Generalized Stokes-Mueller formalism for two-photon absorption, frequency doubling, and hyper-Raman scattering

Yaoming Shi and W. M. McClain
Department of Chemistry, Wayne State University, Detroit, Michigan 48202

R. A. Harris
Department of Chemistry, University of California at Berkeley, Berkeley, California 94720
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We consider processes quadratic in incident intensity, in which two identical photons are annihilated simultaneously. We construct a formalism for these processes that is maximally analogous to the Stokes-Mueller formalism for linear processes. The two-photon properties of the incident beam require nine Stokes-like parameters for their description; the Mueller-like matrix which gives a complete description of frequency doubling or hyper-Raman scattering is of size 4×9. Of the 36 independent observable matrix elements, 12 are activated by pure real elastic dipole susceptibilities, four by an imaginary component in the electric dipole susceptibility (absorption), nine by handedness alone, two by extramultipole mechanisms alone, and nine require both handedness and extramultipole mechanisms.

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I. INTRODUCTION

Molecular optics has benefited greatly in recent years by a change of emphasis away from amplitude-based theoretical quantities, moving instead to intensity-based observable quantities. The formalism that accomplishes this is the Stokes-Mueller formalism [1,2].

The chief advantage of the Stokes description of light is that it puts pure polarized light (with steady polarization vector) and depolarized light (with rapidly fluctuating polarization vector) on the same footing. Stokes introduced his four optical parameters in the early 19th century [3], even before Maxwell put electromagnetic theory into finished form. A relationship between the Stokes parameters and the Pauli matrices was noticed in the early days of quantum mechanics [4] and was developed in detail in the 1950s [5].

The Stokes vector has four elements, each measureable as a sum or difference of intensities observed through various polarization filters. In a linear scattering process, we let the incident light have Stokes vector $\mathbf{s}$ and we measure Stokes vector $\mathbf{s}'$ for a particular ray of the scattered light. Linear scattering theory requires that $\mathbf{s}'$ depend linearly on $\mathbf{s}$, so the most general possible relation between them is

$$\mathbf{s}'=\mathbf{M}\mathbf{s}\ . \tag{1.1}$$

The 4×4 matrix $\mathbf{M}$ is called the Mueller scattering matrix [2]. It characterizes completely the polarization behavior of the scattering process, at the given wavelength(s) and given scattering angle.

Scattered light is nearly always depolarized, even if the incident light is not, but the amplitude-based description fails to capture this essential element of reality. Also, the material properties in matrix $\mathbf{M}$ may be ensemble averaged directly, unlike properties in a susceptibility matrix. This is particularly important in the third row and third column of $\mathbf{M}$, where the off-diagonal elements average to zero for solutions and vapors of small nonabsorbing molecules, even when helicity effects are included. However, several of these predicted zero elements are in reality large and easily measured in scattering by viruses [6]. In fact they are especially useful, being hypersensitive to the size and shape of the viruses and to clustering and partial orientation. This major scattering effect cannot be understood at all within an amplitude framework, but is now well understood within the Stokes-Mueller framework.

It has recently struck us as strange that there is no nonlinear formalism comparable to the Stokes-Mueller formalism for linear optical processes. The density matrix is even more important for nonlinear processes than it is for linear, because temporal incoherence of the light has an important effect on nonlinear phenomena. Incoherence is handled automatically along with depolarization in a formalism based on the density matrix [7].

In a foregoing preliminary paper [8] we supplied the missing Stokes-Mueller-like formalism for processes that are bilinear in each of two incident intensities, taking one photon simultaneously from each incident beam. In this paper we do the same for processes that are quadratic in one incident intensity, taking two photons simultaneously from a single incident beam. These processes include two-photon absorption, incoherent frequency doubling, and hyper-Raman scattering. The main result of this paper is an equation very analogous to (1.1), namely,

$$\mathbf{s}'=\mathcal{M}\mathbf{S}\ , \tag{1.2}$$

where $\mathbf{S}$ is a measureable "double Stokes" vector of nine elements and $\mathcal{M}$ is a "double Mueller" matrix of size 4×9. As in our previous work, we find that $\mathcal{M}$ contains a number of those peculiar elements that orientation average to zero in the central multipole approximation off resonance, no matter how high the multipoles are taken. There is no commonly accepted name for such elements. In the past we have called them "retardation elements," but this captures only one of their aspects. In Ref. [8] we

called them "odd diagonal modulation" (ODM) elements, since in that work they all had an odd number of diagonal modulation indices. However, the ODM rule no longer applies in this work, and we need a new name. We therefore propose the name *extramultipole* because in off-resonance experiments their appearance always indicates an effect that lies outside or beyond the central multipole series.

We have shown in previous papers that nonzero orientation averaged values of the extramultipole elements may be caused by (1) anisotropic orientational distribution of the particles, (2) absorption, (3) retarded dipole-dipole interactions, and (4) constant magnetic field. In view of (3), they will carry important information when light interacts nonlinearly with structures near wavelength size. We may even anticipate that because of the large nonlinear effects near surfaces and because wavelength size particles have relatively very large surfaces, the new extramultipole observables may be even more valuable in nonlinear scattering than they are in linear.

In this paper we treat the polarization dependence of nonlinear effects within the regime where the effects are quadratic in incident intensity. We do not treat phase-matched doubling in crystals, which has a polarization fixed by crystal symmetry and which may have a complicated intensity dependence best treated by coupled wave algebra [9].

In Sec. II we show that for a single beam, there are nine double Stokes parameters that determine its two-photon properties, and we define a particular embodiment of them that is maximally analogous to the linear Stokes parameters.

In Sec. III we treat simultaneous two-photon absorption from a single beam, showing that in the most general case there are nine measurable two-photon absorptivities. In Appendix A we show how the nine parameters collapse to two in the case of small molecules and one laser beam, as is well known.

In Sec. IV we show how to prepare pure polarized, coherent laser light with known double Stokes parameters, using a linear polarizer and two ordinary retarders. In Appendix B we give a complete set of polarization cases that may be used to measure the entire double Mueller matrix $\mathcal{M}$.

In Sec. V we show how to measure the nine double Stokes parameters of any given beam; as from a laser with unsteady (mode locked) output, or from a synchrotron, or from the intense light of a magnetically confined plasma. Details are in Appendix C. If $\mathcal{M}$ is measured using light prepared by the methods of Sec. IV, and if an impure, incoherent incident beam is characterized by the methods of Sec. V, then all the Stokes parameters of its quadratically scattered light may be predicted.

In Sec. VI we develop an unapproximated theory of quadratic scattering using the T-matrix approach. This is required if we are to examine $\mathcal{M}$ in the presence of effects such as damping, line broadening, and retardation, which go beyond perturbation theory.

In Sec. VII we formally justify Eq. (1.2), the Stokes-Mueller-like relation that governs quadratic frequency doubling and hyper-Raman scattering.

In Sec. VIII we derive the relation between the theory for two different incident photons and the theory for two identical incident photons.

In Sec. IX we classify each of the 36 elements of $\mathcal{M}$ in terms of its activating mechanism.

II. THE DOUBLE STOKES PARAMETERS

A. How many one-beam n-photon parameters exist?

We begin with a brief classical overview of the problem. Consider a beam of light with horizontal and vertical amplitudes $\{E_H(t),E_V(t)\}$. The time dependence indicates amplitude fluctuations too fast for any detector to follow, but too slow to be considered part of the optical frequency. These fluctuations are always ignored in elementary presentations, but they are accurately absent only in light from very well stabilized cw lasers. All other sources have them, and they reveal themselves as depolarization and incoherence. In this paper we consider their effect in multiphoton spectroscopy. We will show that for a process involving n simultaneous photons from a single beam, the fluctuating beam must be characterized in general by $(n+1)^2$ intensity-based Stokes-like parameters. An elementary argument follows.

The amplitude for an n-photon process is

$$\begin{aligned}\mathcal{A}&=\sum_{i,j,k,\ldots=H,V}\chi_{i,j,k,\ldots}E_iE_jE_k\cdots\\&=\chi_{H,H,H,\ldots}E_H^n+(\chi_{V,H,H,\ldots}+\chi_{H,V,H,\ldots}+\cdots)\\&\quad\times E_H^{n-1}E_V+\cdots,\end{aligned}\tag{2.1}$$

which contains the same field products that appear in the expansion of $(E_H+E_V)^n$, namely, $E_H^n,E_H^{n-1}E_V$, $E_H^{n-2}E_V^2,\ldots,E_HE_V^{n-1},E_V^n$. As may be easily counted, there are $n+1$ such terms. To calculate an event rate, the amplitude for the process must be multiplied by its own complex conjugate giving $(n+1)^2$ terms, each consisting of a molecular quantity times an amplitude factor of the form

$$m_{pq}=\langle E_H^p(t)E_V^{n-p}(t)E_H^{*q}(t)E_V^{*n-q}(t)\rangle_{\text{time}},\tag{2.2}$$

where the time average over the fluctuations has been taken. But each such factor is a polarization parameter, and, in general, the values of the m_{pq} are independent, save for the Hermitian relation $m_{pq}=m_{qp}^*$ that exists by construction. Therefore, the number of real values needed to specify all the polarization parameters is the same as the number of real values needed to specify a general Hermitian matrix of size $(n+1)\times(n+1)$, and this number is $(n+1)^2$. Therefore, the number of independent polarization parameters for an n-photon process is $(n+1)^2$.

For two-photon processes in a single beam, there must be $(2+1)^2=9$ double Stokes parameters. In contrast, in a previous paper, we showed that there are 16 polarization parameters that govern two-photon effects that take one photon from each of two beams.

B. Review of the Stokes operator theory

We now approach our construction of the nine double Stokes operators. To make it as analogous as possible to the construction of the Stokes operators, we begin by reviewing that paradigm. Let a_H^+ (a_H^-) and a_V^+ (a_V^-) be the creation (annihilation) operators for the horizontally and vertically polarized photons, respectively. Also, let τ_1 be the unit matrix and denote the Pauli matrices by

$$\tau_2=\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix},\quad \tau_3=\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix},\quad \tau_4=\begin{bmatrix}0 & i\\ -i & 0\end{bmatrix}. \tag{2.3}$$

We note the orthogonality

$$\mathrm{Tr}[\tau_\alpha\tau_\beta]=2\delta_{\alpha\beta}\ . \tag{2.4}$$

The four τ matrices are the generators (in the Lie sense [10]) of the irreducible Hermitian representation of group SU(2). We define four operators $\hat{s}_\alpha$ as

$$\hat{s}_\alpha=\sum_{i=H}^{V}\sum_{j=H}^{V}(\tau_\alpha)_{ij}a_i^+a_j^-\quad(\alpha=1,2,3,4)\ . \tag{2.5}$$

To show that these are the Stokes operators, we take their expectation values with respect to the arbitrary photon density matrix, given by

$$\rho=\sum_{(n_H,n_V),(n_H',n_V')}W(n_H,n_V;n_H',n_V')|n_H,n_V\rangle\langle n_H',n_V'|\ . \tag{2.6}$$

The basis functions are eigenfunctions of the photon number operator for horizontally and vertically polarized photons. The W matrix contains all the information about the beam of light. Mathematically it must obey the following rules.

(1) The diagonal elements $W(n_H,n_V;n_H,n_V)$ must be the probability $p(n_H,n_V)$ of finding number densities (n_H,n_V) of (horizontally, vertically) polarized photons if the normalization volume is subjected to a photon number measurement.

(2) The off-diagonal elements determine all the correlation properties of the beam. They must be Hermitian, in the sense that

$$W(n_H,n_V;n_H',n_V')\equiv W^*(n_H',n_V';n_H,n_V)\ . \tag{2.7}$$

The expectation value of any operator (for example, $\hat{s}_\alpha$) is given by

$$s_\alpha=\mathrm{Tr}_{(n)}(\rho\hat{s}_\alpha)\ , \tag{2.8}$$

where subscript n indicates that the trace is taken in the photon number space. Recognizing $a_i^+a_j^-$ in (2.5) as the photon number operator when $i=j$, we can immediately evaluate

$$s_1=\sum_{n_H,n_V}(n_H+n_V)p(n_H,n_V)=I_H+I_V=I_{\text{total}}\ , \tag{2.9}$$

where (I_H,I_V) is optical intensity measured through a (horizontal, vertical) polarizer. To make this strictly true, we implicitly absorbed into the τ matrices a factor which converts from photon number in a given normalization volume to optical signal I, as measured by a phototube. The other operators then yield

$$s_2=\sum_{n_H,n_V}(n_H-n_V)p(n_H,n_V)=I_H-I_V\ , \tag{2.10}$$

$$s_3=\sum_{n_{D^+},n_{D^-}}(n_{D^+}-n_{D^-})p(n_{D^+},n_{D^-})=I_{D^+}-I_{D^-}\ , \tag{2.11}$$

$$s_4=\sum_{n_R,n_L}(n_R-n_L)p(n_R,n_L)=I_R-I_L\ , \tag{2.12}$$

where D^+ and D^- refer to diagonal linear polarizers and R and L refer to right and left circular polarizers. These expectation values are exactly the four polarization parameters defined by Stokes in 1852 [3]; therefore, the $\hat{s}_\alpha$ may reasonably be called the quantum-mechanical Stokes operators. Once the four Stokes parameters are obtained, we may define

$$\rho^{(1)}=\tfrac{1}{2}\sum_{\alpha=1}^{4}\tau_\alpha s_\alpha\ , \tag{2.13}$$

where the s_α trace back to the full density matrix ρ through (2.8). Because of the orthogonality of the τ matrices (2.4), we may isolate the Stokes parameters by the formula

$$s_\alpha=\mathrm{Tr}(\rho^{(1)}\tau_\alpha)\ . \tag{2.14}$$

But this is exactly the formula for calculating the expectation value of operator τ_α in a state represented by density matrix $\rho^{(1)}$. So (2.13) and (2.14) create a formalism in which the Stokes parameter operators are the Pauli matrices and $\rho^{(1)}$ is a special kind of reduced density matrix for the light. Of course, $\rho^{(1)}$ contains far less information about the photon state than the full density matrix ρ, but it does contain all information about the Stokes parameters and anything that depends solely on Stokes parameters. This includes all linear optical properties.

To connect $\rho^{(1)}$ with classical electromagnetic theory, we replace the s_α in (2.13) by the intensity expressions of (2.9)–(2.12) and further replace the intensities by the square modulus of the amplitude for a general plane wave $\{E_H,E_V\}$ after it passes through the appropriate polarizers [11]. The result, after considerable calculation, is

$$\rho^{(1)}=\begin{bmatrix}E_HE_H^* & E_HE_V^*\\ E_VE_H^* & E_VE_V^*\end{bmatrix}_{\text{time avg}}\ . \tag{2.15}$$

Then (2.13) becomes

$$\langle E_iE_j^*\rangle_{\text{time}}=\tfrac{1}{2}(\tau_\alpha)_{ij}s_\alpha \tag{2.16}$$

and using the orthogonality (2.4), the classical formula for the Stokes parameters becomes

$$s_\alpha=(\tau_\alpha)_{ij}^*\langle E_iE_j^*\rangle_{\text{time}}\ , \tag{2.17}$$

which is identical mathematically, though not in form, to the definition of 1852. Here and elsewhere in this paper, double occurrence of an index implies summation over the range of the index.

We have recast these old results in a form that makes particularly clear the path that one must follow to obtain new results for the case of nonlinear properties.

C. Construction of a particular set of double Stokes operators

We now construct a similar set of operators relevant to processes involving two simultaneous, identical photons. There are two procedures that we could use. First, we could reduce the results already obtained for two nonidentical photons and project out those terms consistent with Bose-Einstein statistics. This is the familiar method used in electronic theory. Alternatively, we could redo the theory from the beginning, explicitly using operators that create and annihilate two identical photons simultaneously, traveling essentially the path laid out in Sec. II B. Because of its clarity and simplicity, this is the method we will use.

Only three essentially different double annihilation operators or double creation operators are possible, namely,

$$b_1^{\pm}\equiv a_H^{\pm}a_H^{\pm},\quad b_2^{\pm}\equiv a_V^{\pm}a_V^{\pm},\quad b_3^{\pm}\equiv\sqrt{2}a_H^{\pm}a_V^{\pm}\ , \tag{2.18}$$

where H and V (horizontal and vertical) span all possible polarizations. We rewrite this compactly as

$$b_\mu^{\pm}\equiv a_i^{\pm}a_j^{\pm}g_{ij\mu}\ , \tag{2.19}$$

where the $2\times2\times3$ constant matrix $\mathbf{g}$ is defined such that

$$g_{H,H,1}=g_{V,V,2}=\sqrt{2}g_{H,V,3}=\sqrt{2}g_{V,H,3}=1\ , \tag{2.20}$$

with all other elements equal to zero. This constant matrix has the orthogonality

$$g_{ij\mu}g_{ij\nu}=\delta_{\mu\nu}\ . \tag{2.21}$$

Each double creation operator may be paired with a double annihilation operator to produce nine operators. We define a certain weighted sum of these operators as

$$\hat{S}_\Omega=\sum_{(\mu,\nu)=(1,1)}^{(3,3)}(\lambda_\Omega)_{\mu,\nu}b_\mu^{+}b_\nu^{-}\ , \tag{2.22}$$

where Ω runs 1–9 and (μ,ν) runs from (1,1) to (3,3) like an odometer. The $\boldsymbol{\lambda}$ matrices are the 3×3 analog of the Pauli matrices. In detail,

$$\lambda_1=\sqrt{\tfrac{2}{3}}\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix},\quad \lambda_2=\sqrt{\tfrac{1}{3}}\begin{bmatrix}1&0&0\\0&1&0\\0&0&-2\end{bmatrix},\quad \lambda_3=\begin{bmatrix}1&0&0\\0&-1&0\\0&0&0\end{bmatrix},\quad \lambda_4=\begin{bmatrix}0&1&0\\1&0&0\\0&0&0\end{bmatrix},$$
$$\lambda_5=\begin{bmatrix}0&0&0\\0&0&1\\0&1&0\end{bmatrix},\quad \lambda_6=\begin{bmatrix}0&0&1\\0&0&0\\1&0&0\end{bmatrix},\quad \lambda_7=\begin{bmatrix}0&0&0\\0&0&-i\\0&i&0\end{bmatrix},\quad \lambda_8=\begin{bmatrix}0&0&-i\\0&0&0\\i&0&0\end{bmatrix},\quad \lambda_9=\begin{bmatrix}0&-i&0\\i&0&0\\0&0&0\end{bmatrix}. \tag{2.23}$$

These nine $\boldsymbol{\lambda}$ matrices are the Lie generators of an irreducible Hermitian representation of group SU(3), just as the τ matrices are similar generators for SU(2). Their commutation rules and other properties may be found in standard textbooks [12]. The $\boldsymbol{\lambda}$ matrices have several orthogonalities, namely,

$$\mathrm{Tr}(\lambda_\Lambda\lambda_\Omega)=2\delta_{\Lambda\Omega} \tag{2.24}$$

and

$$(\lambda_\Lambda)_{\alpha,\beta}(\lambda_\Lambda)^*_{\rho,\sigma}=2\delta_{\alpha\rho}\delta_{\beta\sigma}\ . \tag{2.25}$$

The expectation values of the operators defined in (2.22) are to be calculated, as always, according to

$$S_\Omega=\mathrm{Tr}_{(n)}(\rho\hat{S}_\Omega)\ , \tag{2.26}$$

where ρ is the same photon density matrix defined in (2.6). As we will show, the nine parameters S_Ω characterize completely the abilities of the light beam to initiate simultaneous two-photon processes. Therefore, we call them the quantum-mechanical double Stokes parameters.

We now calculate the expectation values of the $\hat{S}_\Omega$. This is most easily done if we rewrite the double Stokes operators in terms of the Stokes operators; such a procedure is ubiquitous in many-body theory. The Stokes operators obey

$$[\hat{s}_2,\hat{s}_3]=2i\hat{s}_4,\quad [\hat{s}_3,\hat{s}_4]=2i\hat{s}_2\ ,$$
$$[\hat{s}_4,\hat{s}_2]=2i\hat{s}_3,\quad [\hat{s}_1,\hat{s}_\alpha]=0\ \ (\alpha=2,3,4) \tag{2.27}$$

and using these commutators we arrive at

$$\begin{bmatrix}\hat{S}_1\\\hat{S}_2\\\hat{S}_3\\\hat{S}_4\\\hat{S}_5\\\hat{S}_6\\\hat{S}_7\\\hat{S}_8\\\hat{S}_9\end{bmatrix}=\begin{bmatrix}\sqrt{\frac{2}{3}}\hat{s}_1^2\\\sqrt{\frac{1}{12}}(3\hat{s}_2^2-\hat{s}_1^2)\\\hat{s}_1\hat{s}_2\\\frac{1}{2}(\hat{s}_3^2-\hat{s}_4^2)\\\sqrt{\frac{1}{2}}(\hat{s}_1-\hat{s}_2)\hat{s}_3\\\sqrt{\frac{1}{2}}(\hat{s}_1+\hat{s}_2)\hat{s}_3\\-\sqrt{\frac{1}{2}}(\hat{s}_1-\hat{s}_2)\hat{s}_4\\\sqrt{\frac{1}{2}}(\hat{s}_1+\hat{s}_2)\hat{s}_4\\\hat{s}_3\hat{s}_4\end{bmatrix}+\begin{bmatrix}-\sqrt{\frac{2}{3}}\hat{s}_1\\-\sqrt{\frac{1}{3}}\hat{s}_1\\-\frac{1}{4}\hat{s}_2\\0\\-\sqrt{\frac{1}{2}}(\hat{s}_3+i\hat{s}_4)\\\sqrt{\frac{1}{2}}(\hat{s}_3-i\hat{s}_4)\\\sqrt{\frac{1}{2}}(\hat{s}_4+i\hat{s}_3)\\\sqrt{\frac{1}{2}}(\hat{s}_4+i\hat{s}_3)\\0\end{bmatrix}. \tag{2.28}$$

The first column is quadratic in number density while the second is linear. In the classical limit of high photon density, the expectation value of the second column is much smaller than that of the first, so the first column alone gives the two-photon absorption operators in all practical situations.

We may now define a reduced 3×3 density matrix formalism for two-photon properties. With the normalization shown in (2.28)

$$\rho^{(2)}=\tfrac{1}{2}\sum_{\Omega=1}^{9}\lambda_\Omega S_\Omega \tag{2.29}$$

from which, using orthogonality (2.24), the expectation values S_Ω may be isolated by the formula

$$S_\Omega = \mathrm{Tr}(\rho^{(2)}\lambda_\Omega) \ . \tag{2.30}$$

Again, this expression has the form of an expectation value calculation in density matrix theory. Matrix $\rho^{(2)}$ plays the role of a density matrix for the light while matrix λ_Ω is the operator for observable S_Ω. The reduced density matrix $\rho^{(2)}$ contains all the information about the light that is relevant to simultaneous two-photon processes, but information about higher processes is missing [13].

To relate $\rho^{(2)}$ to classical electromagnetic theory, we replace the expectation values S_Ω in (2.29) by the quadratic Stokes expressions in the first column of (2.28) (without carets), and we then make further replacements in terms of $\{E_H, E_V\}$ just as we did above Eq. (2.15) for $\rho^{(1)}$. The result, after much calculation, is

$$\rho^{(2)} = \begin{bmatrix} E_H^2 E_H^{*2} & E_H^2 E_V^{*2} & \sqrt{2} E_H^2 E_H^* E_V^* \\ E_V^2 E_H^{*2} & E_V^2 E_V^{*2} & \sqrt{2} E_V^2 E_H^* E_V^* \\ \sqrt{2} E_H E_V E_H^{*2} & \sqrt{2} E_H E_V E_V^{*2} & 2 E_H E_H^* E_V E_V^* \end{bmatrix}_{\text{time avg}} \ . \tag{2.31}$$

Putting this into (2.30), it may be shown by direct calculation that

$$S_\Omega = C^*_{\Omega,ijkl} \langle E_i E_j E_k^* E_l^* \rangle_{\text{time}} \ , \tag{2.32}$$

where

$$C_{\Omega,ijkl} = (\lambda_\Omega)_{\mu\nu} g_{ij\mu} g_{kl\nu} \ . \tag{2.33}$$

The **C** matrix is given explicitly in Table I. Note from the definition of **g** that **C** is symmetric for exchange of i and j, and for exchange of k and l. Thus any exchange of E symbols or of E^* symbols in (2.32) must produce the same S. The **C** matrix also possesses the orthogonality

$$C_{\Omega,ijkl} C^*_{\Lambda,ijkl} = 2\delta_{\Omega\Lambda} \ , \tag{2.34}$$

leading easily to an inverse for (2.32)

$$\langle E_i E_j E_k^* E_l^* \rangle_{\text{time}} = \tfrac{1}{2} C_{\Omega,ijkl} S_\Omega \ , \tag{2.35}$$

which will be used in Sec. VII.

D. A depolarization parameter for double Stokes parameters

Linear Stokes parameters always obey the inequality

$$s_1^2 \geq s_2^2 + s_3^2 + s_4^2 \tag{2.36}$$

in which the equality holds only for pure polarized light. A linear depolarization factor p is then defined via

$$p = \sqrt{(s_2^2 + s_3^2 + s_4^2)/s_1^2} \tag{2.37}$$

and it is always true that $0 \leq p \leq 1$. A similar relation holds among the double Stokes parameters. The density matrix $\rho^{(2)}$ always obeys an inequality [7(a)]

$$\mathrm{Tr}(\rho^{(2)}\rho^{(2)}) \leq \mathrm{Tr}(\rho^{(2)})\mathrm{Tr}(\rho^{(2)}) \ . \tag{2.38}$$

Substitution of (2.29) into (2.38) leads to

$$S_1^2 \geq \sum_{\Lambda=2}^{9} S_\Lambda^2 \ , \tag{2.39}$$

where again the equality holds only for pure polarized light. Perhaps when double Stokes parameters are actually measured for an incoherent beam, it will be useful to quote the single number

$$P = \left[\sum_{\Lambda=2}^{9} S_\Lambda^2 \Big/ S_1^2 \right]^{1/2} \tag{2.40}$$

as its nonlinear depolarization and incoherence parameter, with range $0 \leq P \leq 1$.

TABLE I. The tabulated quantity is the **C** matrix defined by Eq. (2.33).

Ω \ $jklm$	HHHH	HHHV	HHVH	HHVV	HVHH	HVHV	HVVH	HVVV	VHHH	VHHV	VHVH	VHVV	VVHH	VVHV	VVVH	VVVV
1	$\sqrt{\frac{2}{3}}$	0	0	0	0	$\sqrt{\frac{1}{6}}$	$\sqrt{\frac{1}{6}}$	0	0	$\sqrt{\frac{1}{6}}$	$\sqrt{\frac{1}{6}}$	0	0	0	0	$\sqrt{\frac{2}{3}}$
2	$\sqrt{\frac{1}{3}}$	0	0	0	0	$-\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{1}{3}}$	0	0	$-\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{1}{3}}$	0	0	0	0	$\sqrt{\frac{1}{3}}$
3	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1
4	0	0	0	1	0	0	0	0	0	0	0	0	1	0	0	0
5	0	0	0	0	0	0	0	$\sqrt{\frac{1}{2}}$	0	0	0	$\sqrt{\frac{1}{2}}$	0	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	0
6	0	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	0	$\sqrt{\frac{1}{2}}$	0	0	0	$\sqrt{\frac{1}{2}}$	0	0	0	0	0	0	0
7	0	0	0	0	0	0	0	$-i\sqrt{\frac{1}{2}}$	0	0	0	$-i\sqrt{\frac{1}{2}}$	0	$i\sqrt{\frac{1}{2}}$	$i\sqrt{\frac{1}{2}}$	0
8	0	$i\sqrt{\frac{1}{2}}$	$i\sqrt{\frac{1}{2}}$	0	$-i\sqrt{\frac{1}{2}}$	0	0	$-i\sqrt{\frac{1}{2}}$	0	0	0	0	0	0	0	0
9	0	0	0	i	0	0	0	0	0	0	0	0	$-i$	0	0	0

III. THE DOUBLE STOKES DESCRIPTION OF TWO-PHOTON ABSORPTION

As a first application of the double Stokes parameters, we will use them to describe two-photon absorption. We begin with the usual expression for the event rate

$$\dot{N}^{(\uparrow)}_{\text{2-photon}} \propto \langle |E_i T_{ij} E_j|^2 \rangle = \langle E_i E_j E_k^* E_l^* \rangle_{\text{time}} \langle T_{ij} T_{kl}^* \rangle_{\text{ensemble}} , \quad (3.1)$$

where the nine T_{ij} form a true two-photon absorptivity tensor when the absorber is small compared to wavelength. They still make a 3×3 matrix even when this is not true, but one must be careful about how the matrix transforms when the molecule rotates. In propagation frame one component of **E** vanishes (call it z). Thus indices i, j, k, and l run over two values, the two transverse directions. Substitution of (2.35) into (3.1) leads to

$$\dot{N}^{(\uparrow)}_{\text{2-photon}} \approx S_\Lambda D_\Lambda , \quad (3.2)$$

where

$$D_\Lambda = \tfrac{1}{2} C_{\Lambda,ijkl} \langle T_{ij} T_{kl}^* \rangle_{\text{ensemble}} . \quad (3.3)$$

The nine quantities S_Λ are the double Stokes parameters for the light; the nine molecule quantities D_Λ are double Mueller two-photon absorptivity parameters for the material. In Appendix A, we show that for a single absorber in one position, there are three identities among the D_Λ, but that after the ensemble average, all nine D_Λ are independent. Also we perform there the ensemble average for the small molecule case in which T_{ij} rotates like a true tensor, finding the expected formula for a fluid with only two of the D_Λ nonzero. These are linear combinations of the two two-photon absorptivities measurable with linear and circular polarizations [14].

IV. PREPARATION OF A BEAM WITH KNOWN PARAMETERS

A. Known Stokes parameters

When we use light scattering to determine the properties of a molecular system, we want full control of polarization for both the incident light and the scattered light. This goal can be achieved using a half-wave plate, a quarter-wave plate, and a linear polarizer.

We let "vertical" mean perpendicular to the scattering plane and let "horizontal" mean parallel to the scattering plane. All rotation angles for optical elements are measured counterclockwise from the scattering plane to the transverse axis of the element, looking into the source. For polarizers the transverse axis we use is the pass axis; for retarders, the slow axis.

We start with pure polarized linear light at $\pi/4$ to the vertical; at this angle the H and V components are equal, and this has a simplifying effect on the algebra below. The light then passes through the quarter-wave plate [with angular position about the optic axis measured by $(3\pi/4-\omega)$] and then through the half-wave plate [with angular position measured by $(\gamma/2-\omega/2-\pi/8)$]. This train is represented by

$$\mathbf{E}(\gamma,\omega) = \mathbf{H}(\tfrac{1}{2}\gamma - \tfrac{1}{2}\omega - \tfrac{1}{8}\pi)\mathbf{Q}(\tfrac{3}{4}\pi - \omega) \begin{bmatrix} E \\ E \end{bmatrix} , \quad (4.1)$$

where $\mathbf{E}(\gamma,\omega)$ is generally complex. Substituting standard Jones matrices [11] for **H** and **Q**, we obtain

$$\mathbf{E}(\omega,\gamma) = (E/2)(1+i)i^{7/2} \times \begin{bmatrix} \cos(\gamma-\omega)+i\cos(\gamma+\omega) \\ \sin(\gamma-\omega)+i\sin(\gamma+\omega) \end{bmatrix} . \quad (4.2)$$

The linear Stokes parameters are then easily calculated, giving

$$\begin{bmatrix} s_1 \\ s_2 \\ s_3 \\ s_4 \end{bmatrix} = \langle |E|^2 \rangle_{\text{time}} \begin{bmatrix} 1 \\ \cos2\omega\cos2\gamma \\ \cos2\omega\sin2\gamma \\ \sin2\omega \end{bmatrix} . \quad (4.3)$$

The proper value of $\langle |E|^2 \rangle_{\text{time}}$ is measured by any linear detector and will normally be reported in units such that s_1 is total optical intensity $I(J\,\text{cm}^{-2}\,\text{sec}^{-1})$. But if s_1 is normalized to 1, the other Stokes parameters are the Cartesian coordinates of a point on the Poincaré unit sphere if we interpret 2γ and 2ω as the Mercator coordinates. The polar angle (latitude) is 2ω; the equatorial angle (longitude) is 2γ. All linear polarizations lie around the equator at $2\omega=0$, with horizontal linear polarization on the Greenwich meridian ($2\gamma=0$). Right circular polarization is at the North pole ($2\omega=+\pi/2$), left, at the South ($2\omega=-\pi/2$). By varying 2ω over $(-\pi/2,+\pi/2)$ and 2γ over $(-\pi,+\pi)$, the Poincaré point moves to any desired pure polarization.

B. Known double Stokes parameters

Now we construct the two-photon analog. We substitute (4.2) into (2.32). The result is

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \\ S_8 \\ S_9 \end{bmatrix} = \langle |E|^4 \rangle_{\text{time}} \begin{bmatrix} \sqrt{\frac{2}{3}} \\ \sqrt{\frac{1}{12}}(3\cos^2 2\omega\cos^2 2\gamma - 1) \\ \cos2\omega\cos2\gamma \\ \frac{1}{2}(\cos^2 2\omega\sin^2 2\gamma - \sin^2 2\omega) \\ \sqrt{\frac{1}{2}}(1-\cos2\omega\cos2\gamma)\cos2\omega\sin2\gamma \\ \sqrt{\frac{1}{2}}(1+\cos2\omega\cos2\gamma)\cos2\omega\sin2\gamma \\ -\sqrt{\frac{1}{2}}(1-\cos2\omega\cos2\gamma)\sin2\omega \\ \sqrt{\frac{1}{2}}(1+\cos2\omega\cos2\gamma)\sin2\omega \\ \cos2\omega\sin2\gamma\sin2\omega \end{bmatrix} . \quad (4.4)$$

The prefactor $\langle |E|^4 \rangle_{\text{time}}$ is measureable only through the event rate of a simultaneous two-photon process; it depends upon the temporal coherence of the original beam as well as its intensity. If this vector is normalized by $\langle |E|^4 \rangle_{\text{time}}$, S_1 has the value $\sqrt{\frac{2}{3}}$ rather than the 1 that

appears in the analogous linear case. This is traceable to the normalization of matrix λ_1 and has no physical significance. In Appendix B we give examples of the nine-vector **S** for a number of familiar polarization cases, plus several unfamiliar ones that are needed to form a complete set of double Stokes experiments.

V. MEASURING THE DOUBLE STOKES PARAMETERS OF A GIVEN BEAM

In this section we show how the double Stokes parameters may be measured for a given beam of light, even if it is depolarized and incoherent. If the light is prepared by the method of the preceding section, it will be pure polarized with known double Stokes parameters. But intense light near the surface of a star, or from a superhot, magnetically confined plasma will generally be incoherent and only partly polarized. Even synchrotron light, which may be coherent but is generally of mixed polarization, must be dealt with by the principles of this section.

Figure 1 shows the conceptual apparatus. The optical train is inverse to that of Sec. IV; the internal linear polarizer is rotated to 45° from the vertical or horizontal to simplify the algebra.

The detecting material at the focus may be anything that has a response quadratic in intensity at the frequency of the light; it may be fluorescence, ionization, acoustic response, thermal lensing, or anything else. Because of the internal polarizer, the vapor always "sees" light of the same polarization, and the tensorial nature of the two-photon absorption never appears in the measurement process. Absolute excitation rates are not required. The optical train is

$$\mathbf{E}^{(\text{at focus})}(\omega,\gamma)=\mathbf{P}(\tfrac{1}{4}\pi)\mathbf{Q}(\tfrac{3}{4}\pi-\omega)\times\mathbf{H}(\tfrac{1}{2}\gamma-\tfrac{1}{2}\omega-\tfrac{1}{8}\pi)\mathbf{E}^{(\text{incident})}\ , \tag{5.1}$$

where $\mathbf{P}(\pi/4)$ is a diagonal linear polarizer. In Appendix C we show that this results in the formula

$$\dot{\mathcal{N}}(\omega,\gamma)=\eta\mathbf{b}\cdot\mathbf{S}=\eta b_\Lambda(\omega,\gamma)S_\Lambda\ , \tag{5.2}$$

where $\dot{\mathcal{N}}$ is an event rate, η is an efficiency factor, and $b_\Lambda(\omega,\gamma)$ represents the entire optical train, given explicitly as (C11). If we choose nine different sets of retarder angles (ω,γ) and do nine experiments indexed by Ω, then we have

$$\dot{\mathcal{N}}_\Omega=\eta B_{\Omega\Lambda}S_\Lambda\ , \tag{5.3}$$

where **B** is a stack of nine row vectors **b**. If we choose the angles properly, we can make the **B** matrix invertable, and thus

$$S_\Lambda=\frac{1}{\eta}(\mathbf{B}^{-1})_{\Lambda\Omega}\dot{\mathcal{N}}_\Omega\ . \tag{5.4}$$

With this we have measured the nine double Stokes parameters, up to an unknown scale factor $1/\eta$. A good practical set of (ω,γ) angles is specified in Appendix C.

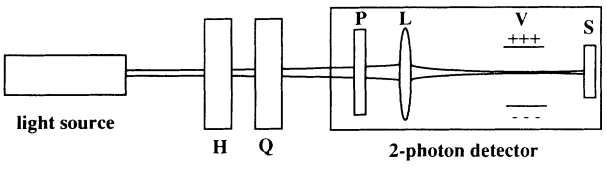

FIG. 1. Apparatus for experimental determination of the nine double Stokes parameters of any kind of light beam, including incoherent depolarized beams. H is a half-wave plate rotatable about the optic axis of the instrument, Q is a similarly rotatable quarter-wave plate, P is a fixed polarizer, L is a lens, V is any kind of detector for two-photon excitations, and S is a beamstop.

VI. NONPERTURBATIVE THEORY OF NONLINEAR LIGHT SCATTERING

We begin our treatment of nonlinear light scattering by examining the basic theory in a form that is free of the usual dipole and perturbative approximations. Our purpose is to display the exact dependence of the quadratic scattering on the experimental vectors $\{\mathbf{k}^{(1)},\boldsymbol{\lambda}^{(1)};\mathbf{k}^{(2)},\boldsymbol{\lambda}^{(2)}\}$, where $\mathbf{k}^{(1)}$ and $\boldsymbol{\lambda}^{(1)}$ are the propagation and polarization vectors of the incident beam and $\mathbf{k}^{(2)}$ and $\boldsymbol{\lambda}^{(2)}$ are the wave vector and polarization passed by filters in front of the detector. These $\boldsymbol{\lambda}$ vectors have nothing to do with the λ matrices of Sec. III.

We follow the convention that the horizontal (upper) element of polarization vectors is always pure real. The vertical (lower) element is real for linearly polarized light, but complex for elliptical light (and pure imaginary for circular light). We take all polarization vectors normalized by $\boldsymbol{\lambda}\cdot\boldsymbol{\lambda}^*=1$, where the asterisk means complex conjugate. The exact vector dependence of quadratic scattering, which we will find, then leads on to an exact Stokes-Mueller-like formalism.

As we did in a previous paper on linear scattering [15], we develop the theory using the Green's operator formalism [16]. Let $d\Omega$ be a small solid angle around scattering angle θ and let $d\sigma$ be the cross section for scattering into $d\Omega$. Then the observable differential cross section $d\sigma/d\Omega$ is to be given by

$$\frac{d\sigma}{d\Omega}=C|\mathcal{A}(\theta)|^2\ , \tag{6.1}$$

where C is a collection of fundamental constants and frequencies and $\mathcal{A}$ is a scattering amplitude. In quadratic scattering, σ will be in $\text{m}^4\,\text{sec photon}^{-1}\,\text{molecule}^{-1}$ (like two-photon absorptivity), whereas the analogous quantity in linear scattering is a true cross section with units $\text{m}^2\,\text{molecule}^{-1}$. The amplitude is the matrix element

$$\mathcal{A}(\theta)=(\text{final}|T|\text{initial}) \tag{6.2}$$

of a scattering operator T, which we now construct. The Hamiltonian of the total system is

$$H=H_R+H_M+H'\ , \tag{6.3}$$

where H_R is for radiation, H_M is for material, and H' is the interaction. The eigenfunctions and eigenvalues of H_R and H_M are, respectively, E_r and $|r\rangle$, and E_m and

$|m)$. The usual treatment then finds a series of approximate perturbative solutions. However, the T-matrix method avoids these and finds a nonperturbative solution for A which is in principle exact.

The most general amplitude for two-photon scattering would be of the form

$$\mathcal{A}=(f|\langle n_1-2n_d,n_2+n_d|T|n_1,n_2\rangle|i)\ , \tag{6.4a}$$

where states $|i)$ and $(f|$ are the initial and final states of the material, and the initial radiation state $|n_1,n_2\rangle$ has n_1 photons at ω_1 in the pump mode and n_2 photons at ω_2 in the observed mode. The final state is $\langle n_1-2n_d,n_2+n_d|$, where n_d photons have been created at ω_2 and $2n_d$ destroyed at ω_1. Any number of other modes may be occupied in any way, but if their occupation numbers do not change, they do not affect the problem, and we suppress them. The intensity dependence of (6.4a) is very complicated, but it is given in principle by the full T-matrix theory. However, it is much better to deal with these complicated cases by (for example) Floquet theory [17] or by Maxwell's equations describing coupled waves in a nonlinear medium [9].

To obtain useful results from T-matrix theory, we must stay in the regime where the amplitude scales with incident photon number, i.e., the event rate scales quadratically with pump intensity. Thus within T-matrix theory we consider only those virtual processes that contribute to intensity-independent damping and coupling of polarization waves. Under these conditions we may use the smallest possible number of photons in the matrix element, rewriting $\mathcal{A}$ as

$$\mathcal{A}\cong n_1(f|\langle 0,1|T|2,0\rangle|i)\ . \tag{6.4b}$$

Energy is conserved according to

$$E_i+2\hbar\omega_1=E_f+1\hbar\omega_2\ . \tag{6.5}$$

When $E_f=E_i$, the process is frequency doubling; when $E_f\neq E_i$, it is hyper-Raman scattering.

From our knowledge of H_R and H_M and their eigensystems we may in principle construct an integral operator inverse to the differential operator $z-(H_R+H_M)$, where z is any complex number. This inverse is the zeroth-order Green's operator

$$G_0(z)=\sum_{r,m}\frac{|r\rangle|m\rangle(m|\langle r|}{z-E_m-E_r}\ . \tag{6.6}$$

It may be shown that the desired matrix T is given by

$$T=H'+H'GH'\ , \tag{6.7}$$

where G is the complete Green's operator, inverse to $z-(H_R+H_M+H')$. It is found by solving for G in the equation

$$G=G_0+G_0H'G\ . \tag{6.8}$$

Using creation operator a_1^+ for mode 1 and annihilation operator a_2^- for mode 2, the radiative part of the amplitude in (6.4b) may be expressed as

$$\langle 0,1|T|2,0\rangle=\sqrt{\tfrac{1}{2}}\langle 0,0|a_2^-Ta_1^+a_1^+|0,0\rangle\ . \tag{6.9}$$

Now a_1^+ and a_2^- commute and $a_2^-|0,0\rangle=0$. Therefore, if we knew the pseudocommutator $(a_2^-T-T'a_2^-)=\hat{C}$, we could write

$$\begin{aligned}a_2^-Ta_1^+a_1^+|0,0\rangle&=(T'a_2^-+\hat{C})a_1^+a_1^+|0,0\rangle\\&=\hat{C}a_1^+a_1^+|0,0\rangle\ ,\end{aligned} \tag{6.10}$$

where half the pseudocommutator expression has been swallowed up by the vacuum. We say *pseudo*commutator because T' is not exactly the same as T. Similarly, if we commute an a_1^+ operator leftwards, we eventually create the fragment $\langle 0,0|a_1^+=0$, making a similar simplification. We must do this twice, and we need the pseudocommutators $(\hat{C}a_1^+-a_1^+\hat{C}')=\hat{D}$ and $(\hat{D}a_1^+-a_1^+\hat{D}')=\hat{E}$. Fortunately, these can be worked out, and the whole radiative matrix calculation, in skeleton form, is

$$\begin{aligned}\langle 1,0|T|0,2\rangle&=\langle 0,0|a_2^-Ta_1^+a_1^+|0,0\rangle\\&=\langle 0,0|\hat{C}a_1^+a_1^+|0,0\rangle\\&=\langle 0,0|\hat{D}a_1^+|0,0\rangle=\langle 0,0|\hat{E}|0,0\rangle\ .\end{aligned} \tag{6.11}$$

In the final expression, all terms containing operators a_2^- or a_1^+ have been consumed by the vacuum, leaving a quantity which can be evaluated numerically (with approximations).

To carry out (6.11), we must specify H' and then use it in the construction of T. In general H' has two parts, one due to the electromagnetic vector potential $\mathbf{A}$ and the other due to spin interaction [18]. In this paper, we do not treat the spin part. The electromagnetic interaction consists of two terms

$$V=\frac{1}{2m}(-2\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{A})\ , \tag{6.12}$$

where $\mathbf{p}$ is the momentum operator for the particle and m is its mass, and where $\mathbf{A}$ is in momentum units. The two interaction terms have different polarization dependence, but as we shall see, they combine to produce only a single common polarization dependence in the final result. The quantum-mechanical form of $\mathbf{A}$ is

$$\mathbf{A}=\sum_\mu[a_\mu^-\mathbf{U}^{(\mu)}+a_\mu^+\mathbf{U}^{*(\mu)}]\ , \tag{6.13}$$

where μ runs over all appropriate modes of the radiation field and

$$\mathbf{U}^{(\mu)}=\left[\frac{e}{c}\right]\left[\frac{c\hbar}{2k^{(\mu)}\mathcal{V}}\right]^{1/2}\boldsymbol{\lambda}^{(\mu)}\exp(i\mathbf{k}^{(\mu)}\cdot\mathbf{r})\ , \tag{6.14}$$

in which $\mathbf{r}$ is the position of the charged particle, e is its charge (e negative for the electron), and $\mathcal{V}$ is the normalization volume for the photons (hereafter taken as unity). The quantities in this definition are in Gaussian units [18], but the Gaussian $\mathbf{A}$ has been converted to momentum units by the factor e/c in $\mathbf{U}$, above. Substituting (6.13) into (6.12), the complete spinless interaction operator is

$$V=-2\sum_{\mu}[a_{\mu}^{-}\mathbf{U}^{(\mu)}\cdot\mathbf{p}+a_{\mu}^{+}\mathbf{U}^{*(\mu)}\cdot\mathbf{p}]+\sum_{\mu,\nu}[a_{\mu}^{-}a_{\nu}^{-}\mathbf{U}^{(\mu)}\cdot\mathbf{U}^{(\nu)}+a_{\mu}^{-}a_{\nu}^{+}\mathbf{U}^{(\mu)}\cdot\mathbf{U}^{*(\nu)}+a_{\mu}^{+}a_{\nu}^{-}\mathbf{U}^{*(\mu)}\cdot\mathbf{U}^{(\nu)}+a_{\mu}^{+}a_{\nu}^{+}\mathbf{U}^{*(\mu)}\cdot\mathbf{U}^{*(\nu)}]\ . \tag{6.15}$$

There should be a sum over all charged particles, with the particle label appearing on $\mathbf{p}$ and on $\mathbf{U}$ (because of the $\mathbf{r}$ inside $\mathbf{U}$). However, this changes nothing essential, and we suppress it.

We now begin detailed implementation of the skeleton calculation (6.11) using this V. With the commutator $[a_{\lambda},a_{\mu}^{+}]=\delta_{\lambda,\mu}$ it may be shown that

$$[V,a_{\mu}^{+}]=-2\mathbf{U}^{(\mu)}\cdot\check{\mathbf{p}} \tag{6.16}$$

where $\check{\mathbf{p}}=(\mathbf{p}-\mathbf{A})$. Similarly,

$$[a_{\mu}^{-},V]=-2\mathbf{U}^{*(\mu)}\cdot\check{\mathbf{p}}\ . \tag{6.17}$$

By a proof very similar to one in an earlier paper on linear scattering [15] it may be shown that G obeys the pseudocommutator relations

$$a_{\mu}^{-}G-G_{\mu}a_{\mu}^{-}=-2G_{\mu}(\mathbf{U}^{*(\mu)}\cdot\check{\mathbf{p}})G \tag{6.18}$$

and

$$Ga_{\mu}^{+}-a_{\mu}^{+}G_{\mu}=G(\mathbf{U}^{(\mu)}\cdot\check{\mathbf{p}})G_{\mu}\ , \tag{6.19}$$

where $G=G(z)$ and $G_{\mu}=G(z-\hbar\omega_{\mu})$. Now $T=V+VGV$ (see 6.7), and we may use (6.16) and (6.17) to show that $\langle 0,1|V|2,0\rangle=0$. This leaves as our whole calculation

$$\sqrt{2}\langle 0,1|T|2,0\rangle=\langle 0,0|a_{2}^{-}VGVa_{1}^{+}a_{1}^{+}|0,0\rangle\ . \tag{6.20}$$

Using (6.16)–(6.19) in the skeleton (6.11), it is now possible to move a_{2}^{-} all the way right and both a_{1}^{+} all the way left [19]. The result is

$$\begin{aligned}\sqrt{2}\langle 0,1|T|2,0\rangle=\langle 0,0|(1+VG_{2})(&2\mathbf{U}^{*(2)}\cdot\check{\mathbf{p}}G\mathbf{U}^{(1)}\cdot\check{\mathbf{p}}G_{1}\mathbf{U}^{(1)}\cdot\check{\mathbf{p}}+2\mathbf{U}^{(1)}\cdot\check{\mathbf{p}}G_{12}\mathbf{U}^{*(2)}\cdot\check{\mathbf{p}}G_{1}\mathbf{U}^{(1)}\cdot\check{\mathbf{p}}\\&+2\mathbf{U}^{(1)}\cdot\check{\mathbf{p}}G_{12}\mathbf{U}^{(1)}\cdot\check{\mathbf{p}}G_{112}\mathbf{U}^{*(2)}\cdot\check{\mathbf{p}}+2\mathbf{U}^{(1)}\cdot\mathbf{U}^{*(2)}G_{1}\mathbf{U}^{(1)}\cdot\check{\mathbf{p}}\\&+2\mathbf{U}^{(1)}\cdot\check{\mathbf{p}}G_{12}\mathbf{U}^{(1)}\cdot\mathbf{U}^{*(2)}+\mathbf{U}^{*(2)}\cdot\check{\mathbf{p}}G\mathbf{U}^{(1)}\cdot\mathbf{U}^{(1)}\\&+\mathbf{U}^{(1)}\cdot\mathbf{U}^{(1)}G_{2}\mathbf{U}^{*(2)}\cdot\check{\mathbf{p}})(1+G_{11}V)|0,0\rangle\ .\end{aligned} \tag{6.21}$$

The big operator is the $\hat{E}$ of (6.11). Terms that contain $\mathbf{U}\cdot\mathbf{p}$ three times come from three passages through $\mathbf{A}\cdot\mathbf{p}$; other terms contain one $\mathbf{U}\cdot\mathbf{p}$ and one $\mathbf{U}\cdot\mathbf{U}$, and they come from one passage through $\mathbf{A}\cdot\mathbf{p}$ and one through $\mathbf{A}\cdot\mathbf{A}$. On each G there is one subscript for each photon energy subtracted from its z, as in $G_{11}=G(z-2\hbar\omega_{1})$ or $G_{12}=G(z-\hbar\omega_{1}-\hbar\omega_{2})$.

We now approach the crucial step of the argument. Every summand in this expression contains, in various orders, the factors $\mathbf{U}^{(1)},\mathbf{U}^{(1)},\mathbf{U}^{*(2)}$. But, as may be seen in the definition (6.14), each of these symbols can be written as

$$\mathbf{U}=U\boldsymbol{\lambda} \tag{6.22}$$

where $\boldsymbol{\lambda}$ is a unit-length polarization vector and U is a scalar plane wave propagating with either $\mathbf{k}^{(1)}$ or $\mathbf{k}^{(2)}$. The $\boldsymbol{\lambda}$'s are just numerical constants and may therefore be factored out of the integrals. Then in tensor subscript notation (with sum over repeated indices understood), the main part of the central sum of (6.21) becomes the polarization factor $\lambda_{i}^{*(2)}\lambda_{j}^{(1)}\lambda_{k}^{(1)}$ times

$$\begin{aligned}F_{ijk}=(&2U^{*(2)}\check{p}_{i}GU^{(1)}\check{p}_{k}G_{1}U^{(1)}\check{p}_{j}+2U^{(1)}\check{p}_{k}G_{12}U^{*(2)}\check{p}_{i}G_{1}U^{(1)}\check{p}_{j}\\&+2U^{(1)}\check{p}_{k}G_{12}U^{(1)}\check{p}_{j}G_{112}U^{*(2)}\check{p}_{i}+2U^{(1)}U^{*(2)}\delta_{ij}G_{1}U^{(1)}\check{p}_{k}+2U^{(1)}\check{p}_{k}G_{12}U^{(1)}U^{*(2)}\delta_{ij}\\&+U^{*(2)}\check{p}_{i}GU^{(1)}U^{(1)}\delta_{jk}+U^{(1)}U^{(1)}\delta_{jk}G_{2}U^{*(2)}\check{p}_{i})\end{aligned} \tag{6.23}$$

and the entire amplitude (6.4b) may be written as

$$\mathcal{A}=n_{1}\lambda_{i}^{*(2)}Q_{ijk}\lambda_{j}^{(1)}\lambda_{k}^{(1)} \tag{6.24}$$

where

$$Q_{ijk}=\frac{1}{\sqrt{2}}\langle 0,0|(f|(1+VG_{2})F_{ijk}(1+G_{11}V)|i)|0,0\rangle\ . \tag{6.25}$$

The simple expression (6.24) displays the main point we have been working toward. The entire exact polarization dependence of the amplitude is one tensorial factor of $\boldsymbol{\lambda}$ for every annihilated photon and one of $\boldsymbol{\lambda}^{*}$ for every created photon. This, of course, is exactly the same as given by the lowest contributing orders of perturbation theory.

The $\mathbf{Q}$ of (6.25) provides everything that perturbation theory provides, plus many important effects that go beyond perturbation theory. In particular, all possible multipole effects fall out quite naturally from $\mathbf{Q}$, as well

as radiative damping and retardation effects, which must be added *ad hoc* to perturbation theory. But these effects alter only the size of the amplitude; none alters the algebraic form of the polarization dependence, even in principle. Therefore (6.24) can be used with complete confidence as the basis of an exact generalization of Stokes-Mueller formalism.

VII. NONLINEAR LIGHT SCATTERING IN GENERALIZED STOKES-MUELLER FORMALISM

We now show how double Stokes parameters describe the simultaneous annihilation of two identical photons and creation of another.

The first step is to resolve a small technical inconsistency. Our Stokes and double Stokes transforms were written using two-component polarization vectors, transverse to their propagation direction in three-dimensional space. But in (6.24), modes 1 and 2 propagate in different directions, so $\boldsymbol{\lambda}^{(1)}$ and $\boldsymbol{\lambda}^{(2)}$ cannot both be transverse in the same coordinate system. We take the system such that $\boldsymbol{\lambda}^{(1)}$ is transverse, and we let $\mathbf{R}$ be a matrix which rotates any vector by the scattering angle about the axis perpendicular to the scattering plane. We can always insert a Kronecker δ into (6.24) in the form

$$\mathcal{A}=n_1\lambda_m^{*(2)}(R_{mI}R_{Ii}^{-1})Q_{ijk}\lambda_j^{(1)}\lambda_k^{(1)} . \tag{7.1}$$

Now $\boldsymbol{\lambda}^{*(2)}\mathbf{R}$ is perpendicular to $\mathbf{k}^{(2)}$, and we can define $\lambda_I^{*(2)}=\lambda_m^{*(2)}R_{mI}$ and $\hat{Q}_{Ijk}=R_{\mathrm{Im}}^{-1}Q_{mjk}$, allowing us to write

$$\mathcal{A}=n_1\lambda_I^{*(2)}\hat{Q}_{Ijk}\lambda_j^{(1)}\lambda_k^{(1)} \tag{7.2}$$

in which all indices run only over two transverse axes; the lowercase indices run in incidence system and uppercase in observation system. Quantity n_1 is the number of photons in mode 1 of the normalization volume. The caret on $\hat{\mathbf{Q}}$ reminds us that it has a different dependence on scattering angle than the original $\mathbf{Q}$, as it has absorbed a rotation through the scattering angle.

Now we are ready to switch from quantum physics to classical physics. The Jones matrix representing the polarizer in front of the detector is the dyad $\mathbf{P}=\boldsymbol{\lambda}^{(2)}\boldsymbol{\lambda}^{*(2)}$, and when field $\mathbf{E}^{(2)}$ is incident on it, the transmitted field is $\mathbf{P}\cdot\mathbf{E}^{(2)}$ or $\boldsymbol{\lambda}^{(2)}(\boldsymbol{\lambda}^{*(2)}\cdot\mathbf{E}^{(2)})$. Therefore the classical electric field amplitude that passes this filter is

$$\mathcal{A}^{(\mathrm{classical})}=\lambda_I^{*(2)}E_I^{(2)} . \tag{7.3}$$

Setting this equal to the quantum amplitude (7.2) we find

$$E_I^{(2)}=n_1\hat{Q}_{Ijk}\lambda_j^{(1)}\lambda_k^{(1)} \tag{7.4}$$

and since $n_1=c\,(E^{(1)})^2$ and $E_i^{(1)}=E^{(1)}\lambda_i^{(1)}$, we have

$$E_I^{(2)}=c\hat{Q}_{Ijk}E_j^{(1)}E_k^{(1)} , \tag{7.5}$$

where c is a constant provided by basic electromagnetic theory. Now it is easy to transform this classical expression to a Stokes-like formalism. Absorbing the c into $\hat{Q}$, we multiply (7.5) by its own complex conjugate, giving

$$E_I^{(2)}E_L^{*(2)}=\hat{Q}_{Ijk}\hat{Q}_{Lmn}^{*}E_j^{(1)}E_k^{(1)}E_m^{*(1)}E_n^{*(1)} . \tag{7.6}$$

We take the time average of the two electrical field product expressions, and also we take the ensemble average of $\hat{\mathbf{Q}}\hat{\mathbf{Q}}^{*}$. In taking the orientational part of the ensemble average, we use the tensorial rotational transform if we can; but if we have to, we use a nontensorial transform with a rotating exponential part, as may be seen explicitly from (6.14). Then we substitute (2.16) to create the Stokes parameters s'_α of the scattered light and (2.35) to create the double Stokes parameters S_Λ of the incident light. Finally, using the orthogonality of the Pauli matrices, we arrive at a formula with the same structure as the Stokes-Mueller formalism, and which was advertised as (1.2):

$$s'_\alpha=\mathcal{M}_{\alpha\Lambda}S_\Lambda , \tag{7.7}$$

where the 4×9 double Mueller matrix $\mathcal{M}$ for nonlinear light scattering is

$$\mathcal{M}_{\alpha\Lambda}(\mathrm{theory})=(\tau_a)_{IL}^{*}C_{\Lambda,jm,kn}\langle\hat{Q}_{Ijk}\hat{Q}_{Lmn}^{*}\rangle_{\mathrm{ensemble}} . \tag{7.8}$$

This is perhaps the central theoretical result of this paper. But we emphasize immediately that $\mathcal{M}$ is also measurable. If we use nine different settings of the retarders for the incident light, we can measure nine different Stokes vectors for the scattered light. Indexing these nine experiments by q, (7.7) becomes

$$s'_{\alpha q}=\mathcal{M}_{\alpha\Lambda}S_{\Lambda q} \tag{7.9}$$

where $s'_{\alpha q}$ is 4×9 and $S_{\Lambda q}$ is 9×9. The latter will have an inverse $S_{q\Lambda}^{-1}$ if the experiments are chosen correctly; a suitable choice is shown in Appendix B. Then an empirically measured $\mathcal{M}$ is given by

$$\mathcal{M}_{\alpha\Lambda}(\mathrm{experiment})=s'_{\alpha q}\mathcal{S}_{q\Lambda}^{-1} . \tag{7.10}$$

Theory and experiment meet when the left-hand sides of (7.8) and (7.10) are compared. The 36 elements of this matrix are all that theory can predict and all that experiment can measure concerning the two-in, one-out process with a single incident beam. This is true whether or not the sample obeys the dipole or any other multipole approximation, whether or not damping and retardative effects are important, or whether or not the sample is perturbed by external fields.

VIII. IDENTICAL INCIDENT PHOTONS vs DIFFERENT INCIDENT PHOTONS

In Ref. [8] we gave a Stokes-Mueller description of two-in, one-out scattering for three coplanar beams, all with different frequencies. We found that with two different incident photons (labeled 1 and 2),

$$s_\alpha^{(3)}=\mathcal{M}_{\alpha,\beta\gamma}^{(3\leftarrow1+2)}s_\beta^{(1)}s_\gamma^{(2)} . \tag{8.1}$$

But if one of the incident beams is turned until it has exactly the same direction as the other incident beam, we have a system very similar to the one described in this paper, except that the two incident beams have different frequencies. If the two frequencies then approach each other, we have exactly the system of this paper. Equation (7.7), in slightly elaborated notation, is

$$s_\alpha^{(3)} = \mathcal{M}_{\alpha\Lambda}^{(3\leftarrow\bar{1}+\bar{1})} S_\Lambda^{(\bar{1},\bar{1})} , \tag{8.2}$$

where photon $\bar{1}$ lies exactly between photons 1 and 2. To clarify the relation between $\mathcal{M}_{\alpha,\beta\gamma}^{(3\leftarrow 1+2)}$ and $\mathcal{M}_{\alpha,\Lambda}^{(3\leftarrow\bar{1}+\bar{1})}$, we eliminate $s_\alpha^{(3)}$ from (8.1) and (8.2), and rewrite in terms of incident field amplitudes [see (2.16) and (2.31)], finding

$$\begin{aligned}\mathcal{M}_{\alpha,\Lambda}^{(3\leftarrow\bar{1}+\bar{1})} C_{\Omega,ijkl}^* \langle E_i E_j E_k^* E_l^* \rangle_{\text{time}} \\ = \mathcal{M}_{\alpha,\beta\gamma}^{(3\leftarrow 1+2)} (\tau_\beta)_{ik}^* \langle E_i^{(1)} E_k^{*(1)} \rangle_{\text{time}} \\ \times (\tau_\gamma)_{jl}^* \langle E_j^{(2)} E_l^{*(2)} \rangle_{\text{time}} .\end{aligned} \tag{8.3}$$

Now if the beams 1 and 2 both become identical to $\bar{1}$, the field averages will be related to each other by some correlation factor κ,

$$\begin{aligned}\kappa \langle E_i E_j E_k^* E_l^* \rangle_{\text{time}} = \tfrac{1}{2} \langle E_i E_k^* \rangle_{\text{time}} \langle E_j E_l^* \rangle_{\text{time}} \\ + \tfrac{1}{2} \langle E_i E_l^* \rangle_{\text{time}} \langle E_j E_k^* \rangle_{\text{time}} .\end{aligned} \tag{8.4}$$

Using (8.4) in (8.3), we find

$$\begin{aligned}\mathcal{M}_{\alpha,\Lambda}^{(3\leftarrow\bar{1}+\bar{1})} C_{\Lambda,ijkl}^* = \tfrac{1}{4}\kappa [\mathcal{M}_{\alpha,\beta\gamma}^{(3\leftarrow 1+2)} + \mathcal{M}_{\alpha,\gamma\beta}^{(3\leftarrow 2+1)}] \\ \times [(\tau_\beta)_{ik}^* (\tau_\gamma)_{jl}^* + (\tau_\beta)_{il}^* (\tau_\gamma)_{jk}^*]\end{aligned} \tag{8.5}$$

or by the **C** orthogonality (2.34)

$$\mathcal{M}_{\alpha,\Lambda}^{(3\leftarrow\bar{1}+\bar{1})} = \frac{\kappa}{2} \mathcal{M}_{\alpha,\beta\gamma}^{(3\leftarrow 1+2)} (\tau_\beta)_{ik}^* (\tau_\gamma)_{jl}^* C_{\Lambda,ijkl} . \tag{8.6}$$

Since α is a free index on both sides, each row α of $\mathcal{M}_{\alpha\Lambda}$ is made from the corresponding plane α of $\mathcal{M}_{\alpha\beta\gamma}$. The transformation matrix $(\tau_\beta)_{ik}^* (\tau_\gamma)_{jl}^* C_{\Lambda,ijkl}$, with free indices β, γ, and Λ, is clearly of size $4\times 4\times 9$. Explicit evaluation shows it to be quite sparse. Suppressing the matrix superscripts and the optical correlation factor κ, the formulas provided by the matrix are

$$\begin{aligned}\mathcal{M}_{\alpha,1} &= \sqrt{\tfrac{1}{6}} (3\mathcal{M}_{\alpha,11} + \mathcal{M}_{\alpha,22} + \mathcal{M}_{\alpha,33} + \mathcal{M}_{\alpha,44}) , \\ \mathcal{M}_{\alpha,2} &= \sqrt{\tfrac{1}{3}} (2\mathcal{M}_{\alpha,22} - \mathcal{M}_{\alpha,33} - \mathcal{M}_{\alpha,44}) , \\ \mathcal{M}_{\alpha,3} &= \mathcal{M}_{\alpha,12} + \mathcal{M}_{\alpha,12} , \\ \mathcal{M}_{\alpha,4} &= \mathcal{M}_{\alpha,33} - \mathcal{M}_{\alpha,44} , \\ \mathcal{M}_{\alpha,5} &= \sqrt{\tfrac{1}{2}} (\mathcal{M}_{\alpha,13} - \mathcal{M}_{\alpha,23} + \mathcal{M}_{\alpha,31} - \mathcal{M}_{\alpha,32}) , \\ \mathcal{M}_{\alpha,6} &= \sqrt{\tfrac{1}{2}} (\mathcal{M}_{\alpha,13} + \mathcal{M}_{\alpha,23} + \mathcal{M}_{\alpha,31} + \mathcal{M}_{\alpha,32}) , \\ \mathcal{M}_{\alpha,7} &= \sqrt{\tfrac{1}{2}} (-\mathcal{M}_{\alpha,14} + \mathcal{M}_{\alpha,24} - \mathcal{M}_{\alpha,41} + \mathcal{M}_{\alpha,42}) , \\ \mathcal{M}_{\alpha,8} &= \sqrt{\tfrac{1}{2}} (\mathcal{M}_{\alpha,14} + \mathcal{M}_{\alpha,24} + \mathcal{M}_{\alpha,41} + \mathcal{M}_{\alpha,42}) , \\ \mathcal{M}_{\alpha,9} &= \mathcal{M}_{\alpha,34} + \mathcal{M}_{\alpha,43} .\end{aligned} \tag{8.7}$$

This would have been difficult to guess in advance. The remaining sections of this paper investigate the patterns of the 4×9 double Mueller matrix $\mathcal{M}_{\alpha\Lambda}$, based on known patterns of $\mathcal{M}_{\alpha\beta\gamma}$ under various simplifying assumptions.

IX. ACTIVATING MECHANISMS FOR THE DOUBLE MUELLER ELEMENTS

The detailed calculation of $\mathcal{M}$ using Kramers-Heisenberg approximation and dipole approximation results in formulas that are given in Appendix D. Under these approximations, the exact nontensor susceptibility $Q_{i,jk}$ becomes a true tensor, namely, the usual second-order susceptibility $\chi_{l,jk}^{(2)}$. We mean that $\chi_{l,jk}^{(2)}$ is the susceptibility of an individual scatterer in a given uniform dielectric environment, not significantly perturbed by other scatterers of the same kind. Thus it holds for low-pressure vapors and dilute solutes. In such a "sparse fluid," the nonlinear scatterer rotates over all orientations with equal probability and the tensor rotation formula is

$$\chi_{ijk}^{(2)} = R_{iI}(\Omega) R_{jJ}(\Omega) R_{kK}(\Omega) \chi_{IJK}^{(2)} \tag{9.1}$$

where $R_{iI}(\Omega)$ is the 3×3 rotation matrix that rotates one uppercase index through Euler angles Ω to lowercase. After performing the operations specified by our major result 7.8, and then taking the orientation average, the result is

$$\begin{aligned}\langle \mathcal{M}^{(\text{dipole, sparse fluid})} \rangle_{\text{orientation}} \\ = \begin{bmatrix} A & B & C & \sqrt{3}C & 0 & 0 & 0 & 0 & l \\ X & D & E & \sqrt{3}E & 0 & 0 & 0 & 0 & m \\ 0 & 0 & 0 & 0 & F & F & n & n & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & G & -G & 0 \end{bmatrix} ,\end{aligned} \tag{9.2}$$

where $X = \sqrt{\frac{3}{2}} B - \sqrt{\frac{1}{2}} E$ and where $A, \ldots, G$ and l, m, n are given in Appendix D in terms of molecular quantities, namely, scalar products of $\chi^{(2)}$ with itself. The θ dependence is simple, and is given explicitly in Appendix D.

The numerous redundancies and zeroes of matrix (9.2) explain why the theory of $\chi^{(2)}$ effects has been able to get along so far without a super Mueller formalism. But all the simple relations within matrix (9.2) will fail whenever the dipole and Kramers-Heisenberg approximations fail, and some of its hitherto unrecognized elements will become important.

The seven observables $A-G$ come from the real part of $\chi^{(2)}$. These observables were enumerated a number of years ago by Bersohn, Pao, and Frisch [20], who gave formulas for certain linear combinations of them.

The three observables l, m, n involve the imaginary part of $\chi^{(2)}$ and have not been previously treated. They may be especially interesting, as they may distinguish between resonant and nonresonant scattering on the basis of polarization. In linear scattering, no such polarization-based criterion for resonance exists.

The remaining 20 vanished elements will take nonzero values if we go beyond the dipole and Kramers-Heisenberg approximations, and none has ever been previously studied. Everything we say below will assume that the sample is an isotropic suspension of arbitrary particles, i.e., that the unweighted average over all orientations obtains. This assumption helps us to characterize several distinctly different subsets among the 20 vanished elements of Eq. (9.2).

By combining the known characteristics of $\mathcal{M}_{\alpha,\beta\gamma}$ with the formulas (8.7), which show how to construct $\mathcal{M}_{\alpha\Lambda}$ from $\mathcal{M}_{\alpha,\beta\gamma}$, we can deduce a number of characteristics of $\mathcal{M}_{\alpha\Lambda}$.

In Ref. [8] we stated the following result as Theorem 1: If the scatterer is achiral, if n_3 is the number of occurrences of Stokes parameter 3 among the indices $\{\alpha,\beta,\gamma\}$, if n_4 is the same for 4, and if n_3+n_4 is odd,

then $\mathcal{M}^{(3\leftarrow 1+2)}_{\alpha,\beta\gamma}$ vanishes on orientation averaging.

Applying this in the formulas (8.7), we find that Theorem 1 implies the following pattern of zeros when the incident photons are identical:

$$\langle \mathcal{M}^{(\text{achiral})} \rangle_{\text{orientation}} = \begin{bmatrix} \cdot & \cdot & \cdot & \cdot & 0 & 0 & 0 & 0 & \cdot \\ \cdot & \cdot & \cdot & \cdot & 0 & 0 & 0 & 0 & \cdot \\ 0 & 0 & 0 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ 0 & 0 & 0 & 0 & \cdot & \cdot & \cdot & \cdot & 0 \end{bmatrix} . \tag{9.3}$$

It is interesting and gratifying that in the nine construction formulas (8.7), the chiral and achiral elements are never mixed.

Theorem 2 of Ref. [8] may be used similarly. It states the following.

If the Green's operators are real, if all relevant molecular states may be taken real, if n_3 is the number of occurrences of Stokes parameter 3 among the indices $\{\alpha,\beta,\gamma\}$, and if n_3 is odd, then $\mathcal{M}^{(3\leftarrow 1+2)}_{\alpha,\beta\gamma}$ vanishes on orientation averaging.

For identical incident photons, the zeros that result from this theorem fall as follows:

$$\langle \mathcal{M}^{(\text{real Green's operators, real states})} \rangle_{\text{orientation}} = \begin{bmatrix} \cdot & \cdot & \cdot & \cdot & 0 & 0 & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & 0 & 0 & \cdot & \cdot & 0 \\ 0 & 0 & 0 & 0 & \cdot & \cdot & 0 & 0 & \cdot \\ \cdot & \cdot & \cdot & \cdot & 0 & 0 & \cdot & \cdot & 0 \end{bmatrix} . \tag{9.4}$$

Again, formulas (8.7) do not mix vanishing with nonvanishing elements. These zeros show the positions of the extra multipole elements; the zero values will persist no matter how far the multipole expansion may be carried, as long as the Green's operators and the molecular eigenstate are pure real.

It is very instructive to look at a matrix which combines the information in these two patterns with that in (9.2). We let *D* characterize an element that is activated by the real part of the dipole susceptibility, *A* (for absorption) by the imaginary part of the dipole susceptibility; *H* by handedness; and *E* by any of the extramultipole mechanisms, namely, (1) anisotropic orientational distribution of the particles, (2) absorption, (3) retarded dipole-dipole interactions, and/or (4) constant magnetic field. The following interesting pattern then emerges:

$$\langle \mathcal{M} \rangle_{\text{orientation}} = \begin{bmatrix} D & D & D & D & HE & HE & H & H & AE \\ D & D & D & D & HE & HE & H & H & AE \\ HE & HE & HE & HE & D & D & AE & AE & H \\ H & H & H & H & E & E & D & D & HE \end{bmatrix} . \tag{9.5}$$

The symbol *HE* means that the element will vanish if there is no handedness and will vanish if there is no extramultipole effect. Therefore, they require both handedness and an extramultipole mechanism. Our experience with linear scattering is that *HE* elements are small and difficult to observe. The single *E* elements, in contrast, are large in linear scattering for particles of wavelength size, but disappear in small molecules like the fifth power of diameter/wavelength [6(c)]. Single *H* elements are never large, but they have certainly been observed in linear scattering; they give Raman circular dichroism [21]. There is no linear analog of the *AE* elements. The *A* does not indicate a vanishing, but rather in an appearance (with absorption). Therefore *AE* elements appear if there is absorption *or* an extramultipole effect, whereas *HE* elements need both handedness *and* an extramultipole effect.

Pattern (9.5) was derived in Ref. [8] using only the $\mathbf{A}\cdot\mathbf{p}$ term in the interaction of radiation and matter; but as always, the same polarization dependence holds when the $\mathbf{A}\cdot\mathbf{A}$ term is included. We have discovered a most remarkable general proof of this assertion, which, however, is too long for the space left on this page.

X. CONCLUSION

In this paper, we have constructed a generalization of the Stokes parameters which describes completely the polarization properties of two simultaneous identical photons. When two identical incoming photons are simultaneously transformed into one outgoing photon a 4×9 matrix relates the nine incoming double Stokes parameters to the four outgoing Stokes parameters. In anisotropic systems we have examined the behavior of this matrix under inversion and near resonance, and we have examined the effects of orientation averaging, which reveals the existence of "extra multipole" effects. These results give new insights into the nonlinear response of chiral systems, systems near resonance, and systems near wavelength size.

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APPENDIX A

Here we investigate the algebraic properties of the nine two-photon absorptivity parameters and their collapse to old, well-known results in the case of absorbers small compared to wavelength. Taking z as the propagation axis and expanding (3.1) we have

$$\dot{N}^{(\uparrow)}_{\text{2-photon}} \propto \langle |E_x^2 T_{xx} + E_x E_y (T_{xy} + T_{yx}) + E_y^2 T_{yy}|^2 \rangle . \tag{A1}$$

Letting

$$\{T_{xx}, (T_{xy}+T_{yx}), T_{yy}\} = \{r_1 \exp[i\varphi_1], r_2 \exp[i\varphi_2], r_3 \exp[i\varphi_3]\} , \tag{A2}$$

we write the nine molecular two-photon absorptivities

D_Λ of (3.3) in terms of the six r,ϕ symbols, finding

$$\begin{bmatrix} D_1 \\ D_2 \\ D_3 \\ D_4 \\ D_5 \\ D_6 \\ D_7 \\ D_8 \\ D_9 \end{bmatrix} = \begin{bmatrix} \sqrt{\frac{2}{3}}(r_1^2+r_2^2+r_3^2) \\ \sqrt{\frac{1}{3}}(r_1^2+r_2^2-2r_3^2) \\ (r_1^2-r_2^2) \\ 2r_1r_2\cos[\varphi_{12}] \\ 2r_2r_3\cos[\varphi_{23}] \\ 2r_3r_1\cos[\varphi_{13}] \\ 2r_2r_3\sin[\varphi_{23}] \\ 2r_3r_1\sin[\varphi_{13}] \\ 2r_1r_2\sin[\varphi_{12}] \end{bmatrix} , \tag{A3}$$

where $\varphi_{12}=\varphi_1-\varphi_2$, etc. These nine equations contain six r,ϕ symbols, which, upon elimination, leave three relations among the D symbols. They are

$$(\sqrt{2}D_1+D_2)^2=3(D_3^2+D_4^2+D_9^2) , \tag{A4a}$$

$$D_1^2-\sqrt{2}D_1D_2-2D_2^2=\tfrac{3}{2}(D_5^2+D_6^2+D_7^2+D_8^2) , \tag{A4b}$$

$$D_1^2-\sqrt{6}D_1D_3+2\sqrt{3}D_2D_3 =\tfrac{3}{2}(D_5^2-D_6^2+D_7^2-D_8^2) . \tag{A4c}$$

These relations hold for a single molecule in a given position. However, upon taking the ensemble average, all nine D's become independent pieces of information.

We now take the ensemble average for small molecules, in which case the two-photon absorptivity rotates like a tensor. In this case

$$\langle T_{IJ}T_{KL}^* \rangle_{\text{ensemble}}=T_{ij}T_{kl}^*\langle R_{iI}R_{jJ}R_{kK}R_{lL} \rangle_{\text{orientation}} , \tag{A5}$$

where **R** is the Euler rotation matrix, an explicit function of the Euler orientation angles. We now substitute the 4-**R** orientation average formula [22]

$$\langle R_{iI}R_{jJ}R_{kK}R_{lL} \rangle_{\text{orientation}} = \tfrac{1}{30}(\delta_{ij}\delta_{kl},\delta_{ik}\delta_{jl},\delta_{il}\delta_{jk}) \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \times \begin{bmatrix} \delta_{IJ} & \delta_{KL} \\ \delta_{IK} & \delta_{JL} \\ \delta_{IL} & \delta_{JK} \end{bmatrix} , \tag{A6}$$

where the δ's are Kronecker delta symbols. This is valid only if the molecule is small compared to wavelength, and the dipole approximation is made. Now combining (3.2), (3.3), (A5), and (A6) and performing the summations that involve Kronecker delta symbols, we find

$$\dot{N}_{\text{2-photon}}^{(\uparrow)} \propto \frac{S_\Lambda}{60}(C_{\Lambda,iijj},C_{\Lambda,ijij},C_{\Lambda,ijji}) \times \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \begin{bmatrix} T_{II}T_{JJ}^* \\ T_{IJ}T_{IJ}^* \\ T_{IJ}^*T_{JI}^* \end{bmatrix} . \tag{A7}$$

There is a more or less standard notation for the three elements of the column vector on the right. They are known [14] as $(\delta_F\delta_G\delta_H)$, a particularly simple way of writing the three rotational invariants of the two-photon absorptivity tensor. Here the letter δ has nothing to do with the Kronecker delta symbol; it was chosen for its proximity in the Greek alphabet to the one-photon molar absorptivity ε. Carrying out the sum over Λ, we write the two-photon absorption rate for small molecules in a familiar form

$$\dot{N}_{\text{2-photon}}^{(\uparrow)}=\tfrac{1}{30}(p_1,p_2,p_3) \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \begin{bmatrix} \delta_F \\ \delta_G \\ \delta_H \end{bmatrix} , \tag{A8}$$

where the δ's characterize the absorbing ensemble of molecules and the p's are polarization parameters that characterize the light. This formula does not depend on any special property of the light. But we may use the formulas implicit in (A7) to trace the p parameters back to double Stokes parameters, and (if the light is pure polarized and coherent) thence back to Stokes parameters, and finally thence to the normalized, complex polarization vector $\boldsymbol{\lambda}$ of the incident light. The final relation is

$$(p_1,p_2,p_3)=(|\boldsymbol{\lambda}\cdot\boldsymbol{\lambda}|^2,1,1) . \tag{A9}$$

Entries 2 and 3 of the **p** vector are identical, and it is also true that for identical photons, entries 2 and 3 of the molecular vector are identical ($\delta_G=\delta_H$). Therefore, (A8) collapses to an even smaller formula

$$\dot{N}_{\text{2-photon}}^{(\uparrow)}=\tfrac{1}{15}(|\boldsymbol{\lambda}\cdot\boldsymbol{\lambda}|^2,1) \begin{bmatrix} 2 & -1 \\ -1 & 3 \end{bmatrix} \begin{bmatrix} \delta_F \\ \delta_G \end{bmatrix} . \tag{A10}$$

Now $|\boldsymbol{\lambda}\cdot\boldsymbol{\lambda}|^2$ is 1 for all linear polarizations and 0 for both circular polarizations, and we find

$$\begin{bmatrix} \dot{N}(\text{linear}) \\ \dot{N}(\text{circular}) \end{bmatrix} \propto \begin{bmatrix} 1 & 2 \\ -1 & 3 \end{bmatrix} \begin{bmatrix} \delta_F \\ \delta_G \end{bmatrix} , \tag{A11}$$

in exact agreement with old results [14].

APPENDIX B

The linear Stokes parameters for nine polarization cases, as calculated by substituting (4.2) into (2.17), are

$$\begin{bmatrix} \mathbf{s}^{(H)} \\ \mathbf{s}^{(V)} \\ \mathbf{s}^{(D+)} \\ \mathbf{s}^{(D-)} \\ \mathbf{s}^{(L)} \\ \mathbf{s}^{(R)} \\ \mathbf{s}^{(QL)} \\ \mathbf{s}^{(E1)} \\ \mathbf{s}^{(E2)} \end{bmatrix} = \langle |E|^2 \rangle_{\text{time}} \begin{bmatrix} \mathbf{s}(0,0) \\ \mathbf{s}\left[0,-\pi/2\right] \\ \mathbf{s}\left[0,\pi/4\right] \\ \mathbf{s}\left[0,-\pi/4\right] \\ \mathbf{s}\left[\pi/4,0\right] \\ \mathbf{s}\left[-\pi/4,0\right] \\ s\left[0,-\pi/8\right] \\ \mathbf{s}\left[-\pi/8,\pi/4\right] \\ \mathbf{s}\left[\pi/8,-\pi/2\right] \end{bmatrix} = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 1 & 0 & -1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & -1 \\ 1 & \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} & 0 \\ 1 & 0 & \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} \\ 1 & -\sqrt{\frac{1}{2}} & 0 & \sqrt{\frac{1}{2}} \end{bmatrix}. \tag{B1}$$

These nine points are picked for their symmetric disposition on the Poincaré sphere. The first six cases (the usual basis cases for linear Stokes work) lie at the apices of an octahedron oriented on the two poles (R and L), with four cases equally spaced around the equator (H, D^+, V, D^-). To these we have added three cases that lie symmetrically with respect to the first six on the surface of the Poincaré sphere. Polarization QL is an oblique linear polarization halfway between V and D^- (22.5° from each); E_1 is an elliptical polarization halfway between H and R; E_2 is an elliptical polarization halfway between D^+ and L. All nine cases are shown on the Poincaré sphere in Fig. 2.

The corresponding double Stokes parameters, as calculated by substituting (4.2) into (2.32), are

$$\begin{bmatrix} \mathbf{S}^{(H)} \\ \mathbf{S}^{(V)} \\ \mathbf{S}^{(D^+)} \\ \mathbf{S}^{(D^-)} \\ \mathbf{S}^{(L)} \\ \mathbf{S}^{(R)} \\ \mathbf{S}^{(QL)} \\ \mathbf{S}^{(E1)} \\ \mathbf{S}^{(E2)} \end{bmatrix} = \langle |E|^4 \rangle_{\text{time}} \begin{bmatrix} \sqrt{\frac{2}{3}} & 1 & \sqrt{\frac{2}{3}} & 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{\frac{2}{3}} & -1 & \sqrt{\frac{2}{3}} & 0 & 0 & 0 & 0 & 0 & 0 \\ \sqrt{\frac{2}{3}} & 0 & -\sqrt{\frac{1}{12}} & \frac{1}{2} & \sqrt{\frac{1}{2}} & 0 & \sqrt{\frac{1}{2}} & 0 & 0 \\ \sqrt{\frac{2}{3}} & 0 & -\sqrt{\frac{1}{12}} & \frac{1}{2} & -\sqrt{\frac{1}{2}} & 0 & -\sqrt{\frac{1}{2}} & 0 & 0 \\ \sqrt{\frac{2}{3}} & 0 & -\sqrt{\frac{1}{12}} & -\frac{1}{2} & 0 & \sqrt{\frac{1}{2}} & 0 & -\sqrt{\frac{1}{2}} & 0 \\ \sqrt{\frac{2}{3}} & 0 & -\sqrt{\frac{1}{12}} & -\frac{1}{2} & 0 & -\sqrt{\frac{1}{2}} & 0 & \sqrt{\frac{1}{2}} & 0 \\ \sqrt{\frac{2}{3}} & \sqrt{\frac{1}{2}} & \sqrt{\frac{1}{48}} & \frac{1}{4} & -\frac{1}{2}a & 0 & -\frac{1}{2}b & 0 & 0 \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{48}} & -\frac{1}{4} & 0 & \frac{1}{2}b & 0 & -\frac{1}{2}a & 0 \\ \sqrt{\frac{2}{3}} & 0 & -\sqrt{\frac{1}{12}} & 0 & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \end{bmatrix}, \tag{B2}$$

where $a = 1+\sqrt{\frac{1}{2}}$ and $b = 1-\sqrt{\frac{1}{2}}$. This matrix is invertable; therefore these polarizations cases form a *complete* set, in the sense that no other polarization case can give linearly independent information. This may or may not be an optimum set to use experimentally.

APPENDIX C

Here we present the details of passage from Eq. (5.1) to Eq. (5.2), followed by a demonstration that the nine retarder plate angle pairs of Appendix B may be used with

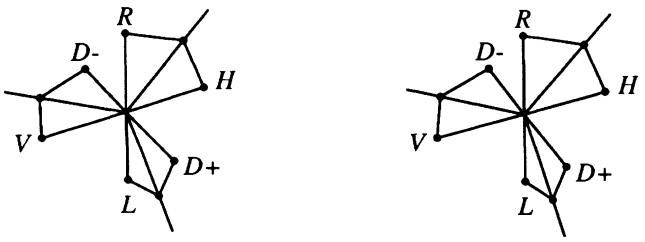

FIG. 2. A stereo pair showing the nine Poincaré points that represent the polarization cases of Eq. (B1). These points make a complete polarization study for two-in, one-out processes with identical incoming photons. All nine points lie on the surface of a Poincaré sphere of unit radius.

the apparatus of Fig. 1 to measure the double Stokes parameter of any light beam, including depolarized incoherent beams. If the double Stokes parameters of such a beam are measured by this method, they may be used in (7.7) to predict the Stokes parameters of the scattered light of a two-in, one-out process. The Jones matrices **H** and **Q** of (5.1) are given by [11]

$$\mathbf{H}(\theta)=i\begin{bmatrix}\cos(2\theta) & \sin(2\theta)\\ \sin(2\theta) & -\cos(2\theta)\end{bmatrix}, \tag{C1}$$

$$\mathbf{Q}(\theta)=\frac{1}{\sqrt{2}}\begin{bmatrix}1+i\cos(2\theta) & i\sin(2\theta)\\ i\sin(2\theta) & 1-i\cos(2\theta)\end{bmatrix}, \tag{C2}$$

while for **P**, a polarizer passing polarization vector $\boldsymbol{\lambda}$, the formula is in general

$$\mathbf{P}=\begin{bmatrix}\lambda_x\\ \lambda_y\end{bmatrix}[\lambda_x^* \quad \lambda_y^*]=\begin{bmatrix}\lambda_x\lambda_x^* & \lambda_x\lambda_y^*\\ \lambda_y\lambda_x^* & \lambda_y\lambda_y^*\end{bmatrix}, \tag{C3}$$

Thus apparatus takes incident vector **E** and turns it into **E′** according to

$$E_i'=I\lambda_i\lambda_j^*Q_{jk}H_{kl}E_l\ , \tag{C4}$$

where I is an intensification factor due to focusing. We now define an "apparatus vector" **A** given by

$$A_l(\omega,\gamma)=\lambda_j^*Q_{jk}\left[\frac{3\pi}{4}-\omega\right]H_{kl}\left[\frac{\gamma}{2}-\frac{\omega}{2}-\frac{\pi}{8}\right]. \tag{C5}$$

The shortest formulas we have found result from the use of a diagonal linear polarizer, i.e., from

$$\boldsymbol{\lambda}=\{1,1\}/\sqrt{2} \tag{C6}$$

in which case the apparatus vector becomes

$$\begin{bmatrix}A_x\\ A_y\end{bmatrix}=\begin{bmatrix}\sin(\gamma+\omega)+i\sin(\gamma-\omega)\\ -\cos(\gamma+\omega)-i\cos(\gamma-\omega)\end{bmatrix}. \tag{C7}$$

In terms of the apparatus vector, the amplitude for two-photon absorption is

$$\mathcal{A}=T_{im}E_i'E_m'=I^2(T_{im}\lambda_i\lambda_m)(A_iA_nE_lE_n)\ , \tag{C8}$$

where **T** is the two-photon absorption tensor of the molecules at the focus. From here, the even rate becomes

$$\dot{\mathcal{N}}(\omega,\gamma)=\eta|\mathcal{A}|^2=\eta I^4\langle|T_{im}\lambda_i\lambda_m|^2\rangle_{\text{ensemble}}\times(A_lA_nA_p^*A_q^*)\langle E_lE_nE_p^*E_q^*\rangle_{\text{time}}\ , \tag{C9}$$

where η is a detection efficiency. Quantities η, I, and the absolute-two-photon absorptivity tensor **T** will usually be unknown; therefore we absorb everything unknown into η. Now trading the four factors of E for an S by (2.32), we find the result promised in (5.2) of the main text:

$$\dot{\mathcal{N}}(\omega,\gamma)=\eta(A_lA_nA_p^*A_q^*C^*_{\Lambda,lnpq})S_\Lambda\ , \tag{C10}$$

where the parenthesis is $[b(\omega,\gamma)]_\Lambda$ of (5.2). Using (2.33) and (C7), this can be evaluated explicitly for the apparatus of Fig. 1. Writing **b** as a column vector, it is symbolically

$$\mathbf{b}(\omega,\gamma)=\begin{bmatrix}\sqrt{\frac{2}{3}}\\ \frac{\sqrt{3}}{48}\{-2+6\cos[4\gamma]+3\cos[4(\gamma-\omega)]+6\cos[4\omega]+3\cos[4(\gamma+\omega)]\}\\ -\frac{1}{2}\{\cos[2(\gamma-\omega)]+\cos[2(\gamma+\omega)]\}\\ \frac{1}{16}\{-2-2\cos[4\gamma]-\cos[4(\gamma-\omega)]+6\cos[4\omega]-\cos[4(\gamma+\omega)]\}\\ -\frac{\sqrt{2}}{16}\{2\sin[4\gamma]+\sin[4(\gamma-\omega)]+4\sin[2(\gamma-\omega)]+4\sin[2(\gamma+\omega)]+\sin[4(\gamma+\omega)]\}\\ \frac{\sqrt{2}}{16}\{2\sin[4\gamma]+\sin[4(\gamma-\omega)]-4\sin[2(\gamma-\omega)]-4\sin[2(\gamma+\omega)]+\sin[4(\gamma+\omega)]\}\\ \frac{\sqrt{2}}{8}\{-\sin[2\gamma-4\omega]+4\sin[2\omega]+\sin[2\gamma+4\omega]\}\\ \frac{\sqrt{2}}{8}\{-\sin[2\gamma-4\omega]-4\sin[2\omega]+\sin[2\gamma+4\omega]\}\\ \frac{1}{4}\{\cos[2\gamma-4\omega]-\cos[2\gamma+4\omega]\}\end{bmatrix}. \tag{C11}$$

Now we perform nine experiments using the nine (ω,γ) pairs of Eq. (B1), and write the nine vectors **b** as rows of matrix

B of (5.3). Numerically, it is

$$\mathbf{B}=\begin{bmatrix} 0.82 & 0.58 & -1.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.82 & 0.58 & 1.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\ 0.82 & -0.29 & 0.00 & 0.50 & -0.71 & -0.71 & 0.00 & 0.00 & 0.00 \\ 0.82 & -0.29 & 0.00 & 0.50 & 0.71 & 0.71 & 0.00 & 0.00 & 0.00 \\ 0.82 & -0.29 & 0.00 & -0.50 & 0.00 & 0.00 & 0.71 & -0.71 & 0.00 \\ 0.82 & -0.29 & 0.00 & -0.50 & 0.00 & 0.00 & -0.71 & 0.71 & 0.00 \\ 0.82 & 0.14 & -0.71 & 0.25 & 0.85 & 0.15 & 0.00 & 0.00 & 0.00 \\ 0.82 & -0.29 & 0.00 & 0.00 & -0.50 & -0.50 & -0.50 & 0.50 & -0.50 \\ 0.82 & 0.14 & 0.71 & -0.25 & 0.00 & 0.00 & 0.15 & -0.85 & 0.00 \end{bmatrix} . \tag{C12}$$

For exact values, use the replacements $0.82\rightarrow\sqrt{2/3}$, $0.58\rightarrow 1/\sqrt{3}$, $0.29\rightarrow 1/\sqrt{12}$, $0.14\rightarrow 1/\sqrt{48}$, $0.71\rightarrow 1/\sqrt{2}$, $0.85\rightarrow(2+\sqrt{2})/4$, $0.15\rightarrow(2-\sqrt{2})/4$, $0.50\rightarrow 1/2$, $0.25\rightarrow 1/4$, and $0.00\rightarrow 0$. Matrix **B** has an inverse, and singular value decomposition shows that it is not close to a singularity. Thus the nine double Stokes parameters are provided by (5.4) of the main text.

APPENDIX D

The quantities presented are symbols used in the double Mueller matrix, Eq. (9.2). These symbols are valid for isotropic suspensions of molecules of any shape, if the molecules are small compared to a wavelength:

$$\begin{aligned} A &= \sqrt{\tfrac{3}{8}}[6a+2c+(3b+3d-2e')(1+\cos^2\theta)] , \\ B &= -4(b+d+e')\sin^2\theta , \\ C &= \sqrt{\tfrac{16}{3}}[c+e'(1+\cos^2\theta)] , \\ D &= 4(b+d+e')(1+\cos^2\theta) , \\ E &= -\sqrt{\tfrac{16}{3}}e'\sin^2\theta , \\ F &= 4\sqrt{2}(b+d+e')\cos\theta , \\ G &= 4\sqrt{2}(-b+d)\cos\theta , \\ l &= -4e''\sin^2\theta , \\ m &= 4e''(1+\cos^2\theta) , \\ n &= -4\sqrt{2}e''\cos\theta , \end{aligned} \tag{D1}$$

where θ is the scattering angle and

$$\begin{bmatrix} a \\ b \\ c \\ d \\ e' \end{bmatrix} = \begin{bmatrix} 8 & -6 & -5 & 11 & -6 \\ -6 & 1 & 2 & -3 & 8 \\ -20 & 8 & 16 & -10 & 8 \\ -6 & 8 & 2 & -3 & 1 \\ 15 & -6 & -5 & 4 & -6 \end{bmatrix} \begin{bmatrix} \beta'_1 \\ \beta'_2 \\ \beta'_3 \\ \beta'_4 \\ \beta'_5 \end{bmatrix} , \tag{D2}$$

$$e''=7\beta''_1 , \tag{D3}$$

$$\begin{bmatrix} \beta'_1 \\ \beta'_2 \\ \beta'_3 \\ \beta'_4 \\ \beta'_5 \end{bmatrix} = (\chi'^{(2,\mathrm{sym})}_{IJK}\chi'^{(2,\mathrm{sym})}_{LMN} + \chi''^{(2,\mathrm{sym})}_{IJK}\chi''^{(2,\mathrm{sym})}_{LMN}) \begin{bmatrix} \delta_{IJ}\delta_{KL}\delta_{MN} \\ \delta_{IJ}\delta_{KM}\delta_{LN} \\ \delta_{IL}\delta_{JK}\delta_{MN} \\ \delta_{IL}\delta_{JM}\delta_{KN} \\ \delta_{IM}\delta_{JL}\delta_{KN} \end{bmatrix} , \tag{D4}$$

$$\beta''_1=(\chi''^{(2,\mathrm{sym})}_{IJK}\chi'^{(2,\mathrm{sym})}_{LMN} - \chi'^{(2,\mathrm{sym})}_{IJK}\chi''^{(2,\mathrm{sym})}_{LMN})\delta_{IJ}\delta_{KL}\delta_{MN} ; \tag{D5}$$

and

$$\chi'^{(2,\mathrm{sym})}_{IJK}=\mathrm{Re}[\chi^{(2,\mathrm{sym})}_{IJK}] , \quad \chi''^{(2,\mathrm{sym})}_{IJK}=\mathrm{Im}[\chi^{(2,\mathrm{sym})}_{IJK}] , \tag{D6}$$

$$\chi^{(2,\mathrm{sym})}_{IJK}\equiv\tfrac{1}{2}(\chi^{(2)}_{IJK}+\chi^{(2)}_{IJK}) . \tag{D7}$$

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