugate to the vector potential, while the longitudinal part was found from the electric polarization field.

B. Second-order contribution

To determine the second-order electric field, $\alpha^{(2)}(t)$, given by Eq. (2.9), is used. The minimal-coupling matrix elements occurring in expression (2.9) are converted to transition multipole moment matrix elements using the identity (3.3) and two further identities [18] (3.11) and (3.12),

$$-\frac{\hbar e^2}{m}\,\delta_{jk}=\sum_{p,n}\,(\omega_{mn}\mu_j^{mn}\mu_k^{np}-\omega_{np}\mu_k^{mn}\mu_j^{np})\,\delta_{mp} \tag{3.11}$$

$$\frac{ie^2}{m}\,e_i\hat{k}_k q_k^{mp}=\frac{ic}{\hbar}\,e_j\hat{k}_k\sum_n\,(k_{np}\mu_i^{mn}Q_{jk}^{np}-k_{mn}Q_{jk}^{mn}\mu_i^{np}) + \frac{1}{\hbar}\,b_j\sum_n\,(\mu_i^{mn}m_j^{np}-m_j^{mn}\mu_i^{np}). \tag{3.12}$$

These are then substituted into the mode expansion (3.1) to give

$$\begin{aligned}
e_i^{\perp(2)}(\vec{r},t)=&\frac{i}{\hbar}\sum_{\substack{\vec{k}',\lambda',\vec{k},\lambda\\ m,n,p}}\left(\frac{1}{2\varepsilon_0 V}\right)\left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2}e_1'\alpha'(0)\beta_m^{\dagger}(0)\beta_p(0)\\
&\times\Bigg[e_i e^{i\vec{k}\cdot\vec{r}}\Bigg(\Bigg\{\mu_l^{mn}\mu_j^{np}\omega_{mn}\omega_{np}\overline{e_j}-ik_k'\overline{e_j}\Bigg[\left(\frac{i}{\hbar}\right)^2E_{mn}E_{np}Q_{kl}^{mn}\mu_j^{np}-\frac{i}{\hbar}\,\varepsilon_{lkt}E_{np}m_t^{mn}\mu_j^{np}-\frac{e}{2m}\,\delta_{kl}\delta_{mn}E_{np}\mu_j^{np}\Bigg]\\
&+i\left(\frac{i}{\hbar}\right)^2\overline{e_j}k_kE_{mn}E_{np}\mu_l^{mn}Q_{jk}^{np}+i\left(\frac{i}{\hbar}\right)k\overline{b_j}E_{mn}\mu_l^{mn}m_j^{np}\Bigg\}\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')(\omega_{mn}-\omega')}-\frac{e^{i\omega_{np}t}-e^{-i\omega t}}{(\omega_{np}+\omega)(\omega_{mn}-\omega')}\right)\\
&+\Bigg\{\mu_j^{mn}\mu_l^{np}\omega_{mn}\omega_{np}\overline{e_j}-ik_k'\overline{e_j}\Bigg[\left(\frac{i}{\hbar}\right)^2E_{mn}E_{np}\mu_j^{mn}Q_{kl}^{np}-\frac{i}{\hbar}\,\varepsilon_{lkt}E_{mn}\mu_j^{mn}m_t^{np}-\frac{e}{2m}\,\delta_{kl}\delta_{pn}E_{mn}\mu_j^{mn}\Bigg]\\
&+i\left(\frac{i}{\hbar}\right)^2\overline{e_j}k_kE_{mn}E_{np}Q_{jk}^{mn}\mu_l^{np}+i\left(\frac{i}{\hbar}\right)k\overline{b_j}E_{np}m_j^{mn}\mu_l^{np}\Bigg\}\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')(\omega_{pn}+\omega')}-\frac{e^{i\omega_{mn}t}-e^{-i\omega t}}{(\omega_{mn}+\omega)(\omega_{pn}+\omega')}\right)\Bigg)\\
&+\Bigg[\Bigg(\frac{e^2\hbar}{im}\,\overline{e_j}\delta_{jl}k_m'q_m^{mp}+\delta_{mp}\overline{e_j}(\omega_{mn}\mu_j^{mn}\mu_l^{np}-\omega_{np}\mu_l^{mn}\mu_j^{np})\\
&+k[ic\overline{e_j}\hat{k}_k(k_{np}\mu_l^{mn}Q_{jk}^{np}-k_{mn}Q_{jk}^{mn}\mu_l^{np})+\overline{b_j}(\mu_l^{mn}m_j^{np}-m_j^{mn}\mu_l^{np})]\Bigg)\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{\omega_{mp}+\omega-\omega'}\right)\Bigg]\Bigg]+\text{H.c.}
\end{aligned} \tag{3.13}$$

Concentrating for the moment on the contribution quadratic in the electric-dipole moments, carrying out the polarization sum and angular average produces

$$\begin{aligned}
e_i^{\perp(2)}(\mu\mu;\vec{r},t)=&\frac{i}{4\pi\varepsilon_0\hbar}\sum_{\substack{\vec{k}',\lambda'\\ m,n,p}}\left(\frac{\hbar}{2\varepsilon_0 ck'V}\right)^{1/2}\beta_m^{\dagger}(0)\beta_n(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\,\frac{1}{2\pi ir}\,e_k'\alpha'(0)\int_{-\infty}^{\infty}\frac{dk}{k}\,(e^{ikr}-e^{-ikr})\\
&\times\Bigg[\mu_k^{mn}\mu_j^{np}k_{mn}k_{np}\left(\frac{e^{i(k_{mp}-k')ct}-e^{-ikct}}{(k_{mp}+k-k')(k_{mn}-k')}-\frac{e^{ik_{np}ct}-e^{-ikct}}{(k_{np}+k)(k_{mn}-k')}\right)\\
&+\mu_j^{mn}\mu_k^{np}k_{mn}k_{np}\left(\frac{e^{i(k_{mp}-k')ct}-e^{-ikct}}{(k_{mp}+k-k')(k_{pn}+k')}-\frac{e^{ik_{mn}ct}-e^{-ikct}}{(k_{mn}+k)(k_{pn}+k')}\right)+\delta_{mp}(k_{mn}\mu_j^{mn}\mu_k^{np}-k_{np}\mu_k^{mn}\mu_j^{np})\\
&\times\left(\frac{e^{i(k_{mp}-k')ct}-e^{-ikct}}{k_{mp}+k-k'}\right)\Bigg].
\end{aligned} \tag{3.14}$$

Integrating subject to $r<ct$ and setting $m=p$ results in

$$e_i^{\perp(2)}(\mu\mu;\vec{r},t)=\frac{i}{4\pi\varepsilon_0}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}e_k\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\,\frac{1}{r}\left[\left(\frac{\mu_j^{mn}\mu_k^{nm}}{E_{nm}-\hbar\omega}+\frac{\mu_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}\right.$$
$$\left.+\frac{\mu_j^{mn}\mu_k^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{mn}}{k}\right)[e^{-ikct}-e^{ik_{mn}ct}+e^{-ik_{mn}(r-ct)}]+\frac{\mu_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)[-e^{-ikct}+e^{-ik_{mn}ct}-e^{ik_{mn}(r-ct)}]\right]$$
$$+\text{H.c.}, \tag{3.15}$$

which, like $e_i^{\perp(1)}(\vec{r},t)$, also contains nonretarded terms. To obtain the retarded, second-order electric-dipole-dependent contribution to the total electric field, the corresponding longitudinal electric field must be added to Eq. (3.15). The latter is obtained from the first term of Eq. (3.7) and by retaining the $\vec{p}^{mn}$ terms of Eq. (2.7) and its Hermitian conjugate, giving

$$p_i^{\perp(2)}(\mu\mu;\vec{r},t)=\sum_{m,p}\mu_j^{mp}\delta_{ij}^{\perp}(\vec{r})e^{-i\omega_{pm}t}[\beta_m^{\dagger(1)}(t)\beta_p(0)+\beta_m(0)\beta_p^{\dagger(1)}(t)]$$
$$=-\frac{e}{i\hbar m}\sum_{\substack{\vec{k},\lambda\\ m,n,p}}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}\delta_{ij}^{\perp}(\vec{r})\beta_m^{\dagger}(0)\beta_p(0)\left\{\left[\overline{e_l}\alpha^{\dagger}(0)p_l^{mn}\left(\frac{e^{i(\omega_{mp}+\omega)t}-e^{-i\omega_{pn}t}}{i(\omega_{mn}+\omega)}\right)\right.\right.$$
$$\left.+e_l\alpha(0)p_l^{mn}\left(\frac{e^{i(\omega_{mp}-\omega)t}-e^{-i\omega_{pn}t}}{i(\omega_{mn}-\omega)}\right)\right]\mu_j^{np}+\mu_j^{mn}\left[e_l\alpha(0)p_l^{np}\left(\frac{e^{i(\omega_{mp}-\omega)t}-e^{-i\omega_{nm}t}}{i(\omega_{pn}+\omega)}\right)\right.$$
$$\left.\left.+\overline{e_l}\alpha^{\dagger}(0)p_l^{np}\left(\frac{e^{i(\omega_{mp}+\omega)t}-e^{-i\omega_{nm}t}}{i(\omega_{pn}-\omega)}\right)\right]\right\}. \tag{3.16}$$

Using relation (3.3), the diagonal term of Eq. (3.16) is

$$p_i^{\perp(2)}(\mu\mu;\vec{r},t)=\frac{i}{4\pi}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\left\{e_k\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)\right.$$
$$\left.\times(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\,\frac{1}{r}\left[\frac{\mu_j^{mn}\mu_k^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{nm}}{k}\right)(e^{-ikct}-e^{ik_{mn}ct})+\frac{\mu_k^{mn}\mu_j^{nm}k}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)(e^{-ikct}-e^{-ik_{mn}ct})\right]\right\}+\text{H.c.} \tag{3.17}$$

Adding Eq. (3.17) to Eq. (3.15) produces the total second-order electric-dipole-dependent electric field

$$e_i^{\text{tot}(2)}(\mu\mu;\vec{r},t)=\frac{i}{4\pi\varepsilon_0}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}e_k\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\,\frac{1}{r}$$
$$\times\left[\left(\frac{\mu_j^{mn}\mu_k^{nm}}{E_{nm}-\hbar\omega}+\frac{\mu_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}+\frac{\mu_j^{mn}\mu_k^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{nm}(r-ct)}+\frac{\mu_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{mn}(r-ct)}\right]+\text{H.c.}, \tag{3.18}$$

which is fully retarded and is applicable for $r<ct$. It is instructive to demonstrate that $\vec{e}^{\text{tot}(2)}(\vec{r},t)$ vanishes for $r>ct$, thus showing the causal nature of $\vec{e}^{\text{tot}(2)}(\vec{r},t)$. Recalling that $\vec{e}^{\perp(2)}(\vec{r},t)$ has nonretarded contributions, by returning to Eq. (3.14) and evaluating the integral for the electric-dipole-dependent part subject to $r>ct$, these are found to be after simplifying

$$\frac{i}{4\pi\varepsilon_0\hbar}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar}{2\varepsilon_0 ckV}\right)^{1/2}e_k\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)$$
$$\times(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\,\frac{1}{r}\left(\frac{\mu_k^{mn}\mu_j^{nm}}{k_{mn}-k}\,k_{mn}(e^{-ikct}-e^{ik_{nm}ct})+\frac{\mu_j^{mn}\mu_k^{nm}}{k_{mn}+k}\,k_{mn}(e^{ik_{mn}ct}-e^{-ikct})\right)+\text{H.c.} \tag{3.19}$$

Adding Eq. (3.19) to the electric-dipole-dependent transverse polarization field (3.17) results in

$$e_i^{\mathrm{tot}(2)}(\mu\mu;\vec{r},t)=e_i^{\perp(2)}(\mu\mu;\vec{r},t)+\varepsilon_0^{-1}p_i^{\perp(2)}(\mu\mu;\vec{r},t)=0, \tag{3.20}$$

so that the total electric field obtained is strictly causal, vanishing for $t<r/c$.

The total second-order fields bilinear in the electric- and magnetic-dipole moments and bilinear in the electric dipole and quadrupole moments can be obtained in a manner similar to that used to obtain the quadratic electric-dipole-dependent contribution. Returning to expression (3.13), performing the appropriate polarization sums and angular averages, evaluating the k integrals subject to $r<ct$, and adding the relevant terms in the second-order electric polarization field (3.21),

$$p_i^{\perp(2)}(\vec{r},t)=\sum_{m,p}(\mu_j^{mp}-Q_{jk}^{mp}\nabla_k)\delta_{ij}^{\perp}(\vec{r})e^{-i\omega_{pm}t}[\beta_m^{\dagger(1)}(t)\beta_p(0)+\beta_m(0)\beta_p^{\dagger(1)}(t)], \tag{3.21}$$

whose diagonal terms after substituting Eqs. (2.7) and (3.3) are

$$\begin{aligned}p_i^{\perp(2)}(\vec{r},t)=&\frac{i}{4\pi}\sum_{\substack{\vec{k},\lambda\\m,n}}\left(\frac{\hbar c}{2\varepsilon_0 kV}\right)^{1/2}\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)\\&\times(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r}\left\{\left[e_k k_{nm}\mu_k^{mn}\mu_j^{nm}-e_k k_{nm}\right.\right.\\&\left.\times\mu_k^{mn}Q_{jl}^{nm}\nabla_l+ie_k k_l k_{nm}Q_{kl}^{mn}\mu_j^{nm}-\frac{1}{c}\,kb_k m_k^{mn}\mu_j^{nm}\right]\left(\frac{e^{-ikct}-e^{ik_{nm}ct}}{E_{mn}-\hbar\omega}\right)+\left[e_k k_{mn}\mu_j^{mn}\mu_k^{nm}-e_k k_{mn}Q_{jl}^{mn}\nabla_l\mu_k^{nm}\right.\\&\left.\left.+ie_k k_l k_{mn}\mu_j^{mn}Q_{kl}^{nm}-\frac{1}{c}\,kb_k\mu_j^{mn}m_k^{nm}\right]\left(\frac{e^{-ikct}-e^{ik_{mn}ct}}{E_{mn}+\hbar\omega}\right)\right\},\end{aligned} \tag{3.22}$$

result in

$$\begin{aligned}e_i^{\mathrm{tot}(2)}(\mu m;\vec{r},t)=&\frac{i}{4\pi\varepsilon_0 c}\sum_{\substack{\vec{k},\lambda\\m,n}}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}b_k\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r}\left[\left(\frac{\mu_j^{mn}m_k^{nm}}{E_{nm}-\hbar\omega}+\frac{m_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}\right.\\&\left.-\frac{\mu_j^{mn}m_k^{nm}}{E_{nm}-\hbar\omega}\,e^{ik_{nm}(r-ct)}-\frac{m_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\,e^{ik_{mn}(r-ct)}\right]+\frac{i}{4\pi\varepsilon_0}\sum_{\substack{\vec{k},\lambda\\m,n}}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}e_k\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)\\&\times(ik\varepsilon_{ijl}\nabla_l)\frac{1}{r}\left[\left(\frac{\mu_k^{mn}m_j^{nm}}{E_{nm}-\hbar\omega}+\frac{m_j^{mn}\mu_k^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}-\frac{\mu_k^{mn}m_j^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{nm}(r-ct)}\right.\\&\left.-\frac{m_j^{mn}\mu_k^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{mn}(r-ct)}\right]+\mathrm{H.c.},\end{aligned} \tag{3.23}$$

$$\begin{aligned}e_i^{\mathrm{tot}(2)}(\mu Q;\vec{r},t)=&-\frac{1}{4\pi\varepsilon_0}\sum_{\substack{\vec{k},\lambda\\m,n}}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}e_k k_l\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{1}{r}\left[\left(\frac{\mu_j^{mn}Q_{kl}^{nm}}{E_{nm}-\hbar\omega}+\frac{Q_{kl}^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}\right.\\&\left.-\frac{\mu_j^{mn}Q_{kl}^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{nm}(r-ct)}-\frac{Q_{kl}^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{mn}(r-ct)}\right]-\frac{i}{4\pi\varepsilon_0}\sum_{\substack{\vec{k},\lambda\\m,n}}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}e_l\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)\\&\times(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\nabla_k\frac{1}{r}\left[\left(\frac{\mu_l^{mn}Q_{jk}^{nm}}{E_{nm}-\hbar\omega}+\frac{Q_{jk}^{mn}\mu_l^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}-\frac{\mu_l^{mn}Q_{jk}^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{nm}(r-ct)}\right.\\&\left.-\frac{Q_{jk}^{mn}\mu_l^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{mn}(r-ct)}\right]+\mathrm{H.c.}\end{aligned} \tag{3.24}$$

As for the electric-dipole case, the instantaneous-type contributions occurring in $\vec{e}^{\perp}(\vec{r},t)$, when added to the transverse polarization field, result in the total electric field in the neighborhood of the source vanishing for $r>ct$, as demanded by causality. It should be noted that the total electric-field quadratic in the magnetic-dipole and electric-quadrupole moments and bilinear in these two moments can be obtained by including higher-order terms in the spatial variation of the vector potential. Comparing the second-order total electric field with the corresponding second-order electric displacement field in the vicinity of a molecule [19,21], the two are seen to differ, although their form is similar, in contrast to the first-order displacement and total electric fields, which are identical. The total electric-field second order in the moments, like the analogous electric displacement field operator [19,21], acts in both the fermion and boson spaces, changing the state of electronic excitation and the number of photons.

IV. MAGNETIC-FIELD OPERATOR

The magnetic-field operator correct to second order in the source moments is now calculated in the minimal-coupling framework using the equations of motion for the photon and electron operators developed in Sec. II. The mode expansion for the magnetic field is given by

$$\vec{b}(\vec{r},t)=i\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}[\vec{b}^{(\lambda)}(\vec{k})\alpha(t)e^{i\vec{k}\cdot\vec{r}-i\omega t}-\overrightarrow{\overline{b}^{(\lambda)}}(\vec{k})\alpha^{\dagger}(t)e^{-i\vec{k}\cdot\vec{r}+i\omega t}], \tag{4.1}$$

where the magnetic polarization vector $\vec{b}^{(\lambda)}(\vec{k})$ is defined by

$$\vec{b}^{(\lambda)}(\vec{k})=\vec{\hat{k}}\times\vec{e}^{(\lambda)}(\vec{k}). \tag{4.2}$$

The free field operator independent of all sources is identical in both the minimal- and multipolar-coupling frameworks, obtained by inserting $\alpha(t)=\alpha(0)$ into Eq. (4.1).

A. First-order contribution

The magnetic field linear in the sources is obtained by substituting the first-order equation of motion for $\alpha(t)$, Eq. (3.4), into the mode expansion (4.1), giving

$$b_i^{(1)}(\vec{r},t)=\frac{i}{\hbar}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar}{2\varepsilon_0 cV}\right)\left\{\beta_m^{\dagger}(0)\beta_n(0)b_i e^{i\vec{k}\cdot\vec{r}}\left[\frac{i}{\hbar}\,\overline{e_j}E_{mn}\mu_j^{mn}-ik\overline{b_j}m_j^{mn}+\frac{1}{\hbar}\,\overline{e_j}k_k E_{mn}Q_{jk}^{mn}\right]\left(\frac{e^{i\omega_{mn}t}-e^{-i\omega t}}{\omega_{mn}+\omega}\right)+\text{H.c.}\right\}. \tag{4.3}$$

Evaluating in the usual manner results in

$$b_i^{(1)}(\vec{r},t)=\begin{cases}\dfrac{1}{4\pi\varepsilon_0 c}\displaystyle\sum_{m,n}\beta_m^{\dagger}(0)\beta_n(0)\left[\mu_j^{mn}(ik_{nm}\varepsilon_{ijk}\nabla_k)+\frac{1}{c}\,m_j^{mn}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)+Q_{jk}^{mn}(ik_{nm}\varepsilon_{ijl}\nabla_l\nabla_k)\right]\dfrac{e^{ik_{nm}(r-ct)}}{r}, & r<ct\\ 0, \quad r>ct.\end{cases} \tag{4.4}$$

Comparing Eq. (4.4) with the analogous result obtained within the multipolar framework [20,21], the two first-order magnetic fields are found to be identical. This is despite the fact that the Heisenberg equations of motion for the fermion and boson operators obtained from the minimal- and multipolar-coupling Hamiltonians are different in both approaches.

B. Second-order contribution

The second-order contribution to the magnetic field is obtained by substituting the second-order operator $\alpha^{(2)}(t)$ given by expression (2.9), after conversion to multipole moments using the identities (3.3), (3.11), and (3.12), into the mode expansion (4.1). Thus

$$b_i^{(2)}(\vec{r},t)=\frac{i}{\hbar c}\sum_{\substack{\vec{k}',\lambda',\vec{k},\lambda\\ m,n,p}}\left(\frac{1}{2\varepsilon_0 V}\right)\left(\frac{\hbar}{2\varepsilon_0 c k' V}\right)^{1/2} e_1'\alpha'(0)\beta_m^{\dagger}(0)\beta_p(0)\Bigg[b_i e^{i\vec{k}\cdot\vec{r}}\Bigg(\Bigg\{\mu_l^{mn}\mu_j^{np}\omega_{mn}\omega_{np}\overline{e_j}-ik_k'\overline{e_j}\Bigg[\left(\frac{i}{\hbar}\right)^2 E_{mn}E_{np}Q_{kl}^{mn}\mu_j^{np}$$

$$-\frac{i}{\hbar}\,\varepsilon_{lkt}E_{np}m_t^{mn}\mu_j^{np}-\frac{e}{2m}\,\delta_{kl}\delta_{mn}E_{np}\mu_j^{np}\Bigg]+i\left(\frac{i}{\hbar}\right)^2\overline{e_j}k_k E_{mn}E_{np}\mu_l^{mn}Q_{jk}^{np}+i\left(\frac{i}{\hbar}\right)k\overline{b_j}E_{mn}\mu_l^{mn}m_j^{np}\Bigg\}$$

$$\times\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')(\omega_{mn}-\omega')}-\frac{e^{i\omega_{np}t}-e^{-i\omega t}}{(\omega_{np}+\omega)(\omega_{mn}-\omega')}\right)+\Bigg\{\mu_j^{mn}\mu_l^{np}\omega_{mn}\omega_{np}\overline{e_j}-ik_k'\overline{e_j}\Bigg[\left(\frac{i}{\hbar}\right)^2 E_{mn}E_{np}\mu_j^{mn}Q_{kl}^{np}$$

$$-\frac{i}{\hbar}\,\varepsilon_{lkt}E_{mn}\mu_j^{mn}m_t^{np}-\frac{e}{2m}\,\delta_{kl}\delta_{pn}E_{mn}\mu_j^{mn}\Bigg]+i\left(\frac{i}{\hbar}\right)^2\overline{e_j}k_k E_{mn}E_{np}Q_{jk}^{mn}\mu_l^{np}+i\left(\frac{i}{\hbar}\right)k\overline{b_j}E_{np}m_j^{mn}\mu_l^{np}\Bigg\}$$

$$\times\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{(\omega_{mp}+\omega-\omega')(\omega_{pn}+\omega')}-\frac{e^{i\omega_{mn}t}-e^{-i\omega t}}{(\omega_{mn}+\omega)(\omega_{pn}+\omega')}\right)\Bigg)+\Bigg[\Bigg(\frac{e^2\hbar}{im}\,\overline{e_j}\delta_{jl}k_m'q_m^{mp}+\delta_{mp}\overline{e_j}(\omega_{mn}\mu_j^{mn}\mu_l^{np}-\omega_{np}\mu_l^{mn}\mu_j^{np})$$

$$+ic\overline{e_j}\hat{k}_k(k_{np}\mu_l^{mn}Q_{jk}^{np}-k_{mn}Q_{jk}^{mn}\mu_l^{np})+k\overline{b_j}(\mu_l^{mn}m_j^{np}-m_j^{mn}\mu_l^{np})\Bigg)\left(\frac{e^{i(\omega_{mp}-\omega')t}-e^{-i\omega t}}{\omega_{mp}+\omega-\omega'}\right)\Bigg]\Bigg]+\text{H.c.} \tag{4.5}$$

Evaluating in the usual manner and extracting the individual contributions quadratic in the moments results in the second-order magnetic fields

$$b_i^{(2)}(\mu\mu;\vec{r},t)=\frac{i}{4\pi\varepsilon_0}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar k}{2\varepsilon_0 c V}\right)^{1/2} e_k\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)(ik\varepsilon_{ijl}\nabla_l)\,\frac{1}{r}\Bigg[\left(\frac{\mu_j^{mn}\mu_k^{nm}}{E_{nm}-\hbar\omega}+\frac{\mu_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}$$

$$-\frac{\mu_j^{mn}\mu_k^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{nm}(r-ct)}-\frac{\mu_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{mn}(r-ct)}\Bigg]+\text{H.c.}, \tag{4.6}$$

$$b_i^{(2)}(\mu m;\vec{r},t)=\frac{i}{4\pi\varepsilon_0 c}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar k}{2\varepsilon_0 c V}\right)^{1/2} b_k\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)(ik\varepsilon_{ijl}\nabla_1)\,\frac{1}{r}\Bigg[\left(\frac{\mu_j^{mn}m_k^{nm}}{E_{nm}-\hbar\omega}+\frac{m_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}$$

$$-\frac{\mu_j^{mn}m_k^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{nm}(r-ct)}-\frac{m_k^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{mn}(r-ct)}\Bigg]+\frac{i}{4\pi\varepsilon_0 c}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar k}{2\varepsilon_0 c V}\right)^{1/2} e_k\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)$$

$$\times(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\,\frac{1}{r}\Bigg[\left(\frac{\mu_k^{mn}m_j^{nm}}{E_{nm}-\hbar\omega}+\frac{m_j^{mn}\mu_k^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}-\frac{\mu_k^{mn}m_j^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{mn}}{k}\right)e^{ik_{nm}(r-ct)}$$

$$-\frac{m_j^{mn}\mu_k^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{nm}}{k}\right)e^{ik_{mn}(r-ct)}\Bigg]+\text{H.c.}, \tag{4.7}$$

$$b_i^{(2)}(\mu Q;\vec{r},t)=-\frac{1}{4\pi\varepsilon_0}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar k}{2\varepsilon_0 c V}\right)^{1/2} e_l k_k\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)(ik\varepsilon_{ijt}\nabla_t)\,\frac{1}{r}\Bigg[\left(\frac{\mu_j^{mn}Q_{kl}^{nm}}{E_{nm}-\hbar\omega}+\frac{Q_{kl}^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}$$

$$-\frac{\mu_j^{mn}Q_{kl}^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{nm}(r-ct)}-\frac{Q_{kl}^{mn}\mu_j^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{mn}(r-ct)}\Bigg]$$

$$+\frac{1}{4\pi\varepsilon_0}\sum_{\substack{\vec{k},\lambda\\ m,n}}\left(\frac{\hbar k}{2\varepsilon_0 c V}\right)^{1/2} e_l\alpha(0)\beta_m^{\dagger}(0)\beta_m(0)(k\varepsilon_{ijs}\nabla_s\nabla_k)\,\frac{1}{r}\Bigg[\left(\frac{\mu_l^{mn}Q_{jk}^{nm}}{E_{nm}-\hbar\omega}+\frac{Q_{jk}^{mn}\mu_l^{nm}}{E_{nm}+\hbar\omega}\right)e^{ik(r-ct)}$$

$$-\frac{\mu_l^{mn}Q_{jk}^{nm}}{E_{nm}-\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{nm}(r-ct)}-\frac{Q_{jk}^{mn}\mu_l^{nm}}{E_{nm}+\hbar\omega}\left(\frac{k_{mn}}{k}\right)^2 e^{ik_{mn}(r-ct)}\Bigg]+\text{H.c.} \tag{4.8}$$

The second-order magnetic fields derived in the minimal-coupling formalism also differ from their analogs calculated in the multipolar approach [19,21]. The electric-dipole-dependent minimal-coupling Maxwell fields are now employed in the calculation of the energy density in a radiation field and the rate of flow of electromagnetic energy from a molecule in an excited electronic state. The expectation values for these processes will be shown to be equivalent to those obtained previously [22] using the multipolar formalism radiation field operators.

V. CALCULATION OF THE ELECTROMAGNETIC ENERGY DENSITY

The expectation value of the electric energy density for the radiation field in the state where no photons are present and with the molecule in the state $|p\rangle$ is

$$\tfrac{1}{2}\varepsilon_0\langle 0;p|e_i^{\mathrm{tot}(1)}e_i^{\mathrm{tot}(1)}+e_i^{(0)}e_i^{\mathrm{tot}(2)}+e_i^{\mathrm{tot}(2)}e_i^{(0)}|p;0\rangle, \tag{5.1}$$

retaining terms second order in the moments only. This is now evaluated for an electric-dipole source. The first term of Eq. (5.1), the contribution from the product of the first-order total electric field of an electric-dipole source, is exactly the same as the corresponding term in the multipolar calculation [22], namely,

$$\frac{1}{32\pi^2\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}k_{pn}^6\overline{f_{ij}}(k_{pn}r)f_{ik}(k_{pn}r), \tag{5.2}$$

where

$$F_{ij}(kr)=\frac{1}{k^3}\,(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\,\frac{e^{ikr}}{r}=f_{ij}(kr)e^{ikr}, \tag{5.3}$$

since ε_0 times the total first-order electric field was shown in Sec. III A to be equal to the first-order transverse displacement field. For the contribution arising from the interference of the vacuum field with the second-order field, only that part of the quadratic field that is diagonal in the electron space is required since the free field operates entirely in the photon space and cannot change the state of the molecule. By taking the diagonal matrix element for a state $|p\rangle$, the second-order electric-dipole-dependent total electric field (3.18) operates solely in the boson space

$$\begin{aligned}&\langle p|e_i^{\mathrm{tot}(2)}(\mu\mu;\vec{r},t)|p\rangle\\&\quad=\frac{i}{4\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{1/2}[e_k\alpha(0)e^{-i\omega t}A_{ki}\\&\quad\quad-\overline{e_k}\alpha^{\dagger}(0)e^{i\omega t}\overline{A_{ki}}],\end{aligned} \tag{5.4}$$

with

$$\begin{aligned}A_{ki}=&\sum_n\frac{\mu_j^{pn}\mu_k^{np}}{E_{np}-\hbar\omega}\left[k^3F_{ij}(kr)-\left(\frac{k_{np}^4}{k}\right)F_{ij}(k_{np}r)e^{i(k_{pn}+k)ct}\right]\\&+\sum_n\frac{\mu_k^{pn}\mu_j^{np}}{E_{np}+\hbar\omega}\left[k^3F_{ij}(kr)-\left(\frac{k_{pn}^4}{k}\right)\right.\\&\left.\times F_{ij}(k_{pn}r)e^{-i(k_{pn}-k)ct}\right].\end{aligned} \tag{5.5}$$

Using the mode expansion for the zeroth-order electric field and Eq. (5.4), the last two terms of Eq. (5.1) are

$$\begin{aligned}&\frac{\varepsilon_0}{2}\sum_{\vec{k},\lambda}[\langle 0;p|e_i^{\mathrm{tot}(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|e_i^{(0)}|p;0\rangle\\&\quad+\langle 0;p|e_i^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|e_i^{\mathrm{tot}(2)}|p;0\rangle]\\&\quad=\frac{1}{8\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar ck}{2V}\right)[e_kA_{ki}\overline{e_i}e^{-i\vec{k}\cdot\vec{r}}+e_ie^{i\vec{k}\cdot\vec{k}}\overline{e_k}\overline{A_{ki}}].\end{aligned} \tag{5.6}$$

After performing the polarization sum and angular integral, the first term of Eq. (5.6), using Eq. (5.5) becomes

$$\begin{aligned}&\frac{\hbar c}{64\pi^3\varepsilon_0 i}\int_0^\infty dk\;k^3[F_{ik}(kr)-\overline{F_{ik}}(kr)]A_{ki}\\&=-\frac{1}{32\pi^2\varepsilon_0}\sum_n\mu_j^{pn}\mu_k^{np}\,\frac{1}{2\pi i}\,\mathrm{P}\int_0^\infty\frac{dk\;k^3}{k+k_{pn}}\left[k^3f_{ik}(kr)f_{ij}(kr)e^{2ikr}-\left(\frac{k_{np}^4}{k}\right)f_{ik}(kr)f_{ij}(k_{np}r)e^{ik(r+ct)}e^{ik_{np}(r-ct)}\right.\\&\quad\left.+\left(\frac{k_{np}^4}{k}\right)\overline{f_{ik}}(kr)f_{ij}(k_{np}r)e^{-ik(r-ct)}e^{ik_{np}(r-ct)}\right]+\frac{1}{32\pi^2\varepsilon_0}\sum_n\mu_j^{pn}\mu_k^{np}\,\frac{1}{2\pi i}\,\mathrm{P}\int_0^\infty\frac{dk\;k^3}{k-k_{pn}}\left[k^3f_{ik}(kr)f_{ij}(kr)e^{2ikr}\right.\\&\quad\left.-\left(\frac{k_{pn}^4}{k}\right)f_{ik}(kr)f_{ij}(k_{pn}r)e^{ik(r+ct)}e^{ik_{pn}(r-ct)}+\left(\frac{k_{pn}^4}{k}\right)\overline{f_{ik}}(kr)f_{ij}(k_{pn}r)e^{-ik(r-ct)}e^{ik_{pn}(r-ct)}\right],\end{aligned} \tag{5.7}$$

where P denotes the principal value. Evaluating the integral for downward transitions from p, with $k_{pn}>0$, produces

$$\frac{1}{64\pi^2\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}k_{pn}^6\overline{f_{ik}}(k_{pn}r)f_{ij}(k_{pn}r) + \frac{1}{32\pi^3\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}\int_0^\infty \frac{du\ u^6e^{-2ur}}{u^2+k_{pn}^2} \times k_{pn}f_{ij}(iur)f_{ik}(iur), \tag{5.8}$$

where the second term is expressed in terms of the imaginary wave vector $k=iu$. For $k_{pn}<0$, the u-integral term remains unchanged while the pole contribution changes sign,

$$-\frac{1}{64\pi^2\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}k_{pn}^6 f_{ik}(k_{pn}r)\overline{f_{ij}}(k_{pn}r). \tag{5.9}$$

The second term of Eq. (5.6) is simply the complex conjugate of the first, so that the total electric-dipole-dependent electric energy density, after adding the term from the product of the first-order fields (5.2) is

$$\frac{1}{16\pi^2\varepsilon_0}\sum_{\substack{n\\E_p>E_n}} \mu_j^{pn}\mu_k^{np}k_{pn}^6\overline{f_{ik}}(k_{pn}r)f_{ij}(k_{pn}r) + \frac{1}{16\pi^3\varepsilon_0} \times \sum_{\substack{n\\\text{all } E_n}} \mu_j^{pn}\mu_k^{np}\int_0^\infty \frac{du\ u^6e^{-2ur}}{u^2+k_{pn}^2}\,k_{pn}f_{ij}(iur)f_{ik}(iur), \tag{5.10}$$

in agreement with that obtained using the electric displacement field [22].

The magnetic energy density of an electric-dipole source using the minimal-coupling magnetic field is given by the expectation value

$$\tfrac{1}{2}\varepsilon_0c^2\langle 0;p|b_i^{(1)}b_i^{(1)}+b_i^{(2)}b_i^{(0)}+b_i^{(0)}b_i^{(2)}|p;0\rangle. \tag{5.11}$$

The contribution from the product of the first-order electric-dipole-dependent magnetic field is easily seen to be

$$\frac{1}{32\pi^2\varepsilon_0}\sum_n \mu_j^{pn}\mu_k^{np}k_{pn}^6\overline{g_{ij}}(k_{pn}r)g_{ik}(k_{pn}r), \tag{5.12}$$

as the minimal-coupling magnetic field linear in the sources (4.4) was shown to be identical to its multipolar counterpart, with

$$G_{ij}(kr)=\frac{i}{k^2}\,\varepsilon_{ijk}\nabla_k\frac{e^{ikr}}{r}=g_{ij}(kr)e^{ikr}. \tag{5.13}$$

For the evaluation of the remaining two terms of expression (5.11) the diagonal matrix element over the molecular space is determined for the magnetic-field quadratic in the electric-dipole moments. From Eq. (4.6),

$$\langle p|b_i^{(2)}(\mu\mu;\vec{r},t)|p\rangle=\frac{i}{4\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0cV}\right)^{1/2} \times[e_k\alpha(0)e^{-i\omega t}B_{ki} -\overline{e_k}\alpha^\dagger(0)e^{i\omega t}\overline{B_{ki}}], \tag{5.14}$$

where

$$B_{ki}=\sum_n \frac{\mu_j^{pn}\mu_k^{np}}{E_{np}-\hbar\omega}\left[k^3G_{ij}(kr)-\left(\frac{k_{np}^4}{k}\right) \times G_{ij}(k_{np}r)e^{i(k_{pn}+k)ct}\right] +\sum_n \frac{\mu_k^{pn}\mu_j^{np}}{E_{np}+\hbar\omega}\left[k^3G_{ij}(kr)-\left(\frac{k_{pn}^4}{k}\right) \times G_{ij}(k_{pn}r)e^{-i(k_{pn}-k)ct}\right]. \tag{5.15}$$

Using the mode expansion for the zeroth-order magnetic field and Eq. (5.14), the contribution to the magnetic energy density arising from the interference of the vacuum and quadratic fields is

$$\frac{1}{2}\,\varepsilon_0c^2\sum_{\vec{k},\lambda}[\langle 0;p|b_i^{(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_i^{(0)}|p;0\rangle +\langle 0;p|b_i^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_i^{(2)}|p;0\rangle] =\frac{c}{8\pi\varepsilon_0}\sum_{\vec{k},\lambda}\left(\frac{\hbar k}{2V}\right)[e_kB_{ki}\overline{b_i}e^{-i\vec{k}\cdot\vec{r}}+b_ie^{i\vec{k}\cdot\vec{r}}\overline{e_k}\overline{B_{ki}}]. \tag{5.16}$$

Evaluating in a manner identical to that in the electric case and adding the contribution from the product of the first-order fields (5.12) results in the magnetic energy density

$$\frac{1}{16\pi^2\varepsilon_0}\sum_{\substack{n\\E_p>E_n}} \mu_j^{pn}\mu_k^{np}k_{pn}^6\overline{g_{ij}}(k_{pn}r)g_{ik}(k_{pn}r) + \frac{1}{16\pi^3\varepsilon_0} \times \sum_{\substack{n\\\text{all } E_n}} \mu_j^{pn}\mu_k^{np}\int_0^\infty \frac{du\ u^6e^{-2ur}}{u^2+k_{pn}^2}\,k_{np}g_{ij}(iur)g_{ik}(iur), \tag{5.17}$$

in agreement with the expression obtained using the multipolar magnetic field [22]. Despite the fact that the second-order radiation field operators are different in both the minimal-coupling and multipolar formalisms, equal expectation values for the electromagnetic energy density are obtained in both schemes. A similar demonstration for the Poynting vector is given in the next section.

VI. CALCULATION OF THE POYNTING VECTOR

The quantum-mechanical Hermitian operator for the Poynting vector $\vec{S}(\vec{r},t)$, expressing the rate of flow of electromagnetic energy from an excited molecule, is [22]

$$S_i(\vec{r},t)\simeq\tfrac{1}{2}\varepsilon_0 c^2\varepsilon_{ijk}[e_j^{\mathrm{tot}(1)}(\mu)b_k^{(1)}(\mu)+e_j^{\mathrm{tot}(2)}(\mu\mu)b_k^{(0)}+e_j^{(0)}b_k^{(2)}(\mu\mu)]+\text{c.c.}, \tag{6.1}$$

concentrating only on terms second order in the electric-dipole moments with c.c. the complex conjugate. The first term, arising from the product of the fields linear in the sources, is identical to that obtained from the corresponding calculation carried out in the multipolar formalism [22], giving

$$\frac{c}{32\pi^2\varepsilon_0}\,\varepsilon_{ijk}\sum_n\,\mu_l^{pn}\mu_m^{np}k_{pn}^6[\overline{f_{jl}}(k_{pn}r)g_{km}(k_{pn}r)+\overline{g_{km}}(k_{pn}r)f_{jl}(k_{pn}r)]. \tag{6.2}$$

Using the mode expansions for the zeroth-order total electric and magnetic fields and the respective second order fields (5.4) and (5.14), the second and third terms of Eq (6.1) become

$$\frac{1}{2}\,\varepsilon_0 c^2\varepsilon_{ijk}\sum_{\vec{k},\lambda}\,[\langle 0;p|e_j^{\mathrm{tot}(2)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(0)}|p;0\rangle+\langle 0;p|e_j^{(0)}|p;\vec{k},\lambda\rangle\langle\vec{k},\lambda;p|b_k^{(2)}|p;0\rangle]+\text{c.c.}$$

$$=\frac{c^2}{8\pi\varepsilon_0}\,\varepsilon_{ijk}\sum_{\vec{k},\lambda}\,\left(\frac{\hbar k}{2V}\right)[e_m A_{mj}\overline{b_k}e^{-i\vec{k}\cdot\vec{r}}+e_j e^{i\vec{k}\cdot\vec{r}}\overline{e_m}\overline{B_{mk}}]+\text{c.c.} \tag{6.3}$$

The first term of Eq. (6.3), after performing the sum over polarization and the angular average and using the definition (5.5), is

$$-\frac{\hbar c^2}{32\pi^2\varepsilon_0}\,\varepsilon_{ijk}\,\frac{1}{2\pi i}\int_0^\infty dk\;k^3[G_{km}(kr)+\overline{G_{km}}(kr)]A_{mj}$$

$$=\frac{c}{32\pi^2\varepsilon_0}\,\varepsilon_{ijk}\sum_n\,\mu_l^{pn}\mu_m^{np}\,\frac{1}{2\pi i}\,\mathrm{P}\int_0^\infty\frac{dk\;k^3}{k+k_{pn}}\left[k^3 g_{km}(kr)f_{jl}(kr)e^{2ikr}-\left(\frac{k_{np}^4}{k}\right)g_{km}(kr)f_{jl}(k_{np}r)e^{ik(r+ct)}e^{ik_{np}(r-ct)}\right.$$

$$\left.-\left(\frac{k_{np}^4}{k}\right)\overline{g_{km}}(kr)f_{jl}(k_{np}r)e^{-ik(r-ct)}e^{ik_{np}(r-ct)}\right]-\frac{c}{32\pi^2\varepsilon_0}\,\varepsilon_{ijk}\sum_n\,\mu_l^{pn}\mu_m^{np}\,\frac{1}{2\pi i}\,\mathrm{P}\int_0^\infty\frac{dk\;k^3}{k-k_{pn}}$$

$$\times\left[k^3 g_{km}(kr)f_{jl}(kr)e^{2ikr}-\left(\frac{k_{pn}^4}{k}\right)g_{km}(kr)f_{jl}(k_{pn}r)e^{ik(r+ct)}e^{ik_{pn}(r-ct)}-\left(\frac{k_{pn}^4}{k}\right)\overline{g_{km}}(kr)f_{jl}(k_{pn}r)e^{-ik(r-ct)}e^{ik_{pn}(r-ct)}\right]. \tag{6.4}$$

The k integration involved in the Poynting vector calculation can be evaluated exactly for the time-independent part by extending the limits to $(-\infty,\infty)$; this results in the pole contributions

$$-\frac{c}{64\pi^2\varepsilon_0}\,\varepsilon_{ijk}\sum_n\,\mu_l^{pn}\mu_m^{np}k_{pn}^6 g_{km}(k_{pn}r)\overline{f_{jl}}(k_{pn}r),\quad k_{pn}<0 \tag{6.5a}$$

$$\frac{c}{64\pi^2\varepsilon_0}\,\varepsilon_{ijk}\sum_n\,\mu_l^{pn}\mu_m^{np}k_{pn}^6\overline{g_{km}}(k_{pn}r)f_{jl}(k_{pn}r),\quad k_{pn}>0. \tag{6.5b}$$

The remaining terms of Eq. (6.3) may be evaluated similarly and added to the contribution from the product of the first-order fields to give the electric-dipole-dependent Poynting vector

$$\frac{c}{16\pi^2\varepsilon_0}\,\varepsilon_{ijk}\sum_{\substack{n\\E_p>E_n}}\,\mu_l^{pn}\mu_m^{np}k_{pn}^6[\overline{f_{jl}}(k_{pn}r)g_{km}(k_{pn}r)+\overline{g_{km}}(k_{pn}r)f_{jl}(k_{pn}r)], \tag{6.6}$$

which is identical to the expectation value obtained with the use of the multipolar Maxwell fields [22].

VII. SUMMARY

The electric and magnetic fields in the proximity of a molecule have been derived in the minimal-coupling framework of nonrelativistic quantum electrodynamics. Beginning with the minimal-coupling radiation-molecule Hamiltonian, the Heisenberg equations of motion for the photon and electron operators were expanded in series of powers of the electronic charge. The spatial variations of the vector potential were partially accounted for by including the first derivative

of $\vec{a}(\vec{r})$. By employing sum rules and identities, minimal-coupling matrix elements were converted to relations explicitly involving molecular multipole moments, enabling the Maxwell field operators correct to second order to include magnetic-dipole- and electric-quadrupole- as well as electric-dipole-dependent terms. Since the dynamical equations of motion in minimal-coupling are different from those occurring in the multipolar formalism, in the former approach the transverse electric-field operator, which is the canonical momentum in minimal coupling, was determined as opposed to the displacement vector field operator. The transverse electric field in both first and second order was found to contain nonretarded contributions. After adding the longitudinal part of the electric field, which was evaluated from the electric polarization field, to the transverse component, the total electric field was shown to be fully retarded. The magnetic-field operator was also calculated in the minimal-coupling approach.

The first-order total electric-field operator and ε_0^{-1} times the transverse displacement field linear in the moments were found to be identical, as were the first-order minimal- and multipolar-coupling magnetic fields. These operators act solely in the electron space, leading to changes of molecular state, and correspond to the classical radiation field emitted by an excited multipole source undergoing real transitions. Unlike the first-order minimal-coupling Maxwell fields, the second-order operators, which act in the combined photon-electron space, when compared to their multipolar counterparts are not equivalent, although similarities do exist, differing by the factor $(k_{mn}/k)^y$, $y=0,1,2$. Despite differences between the second-order multipolar- and minimal-coupling radiation field operators, when the latter are applied to the calculation of a physical process or quantity for which energy is conserved, as in the calculation of the Thomson energy density and the Poynting vector, the resulting expectation value is identical to that obtained within the multipolar formalism.

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[1] M. Göppert-Mayer, Ann. Phys. (Leipzig) **9**, 273 (1931).
[2] P. I. Richards, Phys. Rev. **73**, 254 (1948).
[3] E. A. Power and S. Zienau, Philos. Trans. R. Soc. London, Ser. A **251**, 427 (1959).
[4] R. G. Woolley, Proc. R. Soc. London, Ser. A **321**, 557 (1971).
[5] M. Babiker, E. A. Power, and T. Thirunamachandran, Proc. R. Soc. London, Ser. A **332**, 187 (1973).
[6] M. Babiker, E. A. Power, and T. Thirunamachandran, Proc. R. Soc. London, Ser. A **338**, 235 (1974).
[7] E. A. Power and T. Thirunamachandran, Am. J. Phys. **46**, 370 (1978).
[8] E. A. Power, in *Multiphoton Processes*, edited by J. H. Eberly and P. Lambropoulos (Wiley, New York, 1978).
[9] E. A. Power and T. Thirunamachandran, Proc. R. Soc. London, Ser. A **372**, 265 (1980).
[10] W. P. Healy, *Non-Relativistic Quantum Electrodynamics* (Academic, London, 1982).
[11] E. A. Power and T. Thirunamachandran, Phys. Rev. A **28**, 2649 (1983).
[12] J. R. Ackerhalt and P. W. Milonni, J. Opt. Soc. Am. B **1**, 116 (1984).
[13] D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Academic, London, 1984).
[14] E. A. Power and T. Thirunamachandran, J. Opt. Soc. Am. B **2**, 1100 (1985).
[15] E. A. Power, in *New Frontiers in Quantum Electrodynamics and Quantum Optics*, edited by A. O. Barut (Plenum, New York, 1990).
[16] E. A. Power, in *Physics and Probability, Essays in Honour of Edwin T. Jaynes*, edited by W. T. Grandy, Jr. and P. W. Milonni (Cambridge University Press, Cambridge, 1993).
[17] S. Geltman, Phys. Lett. **4**, 168 (1963).
[18] J. K. Jenkins, Ph.D. thesis, University of London, 1991, (unpublished).
[19] E. A. Power and T. Thirunamachandran, Phys. Rev. A **28**, 2663 (1983).
[20] T. Thirunamachandran, Phys. Scr. **T21**, 123 (1988).
[21] A. Salam and T. Thirunamachandran, Phys. Rev. A **50**, 4755 (1994).
[22] E. A. Power and T. Thirunamachandran, Phys. Rev. A **45**, 54 (1992).
[23] A. Salam, Ph.D. thesis, University of London, 1993 (unpublished).