

Article

# Irreducible Cartesian Tensor Analysis of Harmonic Scattering from Chiral Fluids

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**Abstract:** Symmetry principles of several distinct kinds are revealingly engaged in an analysis focussing on third harmonic scattering, a current focus of research on nonlinear optics in chiral media. Analysis in terms of irreducible Cartesian tensors elucidates the detailed electrodynamical origin and character of the corresponding material properties. Considerations of fundamental charge, parity and time reversal (CPT) symmetry reveal the conditions for an interplay of transition multipoles to elicit a chiral response using circularly polarised pump radiation, and the symmetry of quantised angular momentum underpins the associated selection rules and angular distribution. The intrinsic structural symmetry of chiral scatterers determines their capacity to exhibit differential response. Exploiting permutational index symmetry in the response tensors enables quantitative assessment of the boundary values for experimentally measurable properties, including circular intensity differentials.

**Keywords:** irreducible tensors; angular momentum; multipole expansion; CPT symmetry; conservation laws; ergodic theorem; rotational averages; optical nonlinearity; optical harmonics; scattering

## 1. Introduction

Third harmonic scattering (THS) is an optical process by means of which monochromatic laser light undergoes frequency conversion, producing an output with three times the optical frequency of the input, and accordingly one third of the input wavelength. The efficiency of the conversion varies with the cube of the input intensity, and as such requires intense light for its observation. Unlike the much stronger third harmonic generation (THG) that commonly accompanies this process and is observable in the forward beam direction, the THS process is incoherent, distributing the third harmonic output across a full range of angular deflections, with an angle-dependent intensity. Third harmonic scattering can occur in individual molecules or nanoparticles, often in regular liquids or suspensions. Although the prospect and character of a THS effect were established relatively early in the development of laser science [1,2], the topic has recently acquired new interest [3,4], as the requisite high intensities have now become routinely available in commercial systems. Symmetry principles of several entirely distinct kinds are involved in the mechanism and selection rules for all forms of optical nonlinearity [5,6], and they come powerfully into play in optical frequency conversion. These principles concern both the properties of the input light (known as the pump) and the medium in which conversion to the harmonic takes place. In the case of THS, additional symmetry aspects are elicited when the scattering medium is chiral. To understand the route to those features, and to ascertain the interplay of parameters that determine the experimental observables, the operation of symmetry principles in the general sphere of harmonic conversion should first be appreciated.

## 2. Harmonic Frequency Conversion

The process by means of which laser light undergoes instantaneous conversion to a multiple of its optical frequency  $\omega$  is identifiable in two distinguishable forms: as harmonic generation or

harmonic scattering. No excitation of the medium is involved. At the level of individual photons, the fundamental process in each case engages the cooperative annihilation of an integer number  $n$  of input photons, coupled to photon emission at frequency  $n\omega$ . One immediately significant distinction that can be drawn between the very different characters of harmonic production is that harmonic generation propagates onwards in the “forward” direction, similar to the direction of the pump, whereas harmonic emission is widely distributed over other angles.

In *harmonic generation*, the emission can be strong and as laser-like as the input (the pump). The reason is that the quantum amplitudes for conversion events at different sites within the conversion medium add coherently, which is made possible by the radiation field as a whole conserving energy, linear momentum and angular momentum. Such processes are termed *optically parametric*. As an obvious corollary of Noether’s theorem [7], the same three properties are conserved by the material, due to the isotropy of space and the invariance of the system as a whole to translation in space or time. The conservation of energy in each component, radiation field and matter, identifies the harmonic process as elastic. The conservation of linear momentum requires wave-vector matching to minimise  $\Delta\mathbf{k}$ , the difference between the harmonic output wave-vector and the sum of the pump inputs,  $|\Delta\mathbf{k}| \equiv |\mathbf{k}' - n\mathbf{k}|$ , strongly favouring emission in the forward direction—subject to small deviations to compensate any mismatch of the refractive indices at the input and output optical wavelengths. The distance over which coherence is sustained, and the harmonic signal is additive, is  $\sim |\Delta\mathbf{k}|^{-1} \gg \lambda'$ , where  $\lambda'$  is the wavelength of the emitted harmonic. Any circumstances that compromise the achievement of wave-vector matching blur the distinction between harmonic generation and scattering [8].

For coherent harmonic generation, the conservation of angular momentum by the radiation field is a condition that must be fulfilled by the axial components of photon spin in the input and output. Circularly polarised light is the only case where the axial angular momentum of each photon has a sharp value of  $\pm 1$  [9]. From this it emerges that for systems such as liquids or gases, for which isotropy applies over macroscopic distances  $\gg \lambda'$ , the symmetry of the full rotation group SO(3) applies, and harmonic generation is accordingly forbidden for circularly polarised input [10]. This is because the input photon spin angular momenta add to  $(\pm n)\hbar$ , as determined by the handedness, whereas the harmonic photon can convey away only one unit  $\hbar$ . Equally, if one considers any other state of input polarisation, necessarily expressible as a linear combination of states with  $+1$  and  $-1$  angular momentum (since the left and right circular polarisations constitute a complete basis set) it is clear that no combination of any even number of these states can lead to a sum of unity. The result is that the coherent generation of even optical harmonics is therefore forbidden in isotropic media, irrespective of pump polarisation. By other (isotropic tensor) methods, both conditions have also been proven to apply without constraint on any multipolar nature in the photon–matter interaction [11]. In non-isotropic media, such as solids of much lower symmetry than SO(3), harmonic generation with circularly polarized input is allowed and then follows rules governed by the residual degree of rotational symmetry—see for example reference [12] and references therein.

The other manifestation of optical frequency multiplication, the case of non-forward *harmonic scattering*, is again necessarily elastic—there being no transfer of energy to or from the medium—but linear and angular momentum are no longer conserved by the radiation or matter alone, only in the entire matter + radiation system. Each harmonic conversion event is therefore discrete, additivity applying to only the frequency conversion rates for the individual atoms, molecules, nanoparticles or unit cells—not their quantum amplitudes: in the ensemble average all cross-terms involving separate conversion sites vanish. In the study of molecules the scatterers are commonly randomly oriented. Regular gases and liquids are both suitable media, but to secure a decent measurable signal the latter is experimentally more viable; randomly oriented nanocrystals are also amenable to study (see references [3,4], for example).

The symmetry principles that now determine the selection rules are therefore those applicable to the constituents over a scale of distance, generally  $\ll \lambda'$ . Indeed, these rules apply to both

incoherent harmonic scattering and coherent harmonic generation. No further constraints emerge for the emission of harmonics of any *odd* order—essentially because the number of photons involved in each fundamentally complete frequency conversion event,  $(n + 1)$ , is an even number, and the corresponding nonlinear response tensor (the nonlinear susceptibility, see below) is universally allowed. However, the non-forward emission of *even* harmonics is only possible for non-centrosymmetric (and therefore potentially polar) materials. Amongst the significantly populated symmetry classes, such materials have to possess a structural symmetry belonging to one of these Schoenflies designations:  $S_4, C_{3h}, C_3, C_4, C_6, D_2, D_3, D_4, D_6, D_{3h}, D_{2d}, T, T_d, O$  and  $I$  [13]. This rule, clearly broken at any surface, underpins the use of second harmonic generation as a surface-specific probe [14]. Equally, if the rate of *any* order of harmonic scattering is to exhibit a differential response according to the handedness of the input radiation, the material cannot contain any elements of inversion, mirror, or rotation-reflection symmetry, reducing the list to simply the pure rotation groups  $C_3, C_4, C_6, D_2, D_3, D_4, D_6, T, O$  and  $I$ .

In the following sections these broad principles are specifically developed and applied in the analysis of third harmonic scattering, a current focus of research on nonlinear optics [15]. With striking chiroptical effects having recently been demonstrated in optical second harmonic scattering [16], the focus here, too, is on circularly polarised pump input, for which case important new symmetry rules are established for the specific case of chiral media. Notably, for liquid or randomly oriented media, for the reasons identified above, having a circularly polarised input obviates any possible competition from a process of coherent third harmonic generation followed by conventional scattering, a scenario recently explored by Shelton [17]. Pursuing the analysis in a formulation cast in terms of irreducible Cartesian tensors facilitates the elucidation of the detailed electrodynamical origin, also eliciting the character of the salient material properties. It is shown how considerations of fundamental charge, parity and time reversal (CPT) symmetry reveal the conditions for an interplay of transition multipoles to elicit a chiral response from a circularly polarised pump, and here again it is observed how the symmetry of quantised angular momentum underpins the associated selection rules and angular distribution. As already observed, the intrinsic structural symmetry of chiral media determines their capacity to exhibit differential response. It is also shown how exploiting permutational index symmetry in the response tensors enables quantitative prediction of experimentally prominent properties, including circular intensity differentials.

### 3. Formulation of Third Harmonic Scattering

In the traditional representation of nonlinear optics, the origin of the third harmonic signal that may be produced on irradiating a suitable material with highly intense laser light is cast in terms of a “nonlinear polarisation”  $P$  of the medium, oscillating at three times the input optical frequency. A scalar response might be simply written as:

$$P(3\omega) = \chi^{(3)}(-3\omega; \omega, \omega, \omega)E(\omega)^3 \quad (1)$$

where  $\chi^{(3)}$  is the relevant nonlinear optical susceptibility and  $E$  is the electric field of the input light with optical frequency  $\omega$ . In general, the harmonic field need not be collinear with the input field, and a more accurate form of the relation must engage directional dependence. Casting the input and the nonlinear polarisation as vector quantities, the nonlinear susceptibility is accordingly a fourth rank tensor, and we have:

$$\mathbf{P}(3\omega) = \boldsymbol{\chi}^{(3)}(-3\omega; \omega, \omega, \omega) \odot^3 (\mathbf{E}(\omega)\mathbf{E}(\omega)\mathbf{E}(\omega)) \quad (2)$$

where  $\odot^3$  denotes a tensor inner product. The nonlinear polarisation is strictly an inferred quantity; the true observable in the process is a scalar signal that may represent the conversion efficiency, or the rate of third harmonic production. In the case of incoherent harmonic emission, i.e., where third harmonic scattering, THS, occurs in anything other than the forward direction (which constitutes a very different, coherent case of third harmonic generation, THG) the observable emerges from the scalar product of  $P(3\omega)$  with its complex conjugate.

In the full quantum optical picture, where the input and output radiations are correctly represented in terms of photons, it is simpler and more appropriate to directly deal in terms of a scalar quantum amplitude, or *matrix element*,  $M_{fi}$ —the conventional subscripts denoting progress from an initial system state  $i$  to a final system state  $f$ . This matrix element essentially represents the entirety of the frequency conversion events in the form:

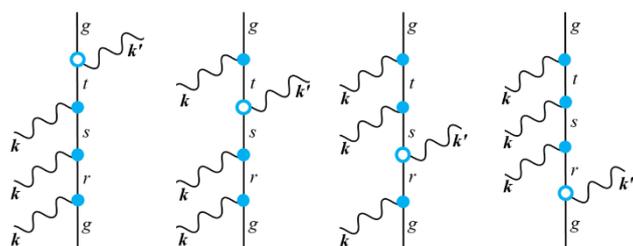
$$M_{fi} \sim \bar{\mathbf{E}}(3\omega) \odot \chi^{(3)}(-3\omega; \omega, \omega, \omega) \odot^3 (\mathbf{E}(\omega)\mathbf{E}(\omega)\mathbf{E}(\omega)) \quad (3)$$

where  $\mathbf{E}(3\omega)$  is the emitted harmonic field and the overbar denotes complex conjugate; the observable THS is related by simple factors to the modulus square of  $M_{fi}$ . It is then more appropriate—especially where distinct molecules or scatterers are involved—to cast the electromagnetic fields and material properties in terms of local fields and the microscopic measure of third harmonic propensity, the “second hyperpolarizability” tensor  $\gamma$ , as follows:

$$M_{fi} \sim \mathbf{E}' \odot \gamma \odot^3 \mathbf{E}^3 \sim \bar{e}'_i \gamma_{ijkl} e_j e_k e_l \quad (4)$$

where the optical fields now acquire the status of quantum operators for the relevant modes, and the second expression on the right is further simplified to an expression written in terms of the input and output polarization vectors  $e$  and  $e'$ , respectively, here adopting the Einstein convention of implied summation over repeated tensor indices—the latter representing components in 3D space. For simplicity, the output field is sufficiently denoted by the prime, and an overbar signifies a complex conjugate. Choosing any specific polarization state for the harmonic allows for determination of the signal detected through corresponding resolving optics.

In the above expressions, the microscopic nonlinear susceptibility (or hyperpolarizability) is formulated in terms of electric dipole (E1) interaction with each optical field—indeed by far the major part of nonlinear optics is based on this often implicit assumption. This accords with the simple appearance of the electric field operator for each of the four photons involved in each distinct frequency conversion interaction, which it will be convenient to represent as  $E1^4$ . The mathematical formulation of the tensor, which comprises four terms, is readily derivable from time-dependent perturbation theory by the use of the Feynman diagrams shown in Figure 1.



Photon interactions:  $\circ$  E1 harmonic emission,  $\vec{e}'$ ;  $\bullet$  E1 pump annihilation,  $e_j, e_k, e_l$

**Figure 1.** Feynman diagrams for the four distinct leading orders, each of which is fourth order in electric dipole (E1) coupling, i.e.,  $E1^4$ , which generate the full set of contributions to the third harmonic scattering (THS) tensor  $\gamma_{i(jkl)}$ . Time progresses upwards, the scatterer progressing from the ground electronic state  $g$  through the virtual intermediate states  $r, s, t$ , before resuming the ground state.

Notably, since the three input photons are identical, only the part of  $\gamma_{ijkl}$  that is symmetric with respect to the interchange of the corresponding three tensor indices can be manifest in THS observations. It is expedient to denote the correspondingly index-symmetric part of  $\gamma_{ijkl}$  as  $\gamma_{i(jkl)}$ , the subscript brackets encompassing the three indices with permutational symmetry. It is not assumed that this tensor has only real components; it is treated as a potentially complex quantity in order to accommodate any damping effects that arise under near-resonance conditions.

The general form of  $\gamma_{ijkl}$  as a fourth-rank tensor in 3D space, comprising in general  $3^4$  independent components, is reducible as a sum of individual tensors that individually transform under irreducible representations of the full rotation group SO(3) [18,19]. This is notwithstanding any axial degeneracies that may arise for scatterers of particular physical shape, such as  $x$ ,  $y$  degeneracy in a particle with a  $z$ -axis of threefold or higher rotational symmetry. Here, the irreducible parts of the susceptibility take the form of natural tensors (tensors whose angular momentum eigenvalues are identically equal to their rank  $J$ , each comprising  $(2J + 1)$  independent components) of order  $J \in \{0, \dots, 4\}$ , embedded in fourth-rank tensor space. Thus, we may write:

$$\gamma_{i(jkl)} = \sum_J \gamma_{i(jkl)}^{[J]} \quad (5)$$

Crucially, the decomposition of  $\gamma_{i(jkl)}$  comprises non-vanishing tensors of all permissible weights  $J$ , all but the highest of these being represented with a multiplicity  $Q_J > 1$ ; the decomposition arises from the outer coupling of four vectors. This reduction simplifies when the triple-index symmetry is introduced, according to the outer product of a vector with an index-symmetric third rank tensor. The number of independent components then reduces to  $\sum_J Q_J(2J + 1) = 30$ . Full details can be found in Appendix 4 of [13].

#### 4. CPT Symmetry and Multipole Interactions

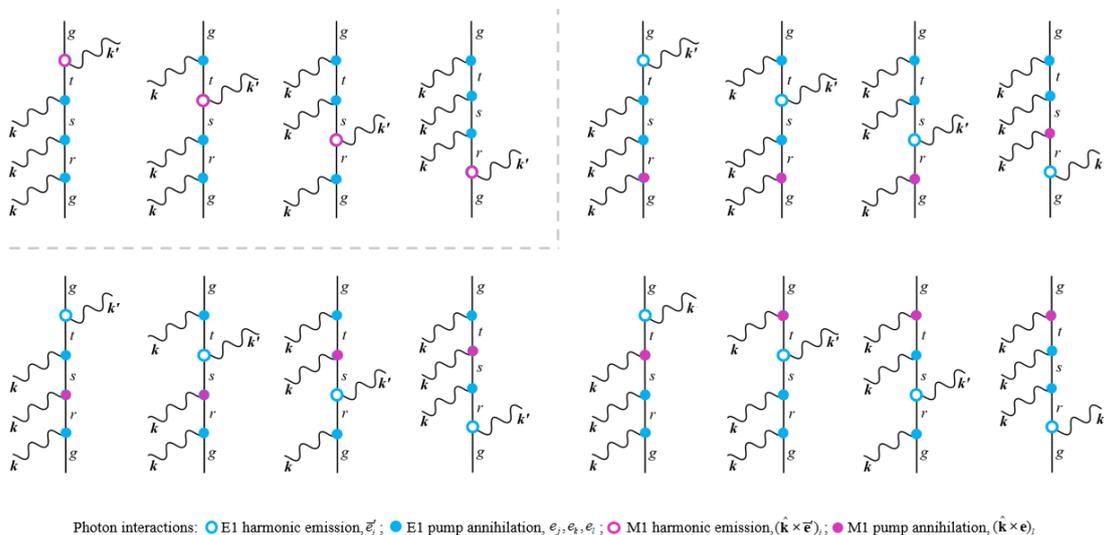
Before proceeding further, it will be helpful to record the signature properties of the susceptibility with respect to fundamental CPT symmetry (conjoining the operations of charge, parity and time inversion) [20,21]. This will prove especially valuable when later identifying the unique features of chiral behaviour. The entire realm of optics satisfies CPT symmetry. In all circumstances the  $E1^4$  third harmonic susceptibility is a tensor of even parity under each of these three operations, and hence under the product CPT. In practice, since replacing all charges with their antiparticle counterparts is of no practical relevance within this sphere of application—as discussed in a recent review—it will suffice here and below to focus exclusively on PT symmetry.

It is well known that in the multipolar representation of electrodynamics, which becomes exact when all terms in its rapidly converging series are accommodated [22], the leading  $E1$  coupling term is derivable as a highly accurate first approximation to the linear “ $p \cdot a$ ” term in the alternative “minimal coupling” form;  $p$  denotes momentum and  $a$  denotes the vector potential. At the next level of approximation to the minimal coupling, accommodating linear field gradients, the corresponding corrections to  $E1$  feature both  $M1$  (magnetic dipole) and  $E2$  (electric quadrupole) forms of interaction. While  $E1$  is odd in spatial parity  $P$ ,  $M1$  and  $E2$  are both even. Equally, while  $E1$  and  $E2$  are even with respect to time inversion,  $M1$  is odd. The latter difference plays into effects that involve electron spin, but it is the spatial parity differences that are crucial in connection with physical structures that are spatially chiral over sub-wavelength, nanoscale dimensions.

At any level of approximation—for any order of perturbation and any kind of multipole—it is clear that, as an energy operator, the interaction Hamiltonian must be even under both  $P$  and  $T$ . Therefore in each contribution to the quantum amplitude, the parity signatures of each type,  $P$  and  $T$ , have to be the same for both the field and the multipole with which it engages. For example in a magnetic dipole interaction term, the dipole is odd in time and even in space; exactly the same applies to the temporal and spatial parities of the magnetic field. To observe a symmetry-breaking chiral effect it is then evident that any observable must entail multipoles of opposite parity, connecting the same initial and final states—which is possible only in materials lacking a centre of symmetry. Again, the equivalent condition applies to the electromagnetic fields, being most clearly satisfied by changes of photon number in states of circular polarisation.

Returning to the specific case of third harmonic scattering, it will now be clear that spatially chirally differential effects can result from the quantum interference of the leading  $E1^4$  term with

any other contribution for which the material tensor has of opposite spatial parity. The two leading and quantitatively most significant terms are evidently of  $E1^3M1$  and  $E1^3E2$  form. The former are illustrated by the diagrams in Figure 2. Here, the magnetic dipole interaction can be associated with the single emitted photon, or with one of the three annihilated input photons. If a chirally sensitive response to the optical input is sought, as would most readily be revealed in a difference in the harmonic conversion rates for left- and right-handed circularly polarised pumps, then clearly only the latter is relevant for further discussion; one may assume the harmonic output is not resolved for polarisation. Here, the appropriately symmetrized tensor  $\gamma_{ij(kl)}^{(m)}$  (the superscript ( $m$ ) denoting the inclusion of a magnetic moment) comprises twelve terms. Their sum again reduces into irreducible tensors spanning all weights  $J = 0 \dots 4$ , though with greater multiplicity accounting for 54 ( $=3 \times 3 \times 6$ ) independent components. The analogous counterpart  $E1^3E2$  tensor with the quadrupole engaging the input is a rank 5 tensor  $\gamma_{i(jkl)m}^{(q)}$  with all weights  $J = 0 \dots 5$  present and 90 ( $=3 \times 10 \times 3$ ) independent components. Both the  $\gamma_{ij(kl)}^{(m)}$  and  $\gamma_{i(jkl)m}^{(q)}$  tensors are supported only by chiral molecules.



Photon interactions:  $\circ$  E1 harmonic emission,  $\vec{e}'_i$ ;  $\bullet$  E1 pump annihilation,  $e_j, e_k, e_l$ ;  $\circ$  M1 harmonic emission,  $(\hat{\mathbf{k}} \times \vec{e})_i$ ;  $\bullet$  M1 pump annihilation,  $(\hat{\mathbf{k}} \times \mathbf{e})_i$

**Figure 2.** Feynman diagrams for the sixteen distinct  $E1^3M1$ , contributions to THS. The four at top left, wherein the M1 (magnetic dipole) interaction is associated with the harmonic photon emission, does not (at this order of approximation) significantly contribute to effects that discriminate the handedness of a circularly polarised input. The remaining twelve terms, with two E1 and one M1 interactions with the pump, all contribute to the tensor  $\gamma_{ij(kl)}^{(m)}$ .

The form of the  $E1^3M1$  and  $E1^3E2$  contributions to the matrix element, representing corrections to the right-hand side of Equation (4) are:

$$\vec{e}'_i \gamma_{ij(kl)}^{(m)} (\hat{\mathbf{k}} \times \mathbf{e})_j e_k e_l; \quad i \vec{e}'_i \gamma_{i(jkl)m}^{(q)} e_j e_k e_l k_m \quad (6)$$

where the  $\mathbf{k} = |\mathbf{k}| \hat{\mathbf{k}}$  is the wave-vector of the input light, whose magnetic polarization vector is cast as  $\hat{\mathbf{k}} \times \mathbf{e}$ . The factor of  $i$  in the second expression, with the  $k_m$  factor, results from the operation of the gradient operator on the optical phase factor  $\exp(i\mathbf{k} \cdot \mathbf{r})$ , associated with quadrupolar coupling. For convenience a factor of  $c$  (speed of light) in the former of the expressions in (6) is here assimilated into the definition of  $\gamma_{ij(kl)}^{(m)}$ .

### 5. Third Harmonic Signal from Fluid Media

The various contributions to the quantum amplitude for THS examined above add together to produce an expression of considerable complexity when expressed explicitly. In principle, the harmonic signal intensity, or conversion efficiency, is determined from the modulus square of this sum, leading to over 30,000, i.e.,  $(30 + 54 + 90)^2$ , terms. However, the virtues of implementing the irreducible tensor decomposition come powerfully into play when the response from any kind of fluid medium is derived. Such media include not only liquids or solutions comprising intrinsically chiral molecules, but also suspensions of helical or other chirally formed nanoparticles, as in recent experimental studies. It is readily proven from the rules of angular momentum coupling that only products of identical weight can contribute to the signal; all cross-terms between irreducible tensors of different weights vanish [23]. Essentially this is because the result has to be a product of scalars, one for the material response and the other for the product of radiation field components.

The leading terms relevant to a chiral observable are now developed in the following form:

$$\begin{aligned}
 S &\sim \left| \vec{e}'_i \gamma_{i(jkl)} e_j e_k e_l + \vec{e}'_i \gamma_{ij(kl)}^{(m)} (\hat{\mathbf{k}} \times \mathbf{e})_j e_k e_l + i \vec{e}'_i \gamma_{ij(klm)}^{(q)} k_j e_k e_l e_m \right|^2 \\
 &= \sum_j \left( \vec{e}'_i \gamma_{i(jkl)}^{[J]} e_j e_k e_l + \vec{e}'_i \gamma_{ij(kl)}^{(m)[J]} (\hat{\mathbf{k}} \times \mathbf{e})_j e_k e_l + i \vec{e}'_i \gamma_{i(jkl)m}^{(q)[J]} e_j e_k e_l k_m \right) \\
 &\times \sum_{j'} \left( e'_n \bar{\gamma}_{n(opq)}^{[J']} \bar{e}_o \bar{e}_p \bar{e}_q + e'_n \bar{\gamma}_{no(pq)}^{(m)[J']} (\hat{\mathbf{k}} \times \bar{\mathbf{e}})_o \bar{e}_p \bar{e}_q - i e'_n \bar{\gamma}_{n(opq)r}^{(q)[J']} \bar{e}_o \bar{e}_p \bar{e}_q k_r \right) \\
 &\Rightarrow \sum_{J=0}^4 \left[ \vec{e}'_i \gamma_{i(jkl)}^{[J]} e_j e_k e_l e'_n \bar{\gamma}_{n(opq)}^{[J']} \bar{e}_o \bar{e}_p \bar{e}_q + 2 \text{Re} \left\{ \vec{e}'_i \gamma_{i(jkl)}^{[J]} e_j e_k e_l \left( e'_n \bar{\gamma}_{no(pq)}^{(m)[J]} (\hat{\mathbf{k}} \times \mathbf{e})_o \bar{e}_p \bar{e}_q - i \vec{e}'_n \bar{\gamma}_{n(opq)r}^{(q)[J]} \bar{e}_o \bar{e}_p \bar{e}_q k_r \right) \right\} \right] + \dots
 \end{aligned} \tag{7}$$

Here, the upper limit on the summation in the bottom line is introduced to highlight the fact that the  $\bar{\gamma}_{no(pqr)}^{(q)[J']}$  contribution with  $J = 5$  vanishes identically, for the reason given above. We can now take advantage of the fact that for L/R (left/right) circular polarization the following relation holds:

$$\hat{\mathbf{k}} \times \mathbf{e}^{(L/R)} = \mp i \mathbf{e}^{(L/R)} \tag{8}$$

affording a simplification of the leading terms shown in Equation (7) into:

$$\begin{aligned}
 S^{(L/R)} &\sim \sum_{J=0}^4 \left[ \vec{e}'_i e'_n \gamma_{i(jkl)}^{[J]} \bar{\gamma}_{n(opq)}^{[J']} e_j e_k e_l \bar{e}_o \bar{e}_p \bar{e}_q + 2 \text{Re} \left\{ \vec{e}'_i e'_n \gamma_{i(jkl)}^{[J]} \left( \pm i n \bar{\gamma}_{no(pq)}^{(m)[J]} - i \bar{\gamma}_{n(opq)r}^{(q)[J]} k_r \right) e_j e_k e_l \bar{e}_o \bar{e}_p \bar{e}_q \right\} \right] \\
 &\equiv \text{Re} \sum_{J=0}^4 \left[ \gamma_{i(jkl)}^{[J]} \bar{\gamma}_{n(opq)}^{[J']} + 2 \left\{ \gamma_{i(jkl)}^{[J]} \left( \pm i n \bar{\gamma}_{no(pq)}^{(m)[J]} - i \bar{\gamma}_{n(opq)r}^{(q)[J]} k_r \right) \right\} \right] \vec{e}'_i e'_n e_j e_k e_l \bar{e}_o \bar{e}_p \bar{e}_q
 \end{aligned} \tag{9}$$

Use is made of the fact that all three input photons are identical, and when the input beam is circularly polarised they should all have the same circular polarization—either all left, or all right, according to the choice of polarising optics in the path of the input beam. At this juncture, using the ergodic theorem, a result for the fluid average can be secured by performing a rotational average on the system. The result can be expressed in several ways; two of them in particular invite pursuit using very different methods.

The first method further exploits the irreducible tensor approach by breaking the radiation vector products into terms that correlate with the irreducible weights of the material tensors with which they are inner-product contracted, leading to:

$$\begin{aligned}
 \langle S^{(L/R)} \rangle &\sim \text{Re} \sum_{J=0}^4 (2J + 1)^{-1} \left[ \gamma_{i(jkl)}^{[J]} \left( \bar{\gamma}_{n(opq)}^{[J']} \pm 2 i n \bar{\gamma}_{no(pq)}^{(m)[J]} \right) \left( e'_n \bar{e}_o \bar{e}_p \bar{e}_q \right)^{[J]} \right. \\
 &\quad \left. - 2 i \gamma_{i(jkl)}^{[J]} \bar{\gamma}_{n(opq)r}^{(q)[J']} \left( e'_n \bar{e}_o \bar{e}_p \bar{e}_q k_r \right)^{[J]} \right] \left( \vec{e}'_i e_j e_k e_l \right)^{[J]}
 \end{aligned} \tag{10}$$

As again shown by Andrews and Blake, all cross-terms involving unequal values of  $J$  vanish [23]. The simplicity of the above expression occludes the complexity of identifying the various weight- $J$  elements of the polarisation vector products in (10). In particular, the general decomposition of a fifth-rank Cartesian tensor into irreducible parts, as is required for evaluating the term  $(e'_n \bar{e}_o \bar{e}_p \bar{e}_q k_r)^{[J]}$ , appears not yet to be known; explicit results are known to be available only up to the fourth-rank case [24,25].

The second method inviting attention follows from casting Equation (9) as follows, without separating out the irreducible parts of the polarisation products:

$$\langle S^{(L/R)} \rangle \sim \text{Re} \sum_{J=0}^4 \left[ \gamma_{i(jkl)}^{[J]} \left( \bar{\gamma}_{n(opq)}^{[J]} \pm 2i \bar{\gamma}_{no(pq)}^{(m)[J]} \right) \langle \bar{e}'_i e'_n e_j e_k e_l \bar{e}_o \bar{e}_p \bar{e}_q \rangle - 2i \gamma_{i(jkl)}^{[J]} \bar{\gamma}_{n(opq)r}^{(q)[J]} \langle \bar{e}'_i e'_n e_j e_k e_l \bar{e}_o \bar{e}_p \bar{e}_q k_r \rangle \right] \quad (11)$$

Here, the complexity shifts to the evaluation of the eighth and ninth rank rotational averages indicated by the angular brackets on the right. The former has long been known, cast in terms of 105 individual isotropic tensor isomers [26,27]; an explicit and general result for the latter, which entails 1260 isotropic tensor isomers, has only been derived much more recently [28].

In the present, symmetry-focused analysis, it is expedient to dwell more substantively on the first terms in (11). In fact, there is a good physical reason to neglect the  $\gamma_{i(jkl)}^{[J]} \bar{\gamma}_{n(opq)r}^{(q)[J]}$  term. As noted earlier, this term specifically involves a quadrupole interaction with an input photon, which, as noted earlier, lends it a  $k_m$  factor, through operation of the gradient operator on the optical phase factor  $\exp(i\mathbf{k}\cdot\mathbf{r})$ . Whilst the E2 and M1 forms of coupling are often considered broadly comparable in significance, it is commonly the case in linear spectroscopies that the former plays a smaller role. However, in the present application a much more substantial difference can be expected to arise, because the third harmonic is generally studied with comparatively long-wavelength light,  $\lambda = 2\pi/k$ , and hence a small wavenumber  $k$ , in order that the third-wavelength output  $\lambda'$  be in an amenable region of the visible spectrum. Any quadrupole interaction with the input is three times less significant than it would be for the emission, but we know the latter plays no part in the chiral resolution of the pump. Accordingly, for both these reasons, it can be anticipated that the  $\gamma_{i(jkl)}^{[J]} \bar{\gamma}_{n(opq)r}^{(q)[J]}$  term will play only a comparatively modest role in modifying the results delivered by the leading terms, and we can proceed on this basis.

It is evident from Equation (11) that the angular distribution of both the  $E1^4$ - $E1^4$  and  $E1^4$ - $E1^3$ M1 terms are in fact the same. This follows from the magnetic field of a circularly polarised beam being merely  $\pi/2$  different in phase from the corresponding electric field, and any such axial shift in phase will not be experimentally resolvable in the perpendicular direction of harmonic emission. The results therefore take the following form, for right-angled scattering and unresolved polarisation in the harmonic (secured by adding the intensity results for two independent output polarisations—any two states with diametrically opposite representations on a Poincaré sphere):

$$\langle S^{(L/R)} \rangle \sim \text{Re} \left[ 144 \gamma^{[2\alpha]} \odot^4 \left( \bar{\gamma}^{[2\alpha]} \mp 2\bar{\gamma}'^{(m)[2\alpha]} \right) + 1800 \gamma^{[2\alpha]} \odot^4 \left( \bar{\gamma}^{[2\beta]} \mp 2\bar{\gamma}'^{(m)[2\beta]} \right) \right. \\ \left. + 900 \gamma^{[2\beta]} \odot^4 \left( \bar{\gamma}^{[2\beta]} \mp 2\bar{\gamma}'^{(m)[2\beta]} \right) + 225 \gamma^{[3]} \odot^4 \left( \bar{\gamma}^{[3]} \mp 2\bar{\gamma}'^{(m)[3]} \right) + 725 \gamma^4 \odot^4 \left( \bar{\gamma}^{[4]} \mp 2\bar{\gamma}'^{(m)[4]} \right) \right] \quad (12)$$

This follows from the sum of Equations (29) and (30) in recent work [15], focused exclusively on  $E1^4$  interactions. In Equation (12), inner products are now denoted in the explicit form  $\gamma \odot^4 \bar{\gamma} \equiv \gamma_{i(jkl)} \bar{\gamma}_{i(jkl)}$ ; the prime on a tensor denotes its imaginary part (recalling that whereas E1 moments are real, M1 are imaginary), i.e.,  $\gamma' = i\gamma$ , and the definitions of the separated  $\gamma^{[2\alpha]}$  and  $\gamma^{[2\beta]}$  parts of the weight-3 tensor are as given in Appendix B of that work. In each irreducible tensor product, the  $\gamma^{(m)}$  tensor is symmetrised in its indices relating to the input photon interactions through the inner products with  $\gamma$ .

It follows that the rotationally averaged differential harmonic intensity, i.e., the change in the harmonic intensity on changing the input from left- to right-handed circular polarisation, is given by:

$$\Delta S \equiv \langle S^{(R)} \rangle - \langle S^{(L)} \rangle \sim 2\text{Re} \left[ 144\gamma^{[2\alpha]} \odot^4 \bar{\gamma}'^{(m)[2\alpha]} + 1800\gamma^{[2\alpha]} \odot^4 \bar{\gamma}'^{(m)[2\beta]} + 900\gamma^{[2\beta]} \odot^4 \bar{\gamma}'^{(m)[2\beta]} + 225\gamma^{[3]} \odot^4 \bar{\gamma}'^{(m)[3]} + 725\gamma^4 \odot^4 \bar{\gamma}'^{(m)[4]} \right] \quad (13)$$

Notably, there are no contribution from weights  $J = 0$  or  $1$ . This feature is readily explicable, and consistent with the rules of quantum angular momentum coupling, running from  $|J_\omega - J_{\omega'}| \dots J_\omega + J_{\omega'}$ . Finally, we can ascertain that the *relative* circular differential—i.e., the fractional change in harmonic intensity compared to the mean for left- and right-handed input,  $\bar{S}^{(L/R)} \equiv \frac{1}{2}[\langle S^{(R)} \rangle + \langle S^{(L)} \rangle]$ —is simply expressible as the following:

$$g_{\text{THSCD}} \equiv \frac{S^{(R)} - S^{(L)}}{\bar{S}^{(R/L)}} = 4\text{Re} \frac{\gamma\bar{\gamma}'^{m[4]} + a\gamma\bar{\gamma}'^{m[3]} + b\gamma\bar{\gamma}'^{m[2\alpha\alpha]} + c\gamma\bar{\gamma}'^{m[2\alpha\beta]} + d\gamma\bar{\gamma}'^{m[2\beta\beta]}}{\gamma\bar{\gamma}'^{[4]} + a\gamma\bar{\gamma}'^{[3]} + b\gamma\bar{\gamma}'^{[2\alpha\alpha]} + c\gamma\bar{\gamma}'^{[2\alpha\beta]} + d\gamma\bar{\gamma}'^{[2\beta\beta]}} \quad (14)$$

-serving to define the THS circular differential ratio  $g_{\text{THSCD}}$  in the same manner as the well-established counterpart differential for linear (i.e., Rayleigh) scattering [29]. Here, a simple adaptation of the concise notation of [15] is adopted, in which, for example  $\gamma\bar{\gamma}'^{m[2\alpha\beta]} \equiv \gamma^{[2\alpha]} \odot^4 \bar{\gamma}'^{(m)[2\beta]}$ . In Equation (14), the numerical coefficients have the values  $a = 0.31$ ,  $b = 0.20$ ,  $c = 2.48$  and  $d = 1.24$ . The numerator of this expression, and hence the whole differential, vanishes if the constituent molecules are achiral. Moreover, whereas the denominator is the same for any pair of chirally opposite enantiomers, all  $\gamma\bar{\gamma}'^{(m)}$  terms in the numerator change their sign in enantiomerically opposite materials (since for inverse structures all electric dipole moments have opposite signs, but the magnetic dipoles are the same). Thus  $g_{\text{THSCD}}$  has an opposite sign for each material. This satisfies the necessity for invariance of the whole radiation + matter system under the space inversion operation P.

## 6. Discussion

The main aim of this paper has been to both exemplify and harness a range of symmetry principles in tackling a system of intrinsic interest in the sphere of modern nonlinear optics. It is well established that the use of irreducible tensor methods proves greatly advantageous in the characterisation of nonlinear molecular media, often through the study of second harmonic scattering [30]. There is additional value and many further advantages to accrue from the use of circularly polarised light as a probe of nonlinear optical systems, generally optimising the amount of information that can be determined [31]. Here considering specific application to the process of third harmonic scattering we have seen how CPT symmetry, quantised angular momentum, irreducible tensors, Cartesian index permutations, conservation laws and structural symmetry all come into play. Moreover, the major simplifications that are thereby brought into effect, mostly without significant approximation, enable new, quantitatively applicable results to be secured.

It is not the purpose here to pursue detailed quantitative results, primarily because in any application the exact values will depend on the material through the ten independent tensor products in Equation (14), and their values will in turn depend on the optical frequency of the pump radiation, as determined by the choice of laser source. However, it is instructive to identify a ballpark figure for the degree of sensitivity to opposite circular polarisations of the pump. A traditional means of estimating typical relative magnitudes for electrodynamic couplings involving M1 and E1 moments takes as its premise the notion that electric dipoles are of the order of  $ea_0$ , where  $e$  is the electron charge and  $a_0$  is the Bohr radius, while magnetic dipoles are of the order of  $e\hbar/m_e$ , where  $m_e$  is the electron mass. From this it emerges that the relative magnitudes of M1/E1 *couplings* (not the moments themselves, which have different physical dimensions) is of the order of  $\alpha$ , the universal fine structure constant whose value is  $\sim 1/137$ . Now each  $E1^3M1 \bar{\gamma}'^{(m)}$  tensor has three times as many contributions

as its  $E1^4$  counterpart  $\gamma$  (compare Figures 1 and 2), and so with the additional factor of 4 at the front of Equation (14) it follows that a  $g_{\text{THSCD}}$  value of around 10% is not unreasonable. Moreover, it may be recalled that the explicitly neglected  $E1^3E2\bar{\gamma}^{(q)}$  terms also have a capacity to add to this result, albeit most likely to a much smaller extent, but still suggesting that  $g_{\text{THSCD}}$  values in excess of 10% are distinctly possible. This encouraging result will be a spur to experimental efforts to determine circular differential THS effects in real chiral systems.

Finally, it is interesting to briefly contemplate potential application of the methods described here to other nonlinear optical processes involving chirality. The most directly similar arise in the same, fourth order of time-dependent perturbation theory; they too entail four photons in each light–molecule interaction. However, departing from the third harmonic focus of the present study—three input photons and one output per interaction—these entail two photons in, and two out. This four-wave mixing (FWM) allows simultaneous inputs from two separate, individually tailored beams, often considered pump and probe. The net input thus comprises two differently polarized fields; either one or both input photons may have circular polarization. Some early “field dressing” approaches considered one such circularly polarized beam to confer chirality on the system probed by the other [32]. As was shown by Craig et al. [33], a molecule can exhibit a circular differential in its response to the secondary beam, not requiring interference of the  $E1^4$  term with any  $E1^3M1$  or  $E1^3E2$  terms of lower magnitude. While the details depend on the relative optical frequencies and polarizations, the theory thus becomes simpler though the molecular tensor  $\gamma_{ijkl}^{\text{FWM}}$  may lack index symmetry, retaining all five weights 0–4. The coherent, wave-matching geometry commonly used enhances the signal, providing signals that can be deployed analytically for optically enhanced detection [34].

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