Comments

Comments are short papers which comment on papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Quantum coherent states and the second-order susceptibility"

E. A. Power
Department of Mathematics, University College London, Gower St., London WC1E 6BT, England
(Received 25 July 1989)

It is shown that the minimal coupling interaction and the multipolar interaction $-\boldsymbol{\mu}\cdot\mathbf{E}$ give identical predictions for the second-order susceptibility. This contrasts with differing results obtained by Hammond [R. T. Hammond, Phys. Rev. A **39**, 2544 (1989)]. The unique answer is obtained in the most straightforward way from the multipolar Hamiltonian. Complicated sum rules are needed to demonstrate the correct result from the minimal coupling form of the interaction.

I. INTRODUCTION

The second-order susceptibility tensor is, for dilute systems, very simply related to the hyperpolarizability of the molecules making up the system. In second-harmonic generation a specialized form of the hyperpolarizability is involved that corresponds to a two-photon absorption and a one-photon emission at double the frequency. It is well known[1] that in the electric-dipole approximation the matrix element for such a process is

$$M=-i\varepsilon_{(\omega)}^2\varepsilon_{(2\omega)}\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)\beta_{ijk} , \tag{1}$$

where $\hat{\mathbf{e}}(\omega)$ and $\hat{\mathbf{e}}(2\omega)$ are the unit vectors describing the polarization of the incident beam and emitted photon, respectively, $\varepsilon_{(\omega)}$ and $\varepsilon_{(2\omega)}$ are the field amplitudes at the corresponding frequencies ω and 2ω, and the overbar represents the complex conjugate. In Eq. (1) β_{ijk} is the hyperpolarizability tensor

$$\beta_{ijk}=\tfrac{1}{2}\sum_{r,s}\left[\frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{ro}}{(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}+2\hbar\omega)}+j\leftrightarrow k\right] , \tag{2}$$

where the $j\leftrightarrow k$ indicates the previous terms with j and k indices interchanged. For a two-level system with energies E_0, E_1 this reduces to

$$\beta_{ijk}=\frac{\Delta_i\mu_j\mu_k}{(E_{10})^2-(\hbar\omega)^2}+\frac{2\Delta_j\mu_k\mu_i[(E_{10})^2+2(\hbar\omega)^2]}{[(E_{10})^2-(\hbar\omega)^2][(E_{10})^2-(2\hbar\omega)^2]} , \tag{3}$$

where $\boldsymbol{\Delta}=\boldsymbol{\mu}^{11}-\boldsymbol{\mu}^{00}$ is the difference between between the permanent moments in the upper and lower states and $\boldsymbol{\mu}=\boldsymbol{\mu}^{01}$ is the transition moment which, without loss of generality, is chosen to be real. It is clear that such three-photon processes involved in β_{ijk} will have a vanishing matrix element if the system is atomic or molecular with no permanent electric moments. We note for later reference that the first symbol in (3) has the second-harmonic photon polarization parallel to the permanent moment difference Δ_i (the i index is that associated with the 2ω photon). On the other hand, there are contributions to the hyperpolarizability from $\boldsymbol{\Delta}$ parallel to the excited beam polarization; the second term in Eq. (3). The former term in the limit $\hbar\omega \gg E_{10}$, $R=0$ gives Eq. (34) of Hammond[2]

$$\frac{\chi^{(2)}}{N}=\frac{-e\Delta}{\omega^2}|\boldsymbol{\mu}\cdot\hat{\mathbf{e}}|^2 , \tag{4}$$

where N is the number of molecules per unit volume.

A recent paper[2] has claimed that this is not the correct prediction of quantum electrodynamics. The two interaction Hamiltonians often used in quantum optics are used and the minimal coupling form $-e\mathbf{p}\cdot\mathbf{A}/m$ is preferred and is claimed to give an $\chi^{(2)}$ which differs from (4) by a multiplicative factor $(E_{10}/\hbar\omega)^2$ in the same limit. The paper implies a different form for β_{ijk} before such a limit is taken. In this Comment we derive the β tensor from the minimal coupling Hamiltonian and show, as is to be expected, that it gives the identical result as that using

 ©1990 The American Physical Society

the $-\boldsymbol{\mu}\cdot\mathbf{E}$ interaction Hamiltonian. It is almost essential to use the $-\boldsymbol{\mu}\cdot\mathbf{E}$ multipolar form when permanent moments of the active molecule are involved in the transition since the momentum operator $\mathbf{p}$ has no diagonal matrix elements. In general, the matrix element of momentum is related to that of position through Eq. (5).

$$\frac{-e}{m}\langle r|\mathbf{p}|s\rangle=\frac{E_{rs}\boldsymbol{\mu}^{rs}}{i\hbar}\ , \tag{5}$$

which vanishes for $E_{rs}=E_r-E_s=0$. It is necessary to use sum rules to convert $-e\mathbf{p}\cdot\mathbf{A}/m$ matrix elements to those involving permanent moments as we demonstrate for two-photon absorption in Ref. 3. It is also easier to model the full quantum-optics Hamiltonian by a two-level system interacting with the electromagnetic field using the multipolar coupling $-\boldsymbol{\mu}\cdot\mathbf{E}$ than using the minimal coupling interaction.

II. CALCULATION OF HYPERPOLARIZABILITY USING MINIMAL COUPLING

The nonlinear polarization involved in Eq. (1) can be written as an energy of interaction of an induced dipole $\mathbf{P}$

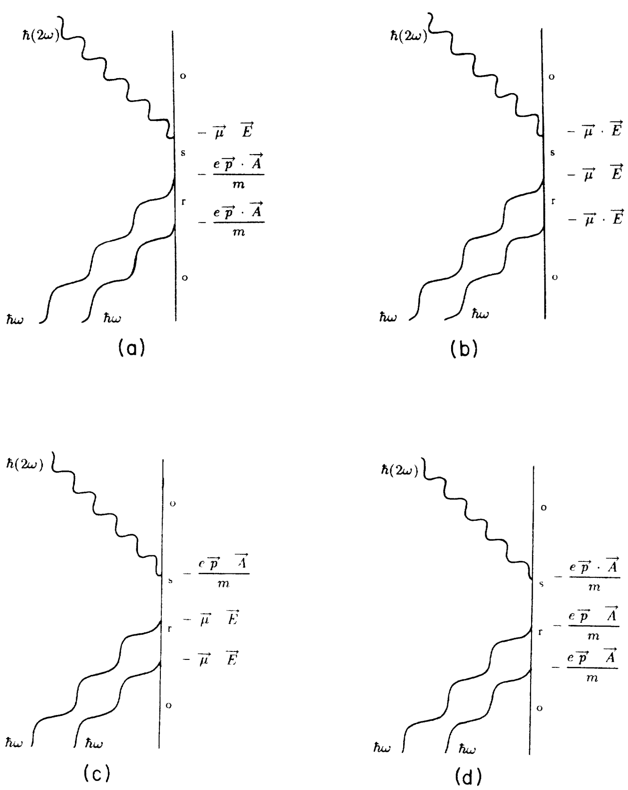

FIG. 1. Time-ordered graph representing one contribution to the matrix element for second-harmonic generation. (a) The emitted photon is dipole coupled with interaction $-\boldsymbol{\mu}\cdot\mathbf{E}$; the absorbed photons are coupled by $-e\mathbf{p}\cdot\mathbf{A}/m$ minimal coupling. (b) All three photons are coupled with the multipolar form of interaction $-\boldsymbol{\mu}\cdot\mathbf{E}$. (c) The complement of (a): the emitted photon is minimally coupled the absorbed photons by the interaction $-\boldsymbol{\mu}\cdot\mathbf{E}$. (d) All three photons are minimally coupled with the interaction $-e\mathbf{p}\cdot\mathbf{A}/m$.

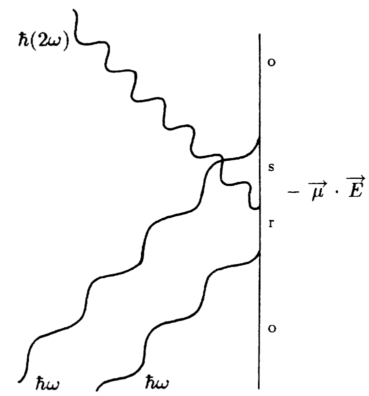

FIG. 2. Time-ordered graph representing a contribution to the matrix element for second-harmonic conversion where the generated photon is emitted between absorptions.

$$W=-\mathbf{P}\cdot\mathbf{E}_{(2\omega)}\ ,$$

when (6)

$$\mathbf{P}=\mathrm{X}^{(2)}:\mathbf{E}_{(\omega)}\mathbf{E}_{(\omega)}\ .$$

The effective induced dipole moment is then already in multipolar form $-\mu_i^{\mathrm{ind}}E_{(2\omega)i}$. The perturbation theory can indeed predict the value of μ_i^{ind} in the form $\beta_{ijk}e_je_k$ using minimal coupling for computing the dynamics involved in absorbing the two photons. This is analogous to Sec. III of Ref. 2 in that it is the changes in the expectation value of $\boldsymbol{\mu}$ that are calculated using the minimal coupling. It clarifies the theory to use diagrammatic techniques. For example, Fig. 1(a) represents the contribution given in Eq. (7) to the full matrix element:

$$M^{[1(a)]}=\frac{-i\mu_i^{0s}ep_j^{sr}ep_k^{r0}\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)}{(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)m^2\omega^2}\varepsilon_{(2\omega)}\varepsilon^2_{(\omega)}\ . \tag{7}$$

This is to be compared with the contribution from Fig. 1(b) when $-\boldsymbol{\mu}\cdot\mathbf{E}$ is used for the dynamics of the two-photon absorption.

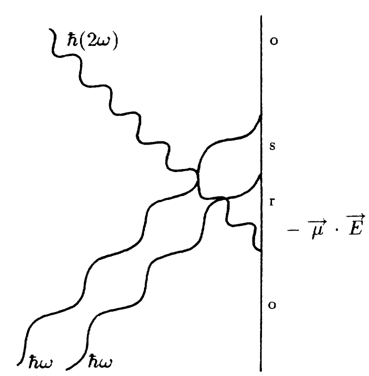

FIG. 3. The third ordering for second-harmonic generation.

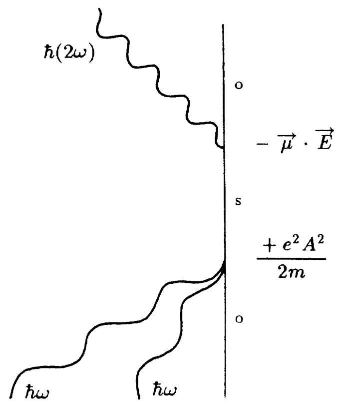

FIG. 4. One sea-gull–interaction graph, with the $e^2A^2/2m$ vertex absorbing the two ω photons.

Then

$$M^{[1(b)]}=\frac{-i\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)}{(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)}\varepsilon_{(2\omega)}\varepsilon_{(\omega)}^2 . \tag{8}$$

The extra factor ω^{-2} in (7) arises from the vector potential $\mathbf{A}$ being the operator that absorbs the ω photons rather than the $\mathbf{E}$. Equation (8), together with (1), immediately determines the first summand in β_{ijk} of Eq. (2). The other two summands shown arise from Figs. 2 and 3 when the ordering of the emitted photon relative to the absorptions is changed. It is of interest to note that the contribution represented by Fig. 2 is the only possible contribution involving a permanent moment in excited states of the molecule along the direction of the polarization of the second-harmonic photon. For example, with a two-level system the component μ_i^{11} (with $r=s=1$) must contribute the term

$$\frac{\mu_i^{11}|\boldsymbol{\mu}^{01}\cdot\hat{\mathbf{e}}|^2}{(E_{10})^2-(\hbar\omega)^2}$$

to $X^{(2)}$. On the other hand, both Figs. 1(b) and 3 represent contributions involving permanent electric moments in the ground state (if either r or $s=0$). In multipolar coupling theory the complete hyperpolarizability β_{ijk} of Eq. (2) can be read off Figs. 1(b), 2, and 3 immediately. This is not so for minimal coupling theory. As an example, if Eq. (5) is used twice, Eq. (7) yields

$$M^{(1)}=-i\sum_{r,s}\frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)} \times\frac{E_{sr}E_{r0}\bar{e}_ie_je_k}{(i\hbar\omega)^2}\varepsilon_{(2\omega)}\varepsilon_{(\omega)}^2 . \tag{9}$$

It is the factor $E_{sr}E_{r0}/(i\hbar\omega)^2$ in Eq. (9), and similar factors for terms derived from the other orderings, which gives rise to the apparent anomaly mentioned in the Introduction [$s=0$, $r=1$ gives $(E_{10}/\hbar\omega)^2$]. The reason that, in minimal coupling theory, the hyperpolarizability tensor β_{ijk} is not determined by Figs. 1(a), 2, and 3 is that there are further contributions due to the quadratic term $e^2\mathbf{A}^2/2m$ in the total Hamiltonian. These, the so-called sea-gull terms, are represented by Figs. 4 and 5. Their contributions to the matrix element are

$$M^{(4)}+M^{(5)}=-i\frac{e^2}{2m}\sum_s\frac{m_i^{0s}\langle s|\,\mathbf{A}^2|0\rangle\bar{e}_i(2\omega)\varepsilon_{2\omega}}{E_{s0}-2\hbar\omega} -i\frac{e^2}{2m}\sum_r\frac{\langle 0|\,\mathbf{A}^2|r\rangle\mu_i^{r0}\bar{e}_i(2\omega)\varepsilon_{2\omega}}{E_{r0}+2\hbar\omega} . \tag{10}$$

In the Appendix we show by explicit calculation that the addition of contribution (10) to the three summands, of which Eq. (9) is typical, does indeed give the identical result β_{ijk}. There is no difference between the predictions made by the two forms of Hamiltonians for the hyperpolarizability; the advantage of the $-\boldsymbol{\mu}\cdot\mathbf{E}$ form of interaction is the immediacy and ease of calculation. This is a well-known[4] feature of the multipolar Hamiltonian. To obtain valid approximations to the full quantum electrodynamics in quantum optics or quantum chemistry that use two-level systems, it is necessary to transform to the multipolar Hamiltonian before making the two-level approximation.

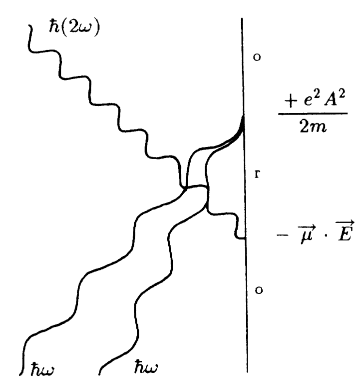

FIG. 5. The other possible ordering for a sea-gull–type interaction.

III. AN ALTERNATIVE DERIVATION

The perturbation theory outlined Sec. II and spelled out in the Appendix is a hybrid, although a perfectly legitimate one. It is a hybrid in so far as the 2ω photon is coupled via the electric field vector, while the ω photons are coupled via the vector potential. The perfect complement of the very simple multipolar calculation would be to use a complete minimal coupling interaction for all three photons. In this section an alternative hybrid is considered where the 2ω photon is coupled with the $-e\mathbf{p}\cdot\mathbf{A}/m$ interaction energy, while the ω photons are multipolar coupled; see Fig. 1(c) for a typical contribution. This combination is of interest since there is no place within this calculation for any sea-gull $e^2\mathbf{A}^2/2m$ terms. However, once again the correct β_{ijk} is obtained. We have

$$M=\frac{e}{2m}\sum_{r,s}\left[\frac{p_i^{0s}\mu_j^{sr}\mu_k^{r0}}{(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{\mu_k^{0s}p_i^{sr}\mu_j^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{\mu_j^{0s}\mu_k^{sr}p_i^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}+2\hbar\omega)}+j\leftrightarrow k\right]$$
$$\times\frac{\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)}{2\omega}\varepsilon_{(2\omega)}\varepsilon_{(\omega)}^2\;, \qquad (11)$$

where the $j\leftrightarrow k$ indicates the previous terms with i and j indices interchanged. The factor $(2\omega)^{-1}$ in Eq. (11) arises from the emission operator within A_i having a frequency dependence $(2\omega)^{-1/2}$ for the 2ω photon, while the electric field for this photon is proportional to $(2\omega)^{1/2}$. If now Eq. (4) is used for the matrix elements of p_i, Eq. (11) becomes

$$M=-\frac{1}{2i\hbar}\sum_{r,s}\left[\frac{E_{0s}\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{E_{sr}\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{E_{r0}\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}+2\hbar\omega)}+j\leftrightarrow k\right]$$
$$\times\frac{\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)}{2\omega}\varepsilon_{(2\omega)}\varepsilon_{(\omega)}^2$$
$$=\frac{-1}{2i\hbar}\sum_{r,s}\left[\left[-1-\frac{2\hbar\omega}{E_{s0}-2\hbar\omega}\right]\frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{(E_{r0}-\hbar\omega)}+\left[\frac{1}{E_{r0}-\hbar\omega}-\frac{1}{E_{s0}+\hbar\omega}-\frac{2\hbar\omega}{(E_{s0}+\hbar\omega)(E_{r0}-\hbar\omega)}\right]\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}\right.$$
$$\left.+\left[1-\frac{2\hbar\omega}{E_{r0}+2\hbar\omega}\right]\frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{E_{s0}+\hbar\omega}+j\leftrightarrow k\right]\frac{\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)}{2\omega}\varepsilon_{(2\omega)}\varepsilon_{(\omega)}^2$$
$$=\left[\frac{1}{2i\hbar}\sum_{r,s}\left[\frac{-\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}+\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}}{E_{r0}-\hbar\omega}+\frac{-\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}+\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{E_{s0}+\hbar\omega}+j\leftrightarrow k\right]-i2\omega\beta_{ijk}\right]\frac{\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)}{2\omega}\varepsilon_{(2\omega)}\varepsilon_{(\omega)}^2\;. \qquad (12)$$

The initial terms on the right-hand side of Eq. (12) vanish since, for example,

$$-\langle 0|\mu_i\mu_j|r\rangle\mu_k^{r0}+\langle 0|\mu_k\mu_i|r\rangle\mu_j^{r0}$$

is antisymmetric in the j,k indices. Hence

$$M=-i\beta_{ijk}\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)\varepsilon_{(2\omega)}\varepsilon_{(\omega)}^2\;. \qquad (13)$$

It is now clear how the calculation that is necessary to determine the hyperpolarizability from a complete use of the minimal-coupling Hamiltonian for each photon should proceed. Figure 1(d) represents a typical contribution to this calculation. The methodology is first to deal with the 2ω-photon vertex as in this section. The result will then have one electric dipole vertex μ_i and two minimal-coupling j,k vertices. These can then be reduced to μ_j,μ_k type vertices using precisely the arguments of Sec. II.

IV. DISCUSSION AND CONCLUSION

We have demonstrated that the hyperpolarizability, and thus the second-order susceptibility, follows independently of the form of Hamiltonian—minimal or multipolar coupling. The additional dependence of the susceptibility on any component of the second harmonic in the incident radiation is not controversial. However, the differences imputed to follow from using the alternatives $-\boldsymbol{\mu}\cdot\mathbf{E}$, $-e\mathbf{p}\cdot\mathbf{A}/m$ as interaction energies are contentious. Since we have shown that there is a unique prediction for $\chi^{(2)}$, the arguments in Ref. 2 suggesting that one should not use the $-\boldsymbol{\mu}\cdot\mathbf{E}$ interaction are fallacious. It is certainly possible to use for the basis states the eigenfunctions of the unperturbed Hamiltonian whatever the interaction energy. The two-level approximation for β_{ijk} is given in Eq. (3) and the resulting susceptibility (in the limit $E_{12}=\hbar\omega_{12}\ll\hbar\omega,\Delta$ parallel to the 2ω-photon polarization) is that given by Eq. (34) of Hammond. This he rejects in favor of Eq. (19) of Ref. 2. We claim that, in the appropriate limit, it is (19) that is incorrect. The reason is that the full interaction of the minimal-coupling Hamiltonian was not used, and the sum rules implicit in the quantum-mechanical properties of molecules were not taken into account.

ACKNOWLEDGMENTS

It is a pleasure to thank T. Thirunamachandran for many discussions on "nonrelativistic" quantum electrodynamics.

APPENDIX

In this appendix the explicit identity is proved that shows that the hyperpolarizability, as predicted by the minimal-coupling interaction Hamiltonian, is precisely β_{ijk} of Eq. (2). The matrix element for the process that absorbs two ω photons, polarizations e_j and e_k, and emits one 2ω-photon polarization $e_i(2\omega)$, leaving the molecule in its ground state is

$$M=-\frac{e^2}{m^2}\sum_{r,s}\left[\frac{\mu_i^{0s}p_j^{sr}p_k^{r0}+\mu_i^{0s}p_k^{sr}p_j^{r0}}{(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{\mu_i^{0s}\langle s|\delta_{jk}m|0\rangle}{2(E_{s0}-2\hbar\omega)}+\frac{p_k^{0s}\mu_i^{sr}p_j^{r0}+p_j^{0s}\mu_i^{sr}p_k^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}-\hbar\omega)}\right.$$
$$\left.+\frac{p_j^{0s}p_k^{sr}\mu_i^{r0}+p_k^{0s}p_j^{sr}\mu_i^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}+2\hbar\omega)}+\frac{\langle 0|\delta_{jk}m|r\rangle\mu_i^{r0}}{2(E_{r0}+2\hbar\omega)}\right]E_i A_j A_k \tag{A1}$$

$$=\sum_{r,s}\frac{(+i)}{\omega^2}\left[\frac{(\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}+\mu_i^{0s}\mu_k^{sr}\mu_j^{r0})E_{sr}E_{r0}}{(i\hbar)^2(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{\mu_i^{0s}(E_{sr}\mu_j^{sr}\mu_k^{r0}-\mu_k^{sr}\mu_j^{r0}E_{r0}+E_{sr}\mu_k^{sr}\mu_j^{r0}-\mu_j^{sr}\mu_k^{r0}E_{r0})}{(i\hbar)(-i\hbar)2(E_{s0}-2\hbar\omega)}\right.$$
$$+\frac{(\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}+\mu_j^{0s}\mu_i^{sr}\mu_k^{r0})E_{0s}E_{r0}}{(i\hbar)^2(E_{s0}+\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{(\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}+\mu_k^{0s}\mu_j^{sr}\mu_i^{r0})E_{0s}E_{sr}}{(i\hbar)^2(E_{s0}+\hbar\omega)(E_{r0}+2\hbar\omega)}$$
$$\left.+\frac{(E_{0s}\mu_j^{0s}\mu_k^{sr}-\mu_k^{0s}\mu_j^{sr}E_{sr}+E_{0s}\mu_k^{0s}\mu_j^{sr}-\mu_j^{0s}\mu_k^{sr}E_{sr})\mu_i^{r0}}{(i\hbar)(-i\hbar)2(E_{r0}+2\hbar\omega)}\right]$$
$$\times\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)\varepsilon_{(\omega)}^{(j)}\varepsilon_{(\omega)}^{(k)}\varepsilon_{(2\omega)}^{(i)}$$

$$=\frac{-i}{(\hbar\omega)^2}\sum_{r,s}\left[\frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{(E_{s0}-2\hbar\omega)}\,\frac{2E_{sr}E_{r0}+(-E_{sr}+E_{r0})(E_{r0}-\hbar\omega)}{2(E_{r0}-\hbar\omega)}-\frac{\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}E_{s0}E_{r0}}{(E_{s0}+\hbar\omega)(E_{r0}-\hbar\omega)}\right.$$
$$\left.+\frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{(E_{r0}+2\hbar\omega)}\,\frac{2E_{0s}E_{sr}+(-E_{0s}+E_{sr})(E_{s0}+\hbar\omega)}{2(E_{s0}+\hbar\omega)}+j\leftrightarrow k\right]\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)\varepsilon_{(\omega)}^{(j)}\varepsilon_{(\omega)}^{(k)}\varepsilon_{(2\omega)}^{(i)}$$

$$=\frac{-i}{(\hbar\omega)^2}\sum_{r,s}\left[\frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{2(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)}(E_{s0}E_{r0}+E_{s0}\hbar\omega-2\hbar\omega E_{r0})\right.$$
$$-\frac{\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}-\hbar\omega)}(E_{s0}+\hbar\omega-\hbar\omega)(E_{r0}-\hbar\omega+\hbar\omega)+\frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{2(E_{r0}+2\hbar\omega)(E_{s0}+\hbar\omega)}$$
$$\left.\times(E_{s0}E_{r0}+2E_{s0}\hbar\omega-\hbar\omega E_{r0})+j\leftrightarrow k\right]$$
$$\times\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)\varepsilon_{(\omega)}^{(j)}\varepsilon_{(\omega)}^{(k)}\varepsilon_{(2\omega)}^{(i)}$$

$$=\frac{-i}{2(\hbar\omega)^2}\sum_{r,s}\left\{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}\left[\left[1+\frac{2\hbar\omega}{E_{s0}-2\hbar\omega}\right]\left[1+\frac{\hbar\omega}{E_{r0}-\hbar\omega}\right]+\left[1+\frac{2\hbar\omega}{E_{s0}-2\hbar\omega}\right]\frac{\hbar\omega}{E_{r0}-\hbar\omega}\right.\right.$$
$$\left.-\left[1+\frac{\hbar\omega}{E_{r0}-\hbar\omega}\right]\frac{2\hbar\omega}{E_{s0}-\hbar\omega}\right]-2\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}\left[1-\frac{\hbar\omega}{E_{s0}+\hbar\omega}\right]\left[1+\frac{\hbar\omega}{E_{r0}-\hbar\omega}\right]$$
$$+\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}\left[\left[1-\frac{\hbar\omega}{E_{s0}+\hbar\omega}\right]\left[1-\frac{2\hbar\omega}{E_{r0}+2\hbar\omega}\right]+\left[1-\frac{\hbar\omega}{E_{s0}+\hbar\omega}\right]\frac{2\hbar\omega}{E_{r0}+2\hbar\omega}\right.$$
$$\left.\left.-\left[1-\frac{2\hbar\omega}{E_{r0}+2\hbar\omega}\right]\frac{\hbar\omega}{E_{s0}+\hbar\omega}\right]+j\leftrightarrow k\right\}\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)\varepsilon_{(\omega)}^{(j)}\varepsilon_{(\omega)}^{(k)}\varepsilon_{(2\omega)}^{(i)}$$

$$=\frac{-i}{2(\hbar\omega)^2}\sum_{r,s}\left[\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}\left[1+\frac{2\hbar\omega}{E_{r0}-\hbar\omega}+\frac{2(\hbar\omega)^2}{(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)}\right]\right.$$
$$-2\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}\left[1+\frac{\hbar\omega}{E_{r0}-\hbar\omega}-\frac{\hbar\omega}{E_{s0}+\hbar\omega}-\frac{(\hbar\omega)^2}{(E_{s0}+\hbar\omega)(E_{r0}-\hbar\omega)}\right]$$
$$\left.+\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}\left[1-\frac{2\hbar\omega}{E_{s0}+\hbar\omega}+\frac{2(\hbar\omega)^2}{(E_{s0}+\hbar\omega)(E_{r0}+2\hbar\omega)}\right]+j\leftrightarrow k\right]$$
$$\times\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)\varepsilon_{(\omega)}^{(j)}\varepsilon_{(\omega)}^{(k)}\varepsilon_{(2\omega)}^{(i)}\ . \tag{A2}$$

Double closure sums on the three lead terms in (A2) give

$$\langle 0|\mu_i\mu_j\mu_k|0\rangle(1-2+1)=0\ . \tag{A3}$$

On the other hand, single sums lead to the contribution

$$\sum_r \frac{\langle 0|\mu_i\mu_j|r\rangle \mu_k^{r0} - \langle 0|\mu_k\mu_i|r\rangle \mu_j^{r0}}{E_{r0}-\hbar\omega}\hbar\omega + \sum_s \frac{\mu_k^{0s}\langle s|\mu_i\mu_j|0\rangle - \mu_j^{0s}\langle s|\mu_k\mu_i|0\rangle}{E_{s0}+\hbar\omega}\hbar\omega \ ,$$

which is antisymmetric in the $j\leftrightarrow k$ interchange. Adding the symmetric contribution in the total matrix element ensures the vanishing of all terms of this form. Thus the final form of the matrix element (A2) is

$$M=-i\sum_{r,s}\left[\frac{\mu_i^{0s}\mu_j^{sr}\mu_k^{r0}}{(E_{s0}-2\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{\mu_k^{0s}\mu_i^{sr}\mu_j^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}-\hbar\omega)}+\frac{\mu_j^{0s}\mu_k^{sr}\mu_i^{r0}}{(E_{s0}+\hbar\omega)(E_{r0}+2\hbar\omega)}+j\leftrightarrow k\right]$$

$$\times\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)\varepsilon_{(\omega)}^{(j)}\varepsilon_{(\omega)}^{(k)}\varepsilon_{(2\omega)}^{(i)} \tag{A4}$$

$$=-i2\beta_{ijk}\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)\varepsilon_{(\omega)}^{(j)}\varepsilon_{(\omega)}^{(k)}\varepsilon_{(2\omega)}^{(i)} \ . \tag{A5}$$

This is precisely the matrix element that directly follows from the use of $-\boldsymbol{\mu}\cdot\mathbf{E}$ at each of the three vertices. We note finally that if the j,k polarizations are equal so that the incident beam is a single mode,

$$\varepsilon_{(\omega)}^{(j)}=\varepsilon_{(\omega)}^{(k)}=\frac{1}{\sqrt{2}}\varepsilon_{(\omega)}$$

and

$$M=-i\beta_{ijk}\bar{e}_i(2\omega)e_j(\omega)e_k(\omega)\varepsilon_{(\omega)}^{(j)}\varepsilon_{(\omega)}^{(k)}\varepsilon_{(2\omega)}^{(i)} \ . \tag{A6}$$

[1] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Persham, Phys. Rev. **127**, 1918 (1962); N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965); C. Flytzanis, *Quantum Electronics,* edited by H. Rabin and C. L. Tang (Academic, New York, 1975), p. 87; D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Academic, London, 1984), p. 227.
[2] R. Hammond, Phys. Rev. A **39**, 2544 (1989).
[3] W. J. Meath and E. A. Power, J. Phys. B **17**, 763 (1984).
[4] E. A. Power and T. Thirunamachandran, J. Phys. B **8**, L170 (1975); Am. J. Phys. **46**, 370 (1978); D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Academic, London, 1984), Chap. 10; J. O. Hirschfelder, R. E. Wyatt, and R. D. Coalson, *Lasers, Molecules and Methods* (Interscience, New York, 1989), p. 45.